Master's thesis

NTNU
Norwegian University of Science and Technology
Faculty of Natural Sciences
Department of Chemistry

Maren Hauknes Ranheim

Crosslinking of Polyesters in Emulsion Droplets

Master's thesis in Chemistry
Supervisor: Solon Economopoulos
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Preface

This master thesis was performed in collaboration with Jotun AS at the Department of Chemistry at Norwegian University of Science and Technology (NTNU) in Trondheim, with specialization in organic chemistry. This work was carried out between August 2018 and June 2020 under supervision of associate professor Solon Economopoulos and co-supervisor Sina Lystvet.

I would sincerely like to thank my supervisor Solon Economopoulos for all support and advice during the past two years. Thank you for your patience and for always being available to answer any questions or concerns. My deepest gratitude to Sina Lystvet and Olav Marstokk for the opportunity to contribute to such a project and for teaching me so much about this field.

I am thankful to Henriette Reinholt Hansen for carrying out measurements at Jotun AS, and to all the others at the Binder department. For your help and guidance at Jotun AS, thank you to Heng Li for the valuable input with the GPC and FTIR analysis; to Marit Dahling and Jamie Foster for the aid with the DSC analysis, and to Sebastien Charles Simon and Jost Ruwoldt at the Department of Chemical Engineering at NTNU for assistance with the GPC and molecular weight calculations. Lastly, I would also like to extend my gratitude to senior engineer Susana Villa Gonzalez for valuable assistance with UPLC/UPC2/MS analysis.

I also want to thank my fellow students, family, and friends for all support during the last two years.

Abstract

Advances in the alkyd emulsions are required to improve shortcomings such as long drying times and softness associated with alkyd paints. Increasing the molecular weight can reduce the curing time and improve the hardness of the films.

A complete study on a simplified base system for an alkyd paint, involving the crosslinker of the alkyd prior to emulsification was carried out. The goal was to identify viable reaction conditions, based on the Diels-Alder reaction mechanism, that can be directly applicable to the industrial production line at Jotun AS. It was found that the choice of crosslinker, concentration and reaction times play crucial roles in the molecular weight of the final product. The largest increase in molecular weight was achieved with increased temperatures, prolonged reaction times and crosslinker pentaerythritol tetraacrylate (PT). This was extrapolated to the emulsified system. However, the emulsion system proved to be much more complex and side-reactions were observed. The main side-reaction is believed to be caused by hydrolysis of the ester backbone in the alkyd.

The study also showed that the crosslinker could be added to the alkyd prior to emulsification without restricting the emulsification process. This bypassed some of the challenges encountered by adding the crosslinker post-emulsification. During this series of experiments, the largest molecular weight was obtained with crosslinker 1,1’(methylenedi-4,1-phenylene)bismaleimide (MPB).

A mechanical study was conducted with the conjugated fatty acid. There were no indications that the Diels-Alder reaction occurred. Instead, an autoxidative reaction between the fatty acid and oxygen from the atmosphere was confirmed. Another reaction detected was the transesterification of the ester bond in the fatty acid by an alcohol species. The role of the crosslinker in the alkyd and alkyd emulsion reactions was not determined although it was found to have a crucial effect on the resulting molecular weight.

Sammendrag

Fremskritt innen alkydemulsjoner er nødvendig for å forbedre svakheter som lange tørketider og myke filmer assosiert med alkydmaling. Å øke molekylvekten kan redusere herdetiden og forbedre hardheten til filmene.

En fullstendig studie på et forenklet base-system for en alkydmaling som involverte alkyden før emulgering ble utført. Målet var å identifisere gjennomførbare reaksjonsforhold, basert på Diels-Alder reaksjonsmekanisme, som direkte kan være anvendelige ved den industrielle produksjonslinjen ved Jotun AS. Et forenklet system ble undersøkt som involverte alkyden før emulgering. Det ble funnet at valg av kryssbinder, konsentrasjon og reaksjonstid spiller avgjørende roller i molekylvekten i sluttproduktet. Den største økningen i molekylvekt ble oppnådd med økte temperaturer, forlengede reaksjonstider og kryssbinder pentaerytritol tetraakrylat. Dette ble ekstrapolert til det emulgerte systemet. Imidlertid viste emulsjonssystemet seg til å være mer komplekst og sidereaksjoner ble observert. Den viktigste sidereaksjonen antas å være forårsaket av hydrolyse av esterbindingen i alkyden.

Studien viste også at kryssbinderen kunne tilsettes alkyden før emulgering uten at dette begrenset muligheten for emulgeringsprosessen. Dette var fordelaktig for noen av utfordringene som oppsto ved å tilsette kryssbinderen etter emulgering. Gjennom dette settet av eksperimenter ble den største økningen i molekylvekt oppnådd med kryssbinder 1,1'(metylendi-4,1-fenylen)bimaleimid (MPB).

En mekanisk studie ble utført med den konjugerte fettsyren. Det var ingen indikasjoner på at Diels-Alder reaksjonen skjedde. I stedet ble en autoksidativ reaksjon mellom fettsyren og oksygen fra atmosfæren bekreftet. En annen reaksjon som ble påvist var transesterifisering av esterbindingen i fettsyren av en alkohol. Kryssbindingens rolle i alkyd- og alkydemulsjonsreaksjonene ble ikke bestemt selv om det ble funnet til å ha en avgjørende effekt på den endelige molekylvekten.

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Symbols and Abbreviations

Abbreviation	**Full name**
A_i	Integrated area in GPC
c	Concentration
cFA	Conjugated fatty acid
COSY	Correlation spectroscopy
CPE	Crosslinker added prior to emulsification
d	Day(s)
dd	Doublet of doublet in NMR
DG	di(Ethylene glycol)diacrylate
DLS	Dynamic light scattering
DPM	di(propylene glycol) methyl ether
DSC	Differential scanning calorimeter
EDG	Electron donating group
EWG	Electron withdrawing group
func%	Concentrations based on functional groups
GPC	Gel permeation chromatography
h	Hour(s)
HD	1,6-hexanediol diacrylate
HMBC	Heteronuclear multiple bond correlation
HPLC	High pressure liquid chromatography
HSQC	Homonuclear single quantum coherence
i	Measuring point
IR	Infrared spectroscopy
LALS	Low angle light scattering
MA	Methyl acrylate
M_i	Molecular weight at measuring point *i*
min	Minute(s)
mM	N,N’-(1,3-Phenylene)dimaleimide
M_n	Number average molecular weight
MPB	1,1’(Methylenedi-4,1-phenylene)bismaleimide

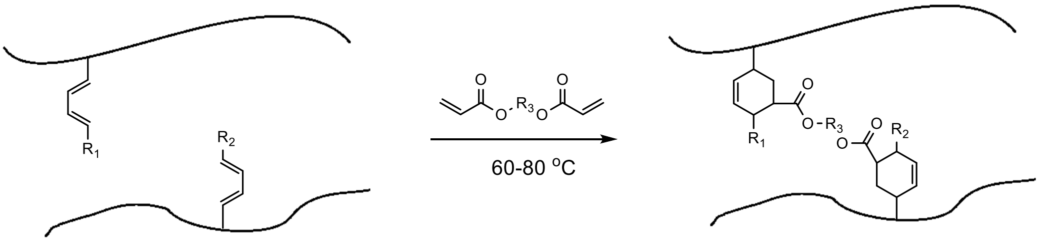
MS	Mass spectroscopy
M_w	Weight average molecular weight
M_x	Molecular weight of molecule corresponding to a specific degree of polymerization
M_z	z-average molecular weight
NMR	Nuclear magnetic resonance
Nu	Nucleophile
N_x	Number of moles corresponding to a specific degree of polymerization
O/W	Oil-in-water
pM	N,N'-(1,4-Phenylene)dimaleimide
ppm	Parts per million
PS	Polystyrene
PT	Pentaerythritol tetraacrylate
RALS	Right angle light scattering
RI	Refractive index
RT	Room temperature
SCF	Supercritical fluid
SEC	Size exclusion chromatography
SEC	Size exclusion chromatography
T	Temperature
t	Reaction time
T_g	Glass transition temperature
THF	Tetrahydrofuran
Tm	Melting temperature
tr	Triplet in NMR
UV	Ultraviolet
VOC	Volatile organic compound
w	Weak
W/O	Water-in-oil
wt%	Weight percentage
x	Degree of polymerization

Table of Content

1 Introduction

The alkyd polymer serves as a binder and is one of the most important components in alkyd paints. The alkyd gives the paint adhesive and drying properties, among others. Commonly, the alkyd consists of a mixture of diacids, polyols, and fatty acids. For water-borne paints, the alkyd is then emulsified.[1] Compared to acrylic systems, alkyds are slow drying and soft. This causes prolonged application time when multiple layers are needed, and increased dirt pick up. Increasing the molecular weight reduces curing time and forms a harder film, minimizing both application time and dirt pick-up.

For the emulsification process there are several experimental restrictions that come into play as alkyds with high molecular weight can be difficult to emulsify. [2-3] The purpose of this project is to crosslink the polymer chains after emulsification to increase the molecular weight and hence the curing rate. This is achieved through a Diels-Alder reaction between conjugated fatty acids in the alkyd and a crosslinker with two or more functional groups (**Scheme 1**).[4] This study deals with establishing that the crosslinking reaction takes place and following that, the ability to control the molecular weight of the resulting polymer through altering parameters such as reaction time/temperature/choice of crosslinker etc.



Scheme 1: *Diels-Alder reaction between two alkyd chains and a difunctional acrylate crosslinker.*

In order to obtain a clearer indication on the crosslinking and the progress of the Diels-Alder reaction a simplified system consisting of the alkyd prior to emulsification and crosslinker was investigated. This allows a more facile monitoring of reaction progress and molecular weight through spectroscopic techniques. The results obtained for the simplified system were used as guidelines for the further emulsion reactions of interest for industrial purposes. The reaction was conducted by adding the crosslinker pre- and post-emulsification. Mechanistic studies were carried out with the fatty acid.

2 Theory

2.1 Polymers

Polymers are macromolecules built up of smaller units or monomers.[5] Polymers can be amorphous where the chains are arranged in a statistically random manner but also, linear chains can pack in a regular three-dimensional fashion, forming crystalline phases. However, polymers never crystallize completely; there are always amorphous regions in polymers. The thermodynamic preference towards the arrangement of the polymer chains can be the result of several factors such as chemical composition, polymer architecture (**Figure 1**), solvent, heat etc.[5-6] Networks can be formed by including at least one monomer with a functionality greater than two, or by chemically linking chains together after formation, known as crosslinking.[5]

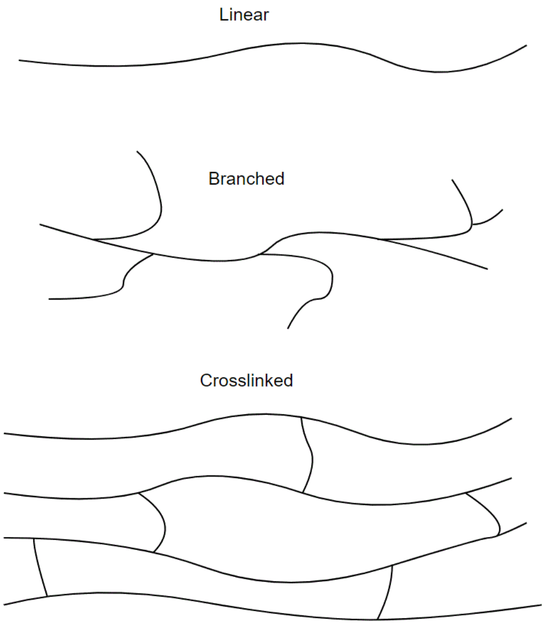


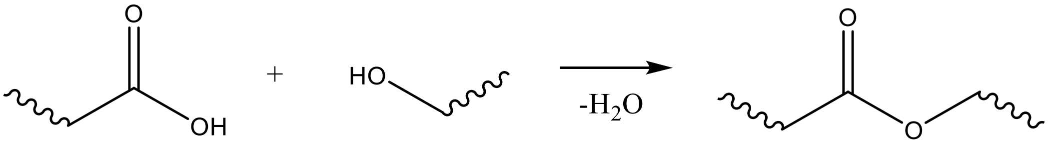
Figure 1: Different polymer structures, including linear, branched, and crosslinked chains.

Elastomers are high-molecular weight polymers which have been subjected to chemical and/or physical crosslinking. Most elastomers are amorphous. Due to the crosslinking, the material possesses a shape-memory effect and can return to its original shape upon deformation.[6]

Homopolymers are commonly synthesized from a single monomer while copolymers are derived from two or more monomers. Depending on the location of the different monomers, block, graft, alternating or random copolymers can be synthesized. Different polymers can also simply be mixed to form polymer blends.[5]

2.1.1 Polymerization Mechanisms

Many polymers can be classified according to two main polymerization mechanisms, namely addition and condensation reactions. In the addition reaction, the molecular formula of the structural units is the same as in the monomers, although the arrangements of bonds are different. The propagation typically involves unsaturated monomers reacting through a free radical mechanism, although other polymer chain-growth mechanisms exist as new polymerization reactions are constantly being developed.[7-9] In the condensation reactions, two functional groups react with the loss of a small end-molecule. These can follow traditional organic synthetic reaction mechanisms such as esterification (**Scheme 2**), Suzuki and Stille coupling, as long as the monomers possess bi-functional end-groups in order to ensure the polymer chain growth. The chemical repeat unit of the resulting polymer in condensation reactions is different from the molecular formula of the monomer.[5, 10] Alternatively, polymerization reactions can be classified as step-growth or chain polymerizations.



Scheme 2: *Esterification reaction.*

2.1.2 Molecular Weight

Although, standard structural characterization techniques such as NMR, FTIR are also applicable in polymer characterization, there is an obvious need for one new property that needs to be defined, the molecular weight or the degree of polymerization. The degree of polymerization represents the number of structural units in the chain and can be used to describe the chain length. For most synthetic polymers, the polymer chains have different chain lengths, resulting in a molecular weight distribution. The molecular weight of a polymer therefore corresponds to an average molecular weight and can be defined in different ways. The definitions of the number average molecular weight (M_n), the weight average molecular weight (M_w) and the z-average molecular weight (M_z) are shown in equations 2.1, 2.2 and 2.3, respectively. The weight average molecular weight takes into consideration the total weight, and is closer to the weight of the largest species.[5, 10]

$$\mathrm{M_n} = \frac{\sum N_x M_x}{\sum N_x} \tag{2.1}$$

$$\mathrm{M_w} = \frac{\sum N_x {M_x}^2}{\sum N_x M_x} \tag{2.2}$$

$$\mathrm{M_z} = \frac{\sum N_x {M_x}^3}{\sum N_x {M_x}^2} \tag{2.3}$$

where x is the degree of polymerization, M_x is the molecular weight of a molecule corresponding to the specific degree of polymerization, and N_x is the number of moles of these. The ratio of the weight average molecular weight to the number average molecular weight provides a measure of the breadth of the distribution, and is called the polydispersity of the sample;[5]

$$Polydispersity = \frac{M_w}{M_n} \tag{1.4}$$

In a monodisperse sample the polydispersity is equal to 1, and all polymer chains are of the same length. Polymers consisting of mixtures of chains with different molecular weight are called polydisperse.[5]

Many physical and mechanical properties of amorphous polymers improve as the molecular weight increases. The properties level off after a moderately high molecular weight is reached.[6]

2.1.3 Viscosity

The viscosity of a fluid is a measure of its resistance to flow, and reflects the frictional forces between the molecules.[5] The viscosity of a polymer increases with increasing molecular weight. The viscosity is proportional to the molecular weight up to a critical threshold.[6] However, there is no clear relationship between the measured parameters and the molecular weight. The method is relative, and the parameters must therefore be determined by standards of known molecular weights. The viscosity measurements depend upon the hydrodynamic radius.[5]

2.1.4 Melting and Glass Transition Temperature

Crystalline polymers exhibit melting temperatures (T_m) which is the transition from an ordered crystalline phase to a disordered liquid phase. This usually occurs at a well-defined temperature. Another characteristic transition observed in polymers is the glass transition temperature (T_g) which is related to the amorphous regions present in all polymers to varying extents.[5] The T_m is always higher than the T_g. Most linear polymers are hard brittle plastics at $T < T_g$, leathery and rubbery at $T_m > T > T_g$, and viscous liquids above the T_m. Highly crosslinked polymers do not melt. Polymers are classified as plastics, fibers, and elastomers in accordance with the T_g values.[6]

The T_g is related to the Brownian motion of the chains which increases with increasing temperature. At the glass transition temperature, the micro-Brownian motion becomes significant. Usually, there is no sharp transition involved, and the temperature range in which the T_g occurs is broader than for the T_m.[6]

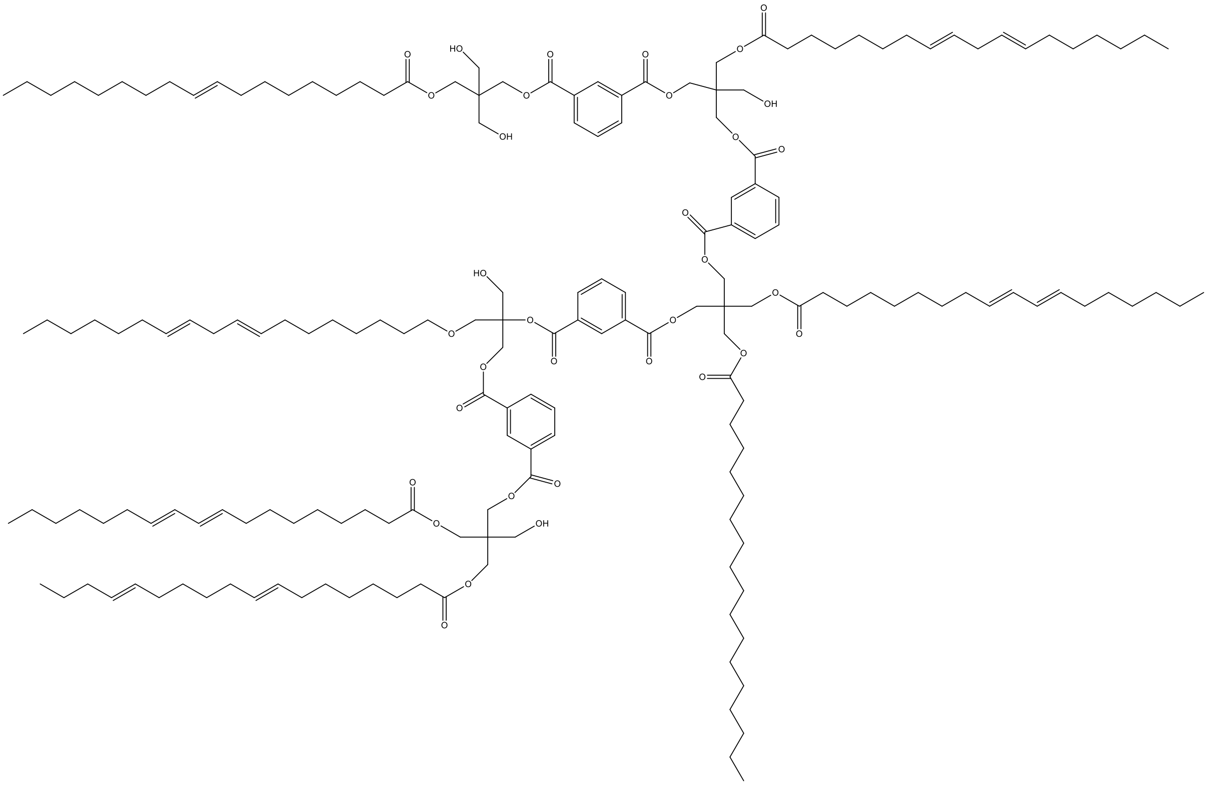
Several factors affect the T_g, including the molecular weight. Initially, the T_g increases sharply with the molecular weight, but levels off at a maximum. Bulky groups in the polymer backbone and bulky pendant groups raise the T_g through hinderance of bond rotations. Increasing the crosslinking density ties the chains more closely together and increases T_g.[5-6]

2.2 Paint

The binding medium in paint is usually called a resin and is the essence of the coating, providing most of the chemical and physical properties.[1] Alkyds have been the most consumed binder used worldwide for over 35 years,[11] in particular for wood and metal applications.[2] To achieve the desired application viscosity, solvents are added to the resin.[12] Paints also contains pigments and fillers, which, among other properties, gives the paint color. Extenders are inert pigments used to extend or increase the bulk of a paint. Paint also contain additives with a variety of functions. This includes paint-drying catalysts, or driers, which enhances the rate of crosslinking formation between the binder molecules.[10, 13]

2.2.1 Alkyds

Alkyd resins are polyesters synthesized by polycondensation reactions, consisting of fatty oils or fatty acids, dibasic acids, and polyols.[12, 14-15] A possible structure is shown in **Scheme 3**. Their advantages include flexibility, durability, good adhesion, and good penetration, and they typically have high gloss.[12, 14, 16] One of the biggest drawbacks is a relatively long drying time. A soft film is formed directly after application, and it takes a long time to reach the drying state of non-tackiness.[16-19]



Scheme 3: Generic structure of an alkyd resin.

The monomer building blocks of an alkyd are selected to provide desired properties in the resulting product. Dibasic acids with rigid structures such as benzene rings or fused rings can improve tensile strength, hardness, thermal stability and water resistance.[14] Alkyds are composed of a large percentage of fatty acids which results in alkyd resins with improved flexibility and toughness.[17] The oils used in alkyds are typically vegetable oils, consisting of fatty acids with different compositions. Such renewable raw materials provides a sustainable and economical coating and reduces the dependency on petroleum products.[15, 20] The alkyds can be classified based on the oil content; long oil (>55%), medium oil (45-55%) and short oil alkyds (<45%). Altering the oil length can provide different properties and applications to the paint. Long oil alkyds are quick drying with low viscosity, and are used in building interiors, marine and maintenance application as primers and finishes. Medium oil alkyds are often used in anticorrosion primers and decorative or maintenance paints, and provide fast drying and rather high viscosity. Short oil alkyds are mainly used in the industrial coating sector, commonly as a finisher, and has a low oxidative drying rate.[10] The alkyd resin can be modified to fit a broad range of applications. They are also compatible with a number of polymers, making them versatile polymers to produce a broad range of coating materials with various desired properties.[2]

There are two main methods for alkyd preparation, namely the monoglyceride and fatty acid process. In the first method, the seed oil is reacted with a polyol, typically glycerol, through a transesterification reaction. This results in monoglyceride products which can react with a polybasic acid to form the alkyd resin. In the second method, the fatty acid, polyols and dibasic acids are reacted in one step.[4]

Alkyds typically consists of a mixture of chains with different molecular weight species. The physical, chemical, and mechanical properties depend on their molecular weights. This include the rate of oxidation, toughness and resistance to degradation.[21]

2.2.2 Emulsions

Traditionally, the alkyd is dissolved in organic solvents to achieve the desired application viscosity.[12] Conventional solvent-borne coating commonly contain 30-60wt% volatile materials.[18] However, the harmful effects of organic solvents have pushed the development of water-based alternatives in paints, such as alkyd emulsions.[3, 22] Water-borne coatings have potential benefits include being environmentally friendly, non-toxic, non-flammable and require low energy curing.[23] Initially, alkyd emulsions were considered inferior to solvent-borne alkyds due to slower drying and somewhat impaired film properties. In recent years, much effort has been done on both synthesis and formulation of alkyd emulsion paints. It has been reported that almost all the beneficial properties are conserved for the alkyd emulsion, with the advantage of no emission of volatile organic compounds (VOCs).[2]

Alkyd emulsions can be made from most alkyds, provided the resin viscosity is not too high.[2] Long oil alkyds, with relatively low viscosity, are suitable for emulsification. Emulsifying medium and short oil alkyds are more complicated, as high temperatures and pressure might be necessary to bring down the viscosity to a suitable level.[3]

For higher viscosity alkyds, phase inversion methods are used. This can be done through mixing the resin, water and emulsion at a temperature in which a water-in-oil (W/O) emulsion is obtained. When the mixture is cooled down the W/O emulsion inverts to an oil-in-water (O/W) emulsion at the phase inversion temperature. Another method is mixing the resin and emulsifier at a constant temperature, then adding water with the same temperature. This forms a W/O emulsion. At a certain water concentration, namely the emulsion inversion point, the emulsion inverts to an O/W emulsion. A mixture of the two methods may also be used.[22]

In a thermodynamic sense, emulsions are always unstable systems. Destabilization can occur through flocculation (aggregation) of the droplets, followed by coalescence to form larger particles. The latter is irreversible and leads to phase separation (**Figure 2**).[24] Achieving small droplets and a narrow droplet size distribution in the emulsification process favors stability. The use of a surfactant surrounding the droplets prevents coalescence and flocculation. Nonionic surfactants can provide steric stabilization while ionic surfactants can provide electrostatic stabilization. The two surfactants can also be combined.[3]

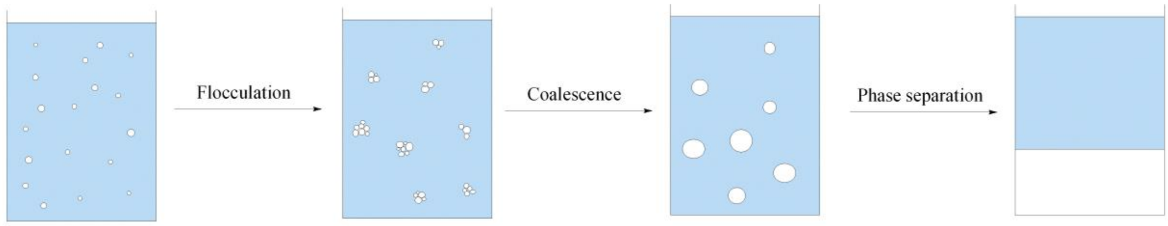
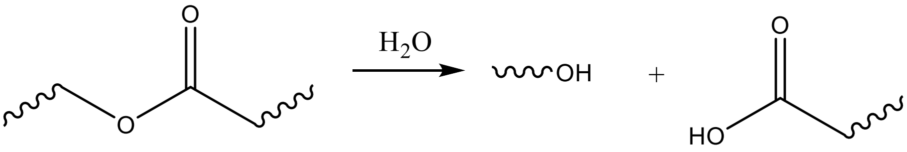


***Figure 2:** Destabilization mechanisms of emulsions though flocculation, coalescence, and phase separation.*

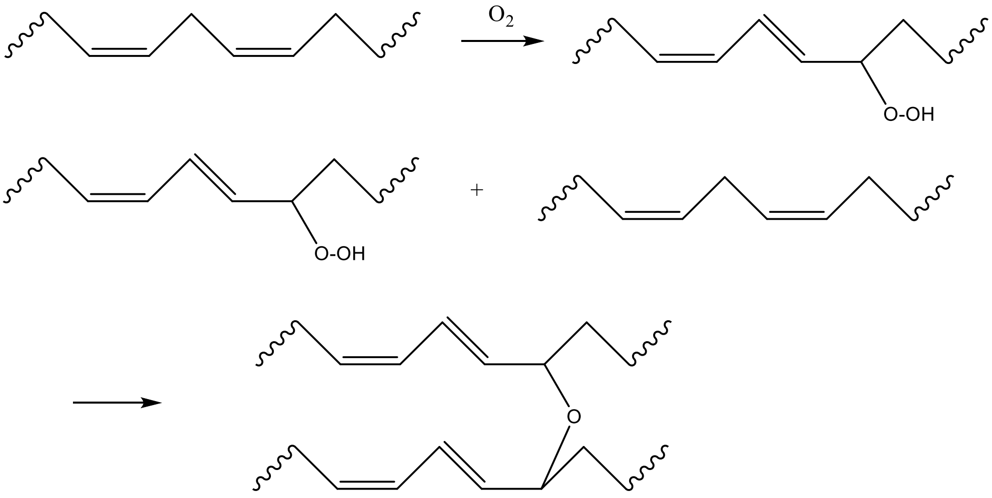
Another potential problem is the hydrolytic stability of the alkyd emulsions, since the ester bondage is susceptible to hydrolysis reaction in water (**Scheme 4**).[12, 24] Initially, the alkyd emulsions tend to have a neutral pH. [22] Acidic or alkaline conditions can catalyze the hydrolysis which leads to a decrease in molecular weight. The reduced molecular weight affects the properties of the film, especially the film hardness. Hydrolysis can also decrease the pH, as carboxylic acids are formed during this reaction which may further catalyze the hydrolysis reaction. The hydrolytic resistance is dependent on the chemical composition of the alkyd, initial pH and temperature.[24]



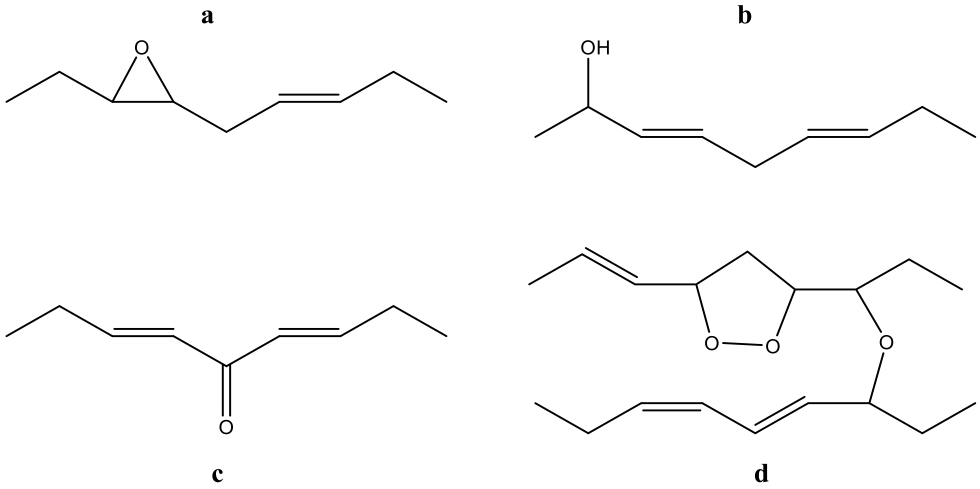
***Scheme 4:** Hydrolysis of the ester bond in alkyd.*

2.2.3 Drying

Alkyd paints dry though an autoxidation process catalyzed by transition metal salts. The most commonly used driers are cobalt compounds, however, their use is limited by their toxicity and bioaccessibility.[13] Other driers include manganese, cerium, vanadium and iron. Without driers, the oxidative drying time of an alkyd paint could take several weeks.[10] The drying of alkyd paints can be divided into two processes. The first stage is physical drying, where the solvent evaporates, and a closed film is formed. For the alkyd emulsions, the physical drying results in an emulsion phase inversion from O/W to W/O.[16, 22] The second process is chemical drying in the presence of oxygen, also called oxidative drying or curing (**Scheme 5**). The reaction proceeds by a free-radical chain mechanism which takes place at the fatty acid groups, resulting in crosslinking of the chains and formation of a continuous film.[12-13] Ether or peroxide crosslinks can be formed, in addition to various oxygenated species, including epoxides, alcohols, ketones and 1,2-dioxolanes (**Scheme 6**), most of which will be further oxidized to alcohols and carboxylic acids.[13] The same film structure is obtained whether the film originated from emulsion or solvent-borne alkyd paint.[2]



Scheme 5: *Oxidative curing of the alkyd.*

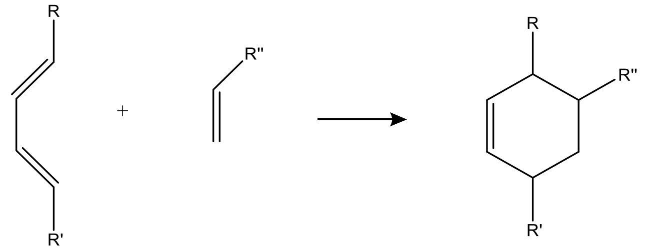


Scheme 6: *Oxygenated species formed from the autoxidation reaction of (E,E) or (Z,Z)-3,6-nonadiene, including **a)** epoxide, **b)** alcohol, **c)** ketone and **d)** 1,2-dioxolane species.*

The film formation depends on the oils or fatty acids used in the alkyd. Oils are divided into drying, semidrying, and non-drying, where the drying oils have the highest percentage of unsaturation. As the number of unsaturated sites increases, the films form more easily. The best drying oils have considerable conjugation as these accelerate the oxidative drying.[10, 12] The large number of double bonds in some oils, such as tung oil, can make the curing occur so rapidly that a highly wrinkled surface is produced.[25] In other vegetable oils, the double bonds are not sufficiently reactive to UV radiation. Terminal double bonds can be introduced to the alkyd resins as they are expected to exhibit higher reactivity than internal double bonds. [12] Such terminal double bonds are found in acrylates, among others.[20] Generally, introducing components with unsaturated bond can provide additional crosslinking sites for the curing process, increasing the drying rate.[4, 12]

2.3 Modifications

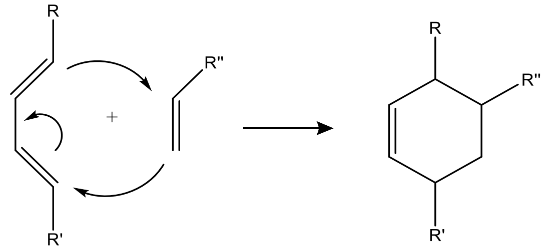
Crosslinked elastomers are polymeric networks capable of absorbing large deformations in a reversible manner. Elastomers can be crosslinked to improve the physical and chemical properties. The crosslinks prevent flow and provide elasticity and toughness. The crosslink density significantly influences the material properties. The two most common methods of crosslinking elastomers are through sulfur vulcanization and peroxide curing. These crosslinking processes are classified as irreversible. Another possibility is through the thermo-reversible Diels-Alder reaction (**Scheme 7**),[26] which has been employed as a useful technique to induce crosslinking of various polymer structures.[27]



Scheme 7: *General Diels-Alder reaction between a conjugated diene and a dienophile where R and R' commonly are electron donating groups and R'' is an electron withdrawing group.*

2.3.1 Diels-Alder

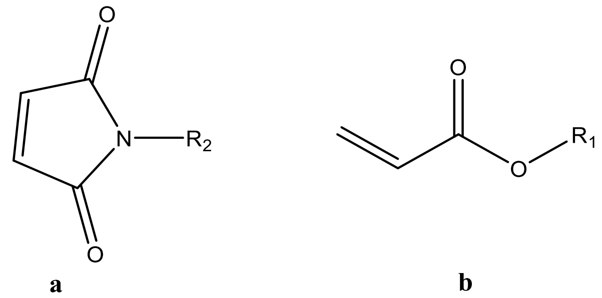
The Diels-Alder reaction is a [4+2] cycloaddition between a conjugated diene and a dienophile (**Scheme 7**). The reaction mechanism is shown in **Scheme 8**. Standard Diels-Alder reactions require an electron-rich diene and an electron-poor dienophile. This can be achieved through electron withdrawing groups (EWG) on the dienophile and electron donating groups (EDG) on the diene.[27-28]



Scheme 8: General reaction mechanism for the Diels-Alder reaction where R and R' commonly are electron donating groups and R'' is an electron withdrawing group.

The Diels-Alder reaction is catalyzed by Lewis-acids and specific-acid catalysts.[29] The increase in rate caused by Lewis-acids is attributed to complex formations between the Lewis acid and the polar groups of the reactants, in addition to the stabilization of the enhanced polarized state.[30] The reaction rate can also be increased by introducing pressure to the system. While increasing the temperature can increase the rate of the forward and reverse reaction, increasing the pressure only increases the forward reaction. Water can have a similar effect on the reaction rate by putting internal pressure on hydrophobic substrates.[30] Surfactants forming micelles and vesicles are common catalysts in water,[29] as hydrophobic packing is promoted.[31] The hydrophobic packing brings the diene and the dienophile together in the transition state. The water molecules can also provide similar effects as the Lewis acids, stabilizing the transition states. Lewis acids can further catalyze the Diels-Alder reactions in aqueous media, given that the catalyst is water-tolerant. Most Lewis acids are decomposed or deactivated in water, however, many Lewis acids have been found to be stable under aqueous conditions and could be employed to increase the rate further.[30]

For this study, two main groups of dienophiles were investigated; dimaleimides and acrylates (**Scheme 9**) with different functionalities. The maleimide consists of an α,β-unsaturated imide group. The delocalization of the double bond gives electron acceptor and dienophile characteristics for Michael additions and Diels-Alder reactions, among others. The maleimides have high reactivity with various functions and the imide part provides good thermal stability to polymers.[32]

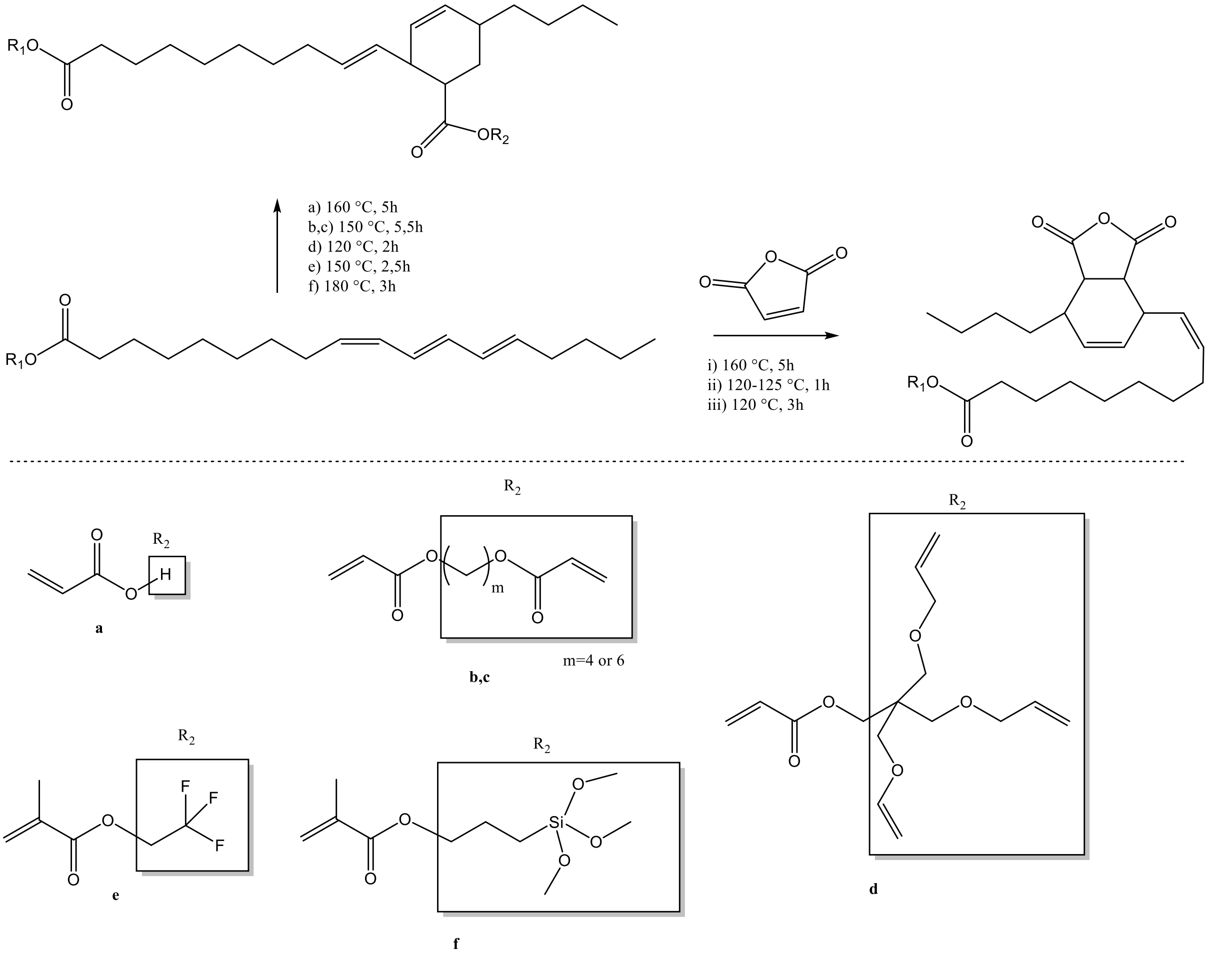


Scheme 9: *Dienophiles for the Diels-Alder reaction, including* ***a)*** *maleimide moiety and* ***b)*** *acrylate moiety.*

Acrylates are commonly used as dienophiles in Diels-Alder reaction due to the activating EWG. [33] Acrylates are widely used for functionalizing materials and can provide distinct properties for the final products.[34]

2.3.2 Modifications of the Fatty Acid

There are several reports of fatty acids or corresponding esters with conjugated double bonds being modified through a Diels-Alder reaction, especially tung oil. The modified fatty acids can have various applications in coatings. Tung oil consist of ≈80% eleostearic acid which can easily react in the Diels-Alder reaction without catalysts.[35] Maleic anhydride has commonly been used as the dienophile in several of these reactions,[20, 34-36] and various acrylates have been successfully employed (**Scheme 10**).[25, 33, 35] Acrylates have also reacted successfully with conjugated soybean oil.[18] In another approach, soybean oil was modified with furan derivatives, which were then further reacted with phenolic maleimide in a Diels-Alder reaction.[28] Similarly, acrylated soybean oil was successfully reacted with a bismaleimide.[37] This shows that conjugated fatty acids can be modified through this route, although the reaction conditions are expected to be significantly different in the alkyd emulsion system. FTIR and NMR have been used to monitor the disappearance of characteristic peaks and appearance of new peaks related to the Diels-Alder adduct.



Scheme 10: *Diels-Alder reactions between eleostearic acid or ester and maleic anhydride*[20, 34-36] *or acrylates a-f.*[25, 33, 35]

The increase in viscosity can cause local variations of the reactive species, resulting in broad molecular weight distributions. In a study by Trumbo and Mote,[25] copolymers of tung oil and diacrylates were synthesized through a Diels-Alder reaction. It was discovered that the reaction conducted in solution resulted in a more narrow molecular weight distribution as the solvent provides a more uniform concentration of reactants.

2.3.3 Modifications of the Alkyd

There have also been reports on modifying alkyds to alter properties, although for other purposes than increasing the molecular weight. Often the modifications are carried out to reduce the VOCs required to achieve the desired application viscosity, as an alternative to alkyd emulsions. The reactive dilutants serve as solvents and also participates in the film formation through the during process.[18]Among others, this was achieved by an isocyanate functionality reacting with hydroxyl groups in the alkyd.[38] In another study by Gandini *et al.*, acrylate functionalities were introduced to the alkyd to improve the curing rate. The alkyd resins were functionalized with methacrylate groups through direct acrylation of the alkyd and through epoxidation of the alkyd followed by ring opening reaction with the acrylate.[17] Alkyds have also been successfully modified though Diels-Alder reactions with different acrylates as dienophiles.[4, 14]

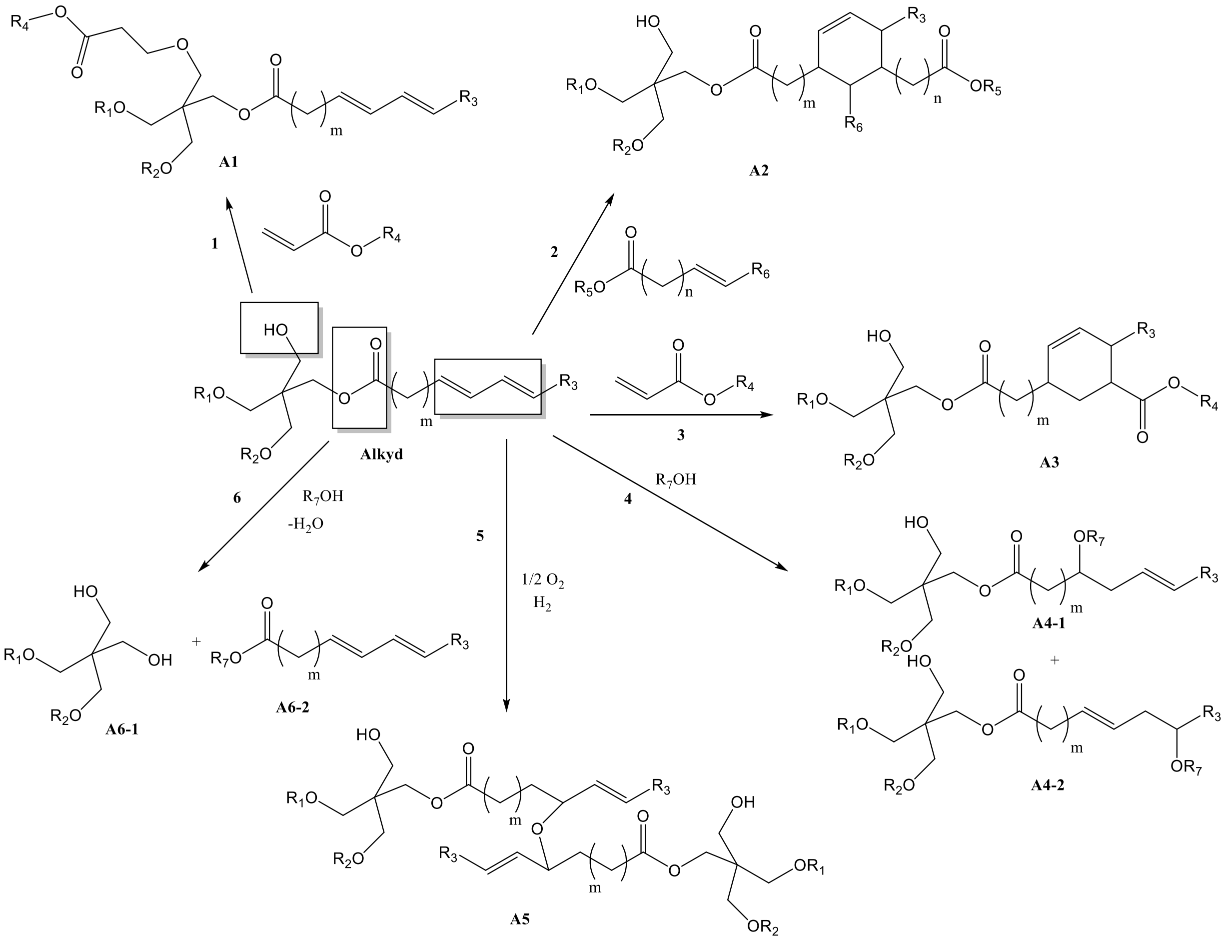
Crosslinking of other polymer chains using the Diels-Alder reaction has been reported previously. Gandini *et al.*, reported elastomeric polymers with furan heterocycles or maleimide functions as pendant groups which were crosslinked with oligomeric bi(maleimide)s or difuran moieties, respectively.[27]

2.3.4 Modifications of the Emulsion

Hybrids of alkyd resins and acrylic resins have been investigated as a way to overcome the shortcomings associated with each. The hybrid systems can be achieved in several ways. Since the resins are not always miscible compatible, chemically connecting the alkyd and the acrylic is the most common way to overcome this issue, through e.g. grafting an acrylic type monomer to the unsaturated fatty acid. However, this could impair the autoxidative drying of the alkyd.[2] In a study by Heiskanen *et al.*, copolymers were made from alkyd emulsion and acrylic monomers. Emulsion polymerization techniques were applied reacting acrylic monomers and unsaturated alkyd resins via free radical polymerization. The acrylic monomers were successfully emulsified and blended with the alkyd emulsions, while some alkyd double bonds remained unreacted to be utilized for oxidative crosslinking.[16] In another approach by Nabuurs *et al.*,[19] the acrylic phase was polymerized in the emulsion with colloidal alkyd droplets. However, this was conducted for the purpose of achieving a homogeneously mixed hybrid, and not for chemically reacting the two polymers.

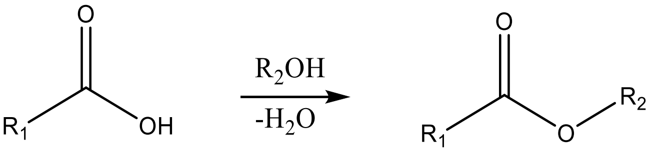
2.3.5 Competing Reactions

There are several possible competing reactions to the desired Diels-Alder reaction between the conjugated fatty acid and the dienophile (Reaction **3**, **Scheme 11**). The Diels-Alder can occur during prolonged heating of drying oils or alkyd (Reaction **2**, **Scheme 11**).[4] For simplicity, only one of the possible Diels-Alder adducts are shown, although regioisomers can be formed. Reaction **1** and **3** (**Scheme 11**) are shown with an acrylate functionality but maleimides can react in the same reactions.



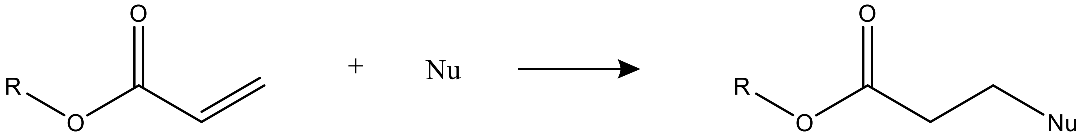
Scheme 11: *Possible reactions for the alkyd, including Michael addition (**1**), Diels-Alder with another alkyd polymer or fatty acid (**2**), Diels-Alder with an acrylate crosslinker (**3**), addition of alcohol or water (**4**), autoxidative curing (**5**) and hydrolysis or transesterification (**6**). R_5=H or alkyd moiety and R_7=H, residual alcohol or alkyd moiety.*

The alkyd contains alcohol and ester moieties and may undergo transesterification (Reaction **6**, **Scheme 11**) which usually requires a protic or Lewis acid. Residual carboxylic acid and alcohol moieties may undergo Fischer esterification (**Scheme 12**), also catalyzed by acids.[39]



Scheme 12: *Fischer esterification.*

Water or alcohols can also be added to the double bond, catalyzed by acid (Reaction **4**, **Scheme 11**).[40-41] Another possible competing reaction may be the Michael addition (Reaction **1**, **Scheme 11**). The Michael addition is a reaction between a nucleophile and an activated olefin (**Scheme 13**), called Michael donors and acceptors, respectively. α,β-Unsaturated acrylate esters and maleimides can act as acceptors to various nucleophile donors, among others. Hetero-Michael addition reactions include oxa-Michael additions, where the donor is an oxygen nucleophile, commonly an alcohol.[42] The addition of alcohols to alkenes is often catalyzed by metal complexes or Brönsted acid catalysts. These reactions are often competing with hydration in water.[30] Drawbacks with the oxa-Michael addition include the reversibility of the alcohol addition step and the relatively poor nucleophilicity of the alcohols.[43] Acrylic acid esters have been used as Michael acceptors for alcohol nucleophiles. Rehberg *et al.* reported on alcohols reacting with the olefinic linkage of acrylates, using a sodium alkoxide catalyst. Simultaneous addition and hydrolysis occurred in some cases.[44] In another study conducted by Serra *et al.*, acrylated soybean oil reacted with a variety of nitrogen or sulfur nucleophiles. The reaction proceeded under mild conditions in the absence of catalyst.[37]



Scheme 13: *Michael addition of an α,β-unsaturated acrylate ester and a nucleophile (Nu).*

2.4 Scope of Thesis

The objective of the thesis is to achieve a specific degree of crosslinking on a polymer supplied by Jotun AS. In order to tackle that problem, specific materials need to be used that should be “compatible” with industrial manufacturing and up-scaling processes. The degree of the crosslinking is also an unknown variable as this is the first time that this problem has been investigated. Starting materials/emulsions have been synthesized at Jotun AS at the R&D small-scale production line at Sandefjord, during our scientific visit and are provided “as is”. While the general chemical structure of the starting polymers is known, no purification of the product from residual reagents/byproducts is performed as this would interfere with the intended production line. In order to solve this problem, the Diels-Alder reaction conditions were chosen as a facile and scalable route for crosslinking polymers. To that end, a series of suitable and cost-effective crosslinkers have been identified as potential candidates of interest. A clear breaking-down of this project consists in the elucidation the following 3 main categories that each possess a number of variables;

1) Suitable crosslinker
    1a) Feasibility of reaction
    1b) Toxicity of chemical (as this will remain as residual in the paint product)
    1c) Identify the reactivity of a selection of crosslinkers
2) Suitable degree of crosslinking
    2a) Identify an effective and facile characterization technique to provide fast monitoring or reaction progress
    2b) Identify the actual desirable degree of crosslinking for the final product
3) Reaction parameters (time, temperature etc.)
    3a) Identify the effect of the temperature on the degree of crosslinking
    3b) Identify reaction times necessary to provide an adequate degree of crosslinking
    3c) Identify a suitable crosslinker concentration

3 Methods

The main methods utilized for characterization of the modified alkyds include FTIR, NMR and GPC. Pendulum hardness tests were conducted to test the resulting properties of the modified alkyds. The stability of the emulsions were also tested, including the drop size, polydispersity index (PDI) and pH.

3.1.1 FTIR

The acrylates show characteristic peaks at 1635 and 1619 cm^{-1} associated with C=C stretches and at 1407 cm^{-1} associated with alkene C-H bending vibrations (**Table 2**) (see FTIR of acrylate crosslinker in Appendix **A.2**). While the peak at 1619 cm^{-1} overlaps with a signal from the alkyd (**Figure 165**), the peaks at 1635 and 1407 cm^{-1} were well separated and could be used to monitor the reaction progression.

Three parallels were analyzed by FTIR for each reaction mixture. Each analyte was extracted from different locations in the vial in order to get a reliable estimation as well as an indication of the homogeneity of the reaction mixtures. Excess sample was removed from the FTIR crystal prior to the analysis, and the analysis was conducted 1-2 minutes after the sample application to allow for evaporation of any residual solvent.

For simplicity, only one parallel was shown for each reaction mixture. Although several measurements were conducted for each reaction mixture, only some of the samples at different reaction times are shown to give an estimation of the relevant changes which were observed with time.

Table 1: *Selected functional groups and their FTIR frequencies.*[45]

Frequency (cm^{-1})	Signal origin
2975-2950, 2885-2860	CH_3 out-of-phase and in-phase stretches
2936-2915, 2865-2833	CH_2 out-of-phase and in-phase stretches
3100-3000	Aryl CH stretch
3400-3200	OH stretch

Table 2: A selection of FTIR adsorption bands related to alkene vibrations. [45-46]

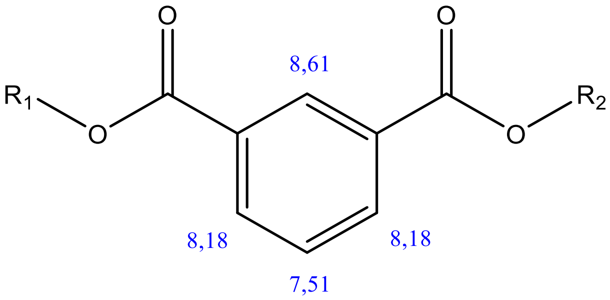
Frequency (cm^{-1})	Signal origin
1667-1640	C=C stretching vibration (unconjugated)
1650, 1600	C=C stretching vibration (conjugated, unsymmetrical)
>3000	Alkene C-H stretching vibration
1420-1400	Alkene CH_2 bend
1000-650	Out-of-plane alkene C-H bending vibration

Table 3: FTIR adsorption bands related to C=O stretches in ketones, aldehydes and esters.[46]

Frequency (cm^{-1})	Signal origin
≈1715	Ketone, saturated and aliphatic
1685-1666	Ketones, conjugated
1740-1720	Aldehydes
≈1760	Carboxylic acids
1720-1706	Carboxylic acids, hydrogen bonded (dimerized)
1710-1680	Carboxylic acids, conjugated
1750-1735	Saturated aliphatic esters
1730-1715	α,β-Unsaturated esters

3.1.2 NMR

^1H NMR was employed as a characterization method to monitor the reaction progression for the acrylate crosslinkers. The acrylates showed signals from the vinylic protons (Appendix **A.2**) which did not overlap with the vinylic protons from the alkyd (Appendix **2.1**), allowing for the reaction to be monitored through the integral of the crosslinker vinylic protons. The aromatic signals from the alkyd (**Scheme 14**) were not expected to change during the reaction and their integral could therefore be used as a reference. This method was limited by solubility of the polymers, excluding measurements at a certain crosslinking density. The maleimide crosslinkers were not soluble in any deuterated solvent, further limiting the method to the acrylate crosslinkers.



Scheme 14: Isophthalic acid in alkyd backbone.

3.1.3 GPC

Size exclusion (SEC) or gel permeation chromatography (GPC) can provide the entire molecular weight distribution of a polymer mixture. SEC is a relative method, and calibration of the instrument is required to establish a relationship between the elution volume and the molecular size. The GPC instruments are often coupled to absolute molecular weight devices, such as laser light scattering.[5] While the measurements conducted at NTNU were limited to the relative method, the measurements conducted at Jotun AS utilized both the relative (conventional) and absolute method. The absolute method might supply more accurate measurements as more detectors than the refractive index (RI) are used.

For the GPC measurements conducted at NTNU with the HPLC-SEC method, some of the polymers showed molecular weights above the separation limit for the column and outside the range of the polystyrene standards (**Figure 3**). This could result in calculated molecular weights lower than the actual molecular weight. Additionally, some of the polymers formed aggregates in THF, which could not be separated using GPC. The aggregates are believed to be of high molecular weight polymers. This could also result in calculated molecular weights below the actual molecular weight.

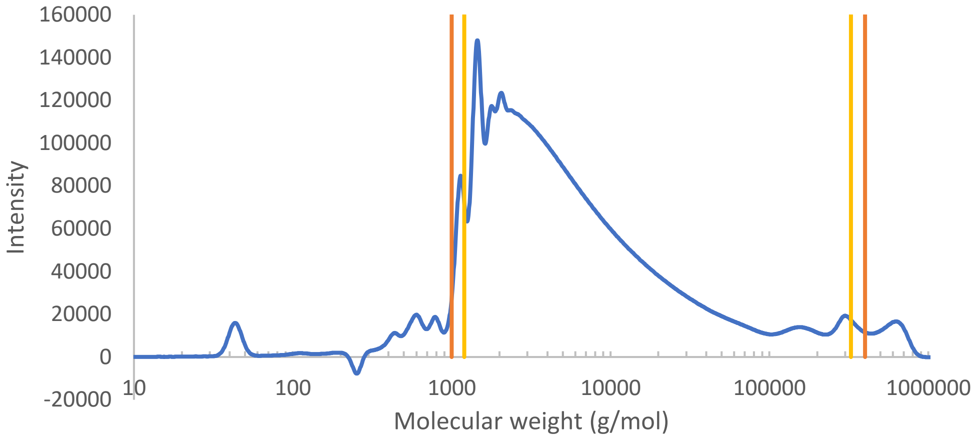


Figure 3: *Chromatogram for emulsion with 20func% 1,1'(methylenedi-4,1-phenylene)bismaleimide (MPB) heated at 80 °C for t=24h. The exclusion limits for the column (orange lines) and standards (yellow line) are shown.*

The polystyrene (PS) standards were analyzed for each set of experiments to get an accurate calibration curve (**Figure 4a**). Including the PS standard with molecular weight of 669 000 g/mol shows that some separation is still achieved (**Figure 4b**) which indicates that some separation can still be achieved despite being outside of the range of the column. However, for the calibration curves, the molecular weight of this standard was excluded. The M_n and M_w were calculated by equations (3.1) and (3.2), respectively.

$$M_n = \frac{\sum_i A_i}{\sum_i \frac{A_i}{M_i}} \tag{3.1}$$

$$M_w = \frac{\sum_i A_i M_i}{\sum_i A_i} \tag{3.2}$$

Where M_i refers to the PS-equivalent molecular weight at measuring point i. Trapezoidal integration is used to calculate the area A_i.[47]

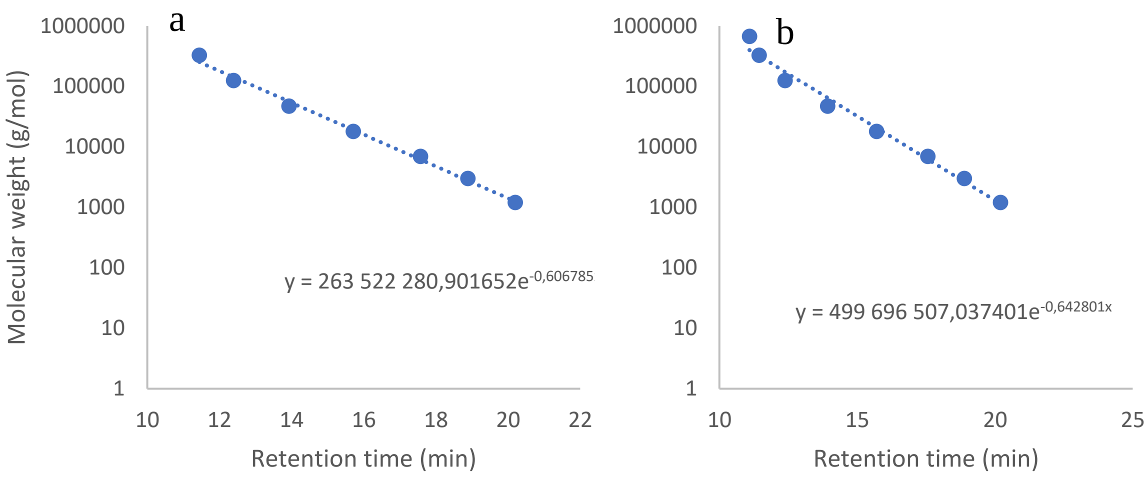


*Figure 4: Standard curve for molecular weight of the polystyrene (PS) standards and retention time, **a)** applied for calculating molecular weights and **b)** including standard with molecular weight 669 000 g/mol.*

The GPC measurements conducted by Jotun AS were commonly conducted using both the conventional and absolute method. The absolute method might supply more accurate measurements as more detectors than the refractive index (RI) are used. For these measurements, the molecular weight was calculated over the entire area. Higher concentration of crosslinker, which have low molecular weights, might therefore affect the average molecular weight, especially M_n. This may also explain the initial decrease in molecular weight observed for the alkyd or alkyd emulsion as the crosslinker is added. For the M_w and M_z, the effect of residual crosslinker is expected to be smaller, as these represent the large molecular weight species to a greater extent. For the calculations of the molecular weight conducted on the GPC at NTNU, limits were applied to exclude the lower molecular weight species (**Figure 5**).

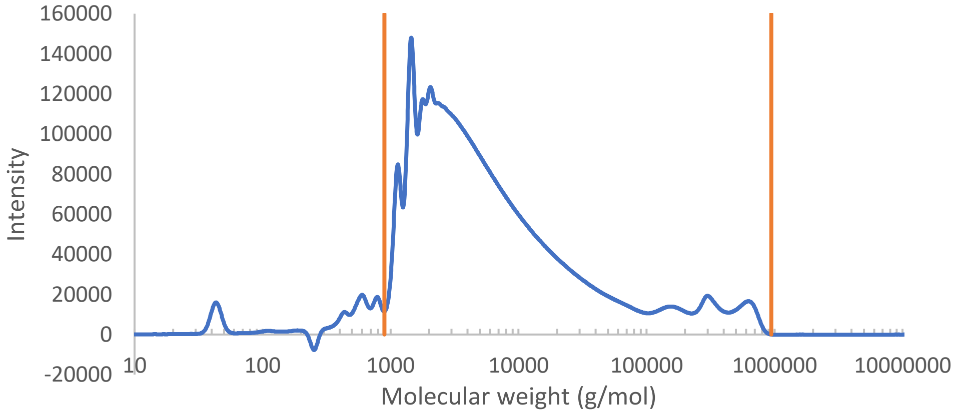


Figure 5: Area over which the molecular weight was calculated.

3.1.4 Drying

The emulsions contain approximately 48wt% water which had to be removed prior to the GPC and NMR measurements. The emulsions were dried using a desiccator and vacuum until the mixtures changed from white to transparent and 38-45wt% had been removed. Different parameters such as the initial sample volume resulted in varying drying times required for the samples. While some samples were dried for t=1 week, others were dried for up t=1.5 months. However, within each set of experiments, the drying time was the same. The emulsion might have reacted during the drying time, either with the crosslinker, oxygen from the air or other side reactions.

The reaction mixtures at the top of each vial were expected to be the most affected by the autoxidation reaction. Therefore, the sample to be analyzed was extracted from the bottom of each vial.

3.1.5 Emulsion Stability Tests

The drop size, polydispersity index of the drop sizes (PDI) and pH were employed as methods to monitor the stability of the emulsions. The drop size and PDI could reveal information whether the crosslinking reaction would occur within the droplets or if the drops were to coalesce.

3.1.6 Pendulum Hardness

The pendulum hardness measures the hardness of the films and is related to the initial molecular weight and the ability of the alkyd mixture to undergo the autoxidation reaction. The hardness commonly increases initially as the solvent evaporates and the autoxidation reactions are initiated. After the completion of the autoxidation reaction, high molecular weight polymeric networks are formed. Observing the initial hardness of the films, prior to the completion of the autoxidation reaction, is expected to reveal the most information regarding the changes attributed to the crosslinking reaction. The hardness can be decreased if the film is affected by the moisture from the environment.

3.2 Reaction Concentrations in Experiments

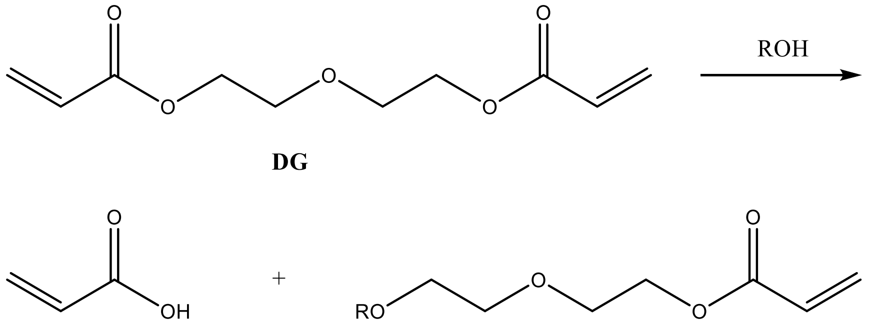
In the preliminary emulsion reactions, the concentration of the crosslinker was determined through the weight percentage (wt%). For the latter experiments, the concentration was calculated based on the number of functional groups in the alkyd and crosslinker (func%) to provide a more accurate representation of the reactive species present. For the alkyd, this included the number of moles of the conjugated fatty acid incorporated in the alkyd. For the crosslinker, this included the number of unsaturated bonds present. The concentration in the initial emulsion experiments is given through both methods to be comparable to the following experiments while only the functional groups concentration is given for the latter reactions.

4 Results and Discussion

For the Diels-Alder reactions between the conjugated fatty acid and the various dienophiles, the temperature was between 120-180 °C, as described in literature.[18, 20, 25, 33-36] The exceptions were the Diels-Alder reactions with modified soybean oils, where the reaction were reported to occur at 50 °C [28] and 30 °C, [37] although the reaction times were significantly longer than the previously reported. [28] For the Diels-Alder reactions between the alkyd resins and dienophiles, the temperatures in all studies were between 150-170 °C. [4, 14] Due to the limited stability of the emulsion and the evaporation of water, the following reactions were subjected to temperatures of 80 °C or lower.

Previous reports include modification of the alkyd by introducing more double bonds to improve curing. [4, 12, 17] This indicates that the dienophiles introduced in the following reactions can improve the curing rate even if only one of the functional groups in the crosslinker react.

Hydrolysis of the ester bonds in the alkyd or in the crosslinker is a possible side reactions and is highly undesirable as it decreases the molecular weight (see Reaction **6**, **Scheme 11**, where R_7=H). Fischer esterification (see **Scheme 12**), on the other hand, can increase the molecular weight. A transesterification reaction (see Reaction **6**, **Scheme 11**, where R_7=alkyd moiety) might increase or decrease the molecular weight of the alkyd, depending on the relative size of the species involved. As the unsaturated bonds are not affected in such reaction, this would not affect the crosslinking reaction. Transesterification (R=alkyd moiety) or hydrolysis (R=H) of the acrylate crosslinker would prevent the crosslinking reaction by reducing the functionality of the crosslinker, illustrated by crosslinker di(ethylene glycol) (DG) (**Scheme 15**).



Scheme 15: Hydrolysis (R=H) or transesterification (R=alkyd moiety) of crosslinker di(ethylene glycol)diacrylate (DG).

Addition of alcohol moieties to unsaturated bonds in the alkyd may occur in acidic conditions and may increase the molecular weight (see Reaction **4**, **Scheme 11**). However, the loss of unsaturated bonds may affect the crosslinking reaction. The Michael addition reactions (see Reaction **1**, **Scheme 11**) between a residual hydroxyl group in the alkyd and an unsaturated bond in the dienophile will serve the purpose of increasing the molecular weight.

The Diels-Alder between alkyd chains (see Reaction **2**, **Scheme 11**) is expected to occur at a lower rate than the Diels-Alder reaction with the crosslinker, due to increased reactivity induced by the EWGs. Although the autoxidative curing is slow without the addition of the catalyst, this may occur to some extent during prolonged heating and exposure to oxygen (see Reaction **5**, **Scheme 11**). The Diels-Alder and autoxidation reaction will increase the molecular weight of the alkyd.

4.3 Reagents

4.3.1 Alkyds and Emulsions

Different alkyds and alkyd emulsions were used throughout the project. Although the reagents and synthetic route were the same for all the resulting polymers and emulsions, small variations could be found (**Table 4** and **Table 5**). In the cases where the properties were measured multiple times over the course of the project, the initial properties are given.

Alkyd MH-5 and emulsion MHE-1 were used for the preliminary reactions (Section **4.4**), MH-5e and MHE-5 were used for the reaction where the crosslinker was added prior to emulsification (CPE) (Section **4.12**), and MH-5mix and MHE-1mix were used for all other reactions (Sections **4.4-4.11**).

Table 4: Molecular weight for the alkyds employed in the projects, analyzed by the conventional method.

	M_n	M_w	M_z
MH-5	2820	15860	92090
MH-5mix	2689	11698	45680
MH-5e	2617	8575	26010

***Table 5**: Initial properties for the alkyd emulsions. The molecular weights were measured with the conventional method.*

	Alkyd	Solid content	Drop size	pH	M_n	M_w	M_z
MHE-1	MH-5	55.68	191.2	8.6	2822*	25920*	170000*
MHE-1mix	MH-5mix	56.49	194.8	8.2	2762*	14731*	73150*
MHE-5	MH-5e	55.6	185	8.3	2720	11225	43260

*Measured 10 months after preparation
**Measured after 6 months

FTIR and ^{1}H NMR spectra of alkyd MH-5mix and emulsion MHE-1 are shown Appendix **A.1**. These are representative for all alkyd and alkyd emulsions employed during this project although small variations might be evident. The FTIR spectra of the conjugated fatty acid used for the alkyd synthesis (Appendix **A.1**) shows a signal at 3006 cm^{-1}, associated with =C-H stretches (see **Table 2**). This peak is also evident in the FTIR spectra of the MH-5mix.

Small variation in properties such as the molecular weight could be affected by increased storage time (**Figure 6**). Properties of the emulsion are also affected by storage time, including drop size (**Figure 7a**), PDI (**Figure 7b**) and pH (**Figure 8**). Some of the properties change more rapidly by exposing the emulsion to higher temperatures (50 °C) such as pH. Measurements of properties such as the pH is also dependent on the temperature in the mixture. Therefore, the properties of the corresponding unreacted alkyd or emulsion were measured simultaneously as the modified polymers, and the measurements of each set of experiments were conducted on the same day.

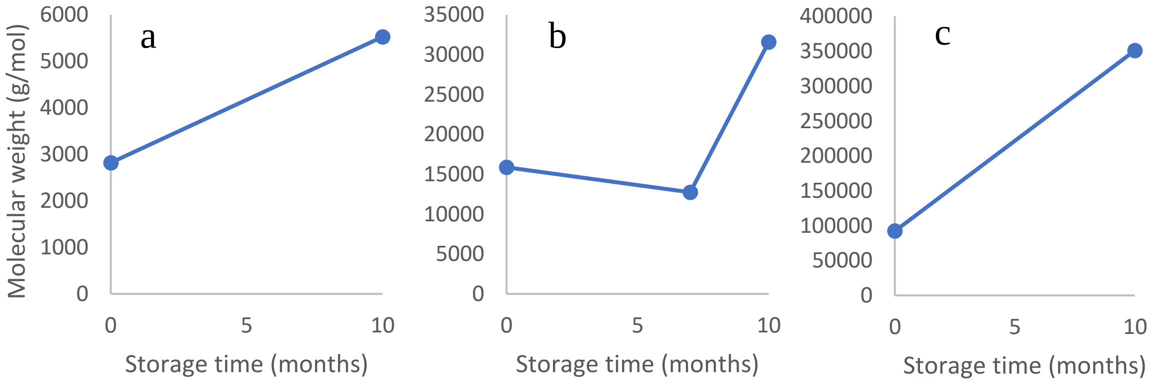


***Figure 6: a)** Number average molecular weight (M_n), **b)** weight average molecular weight (M_w) and **c)** z-average molecular weight (M_z) of alkyd MH-5 initially and after storing for up to 10 months.*

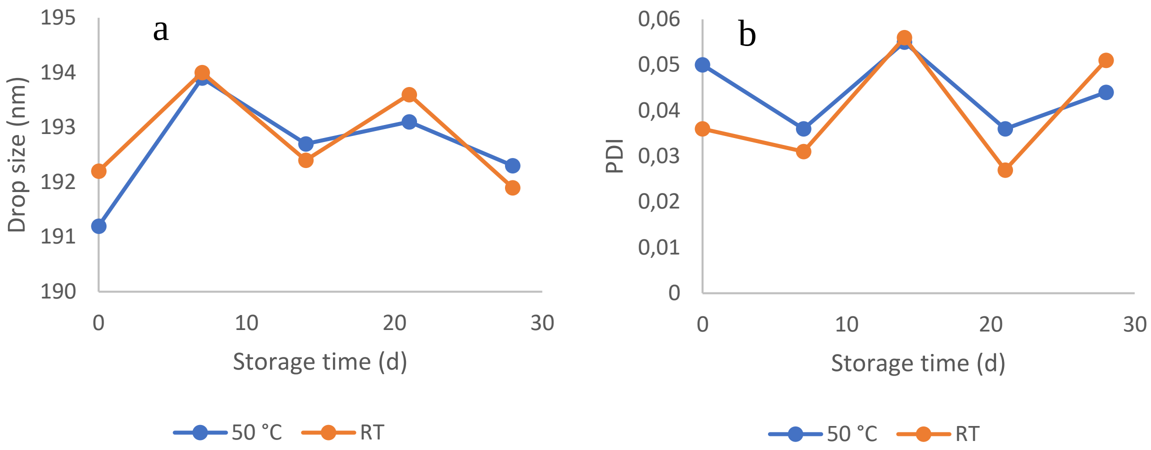


Figure 7: a) *Drop size and* ***b)*** *PDI of emulsion MHE-1 after storing at room temperature (RT) and 50 °C for t=0d, 7d, 14d, 21d and 28d.*

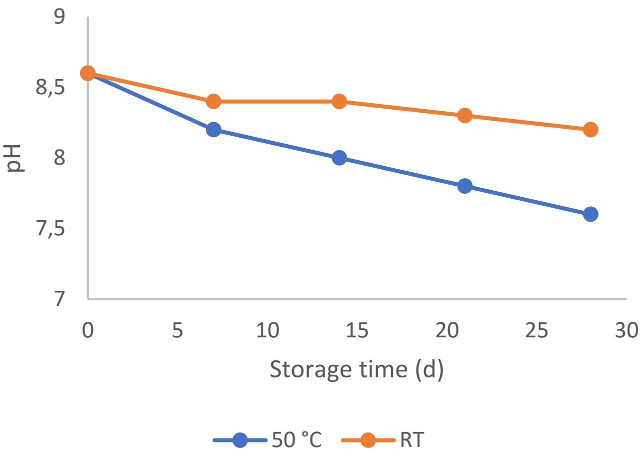
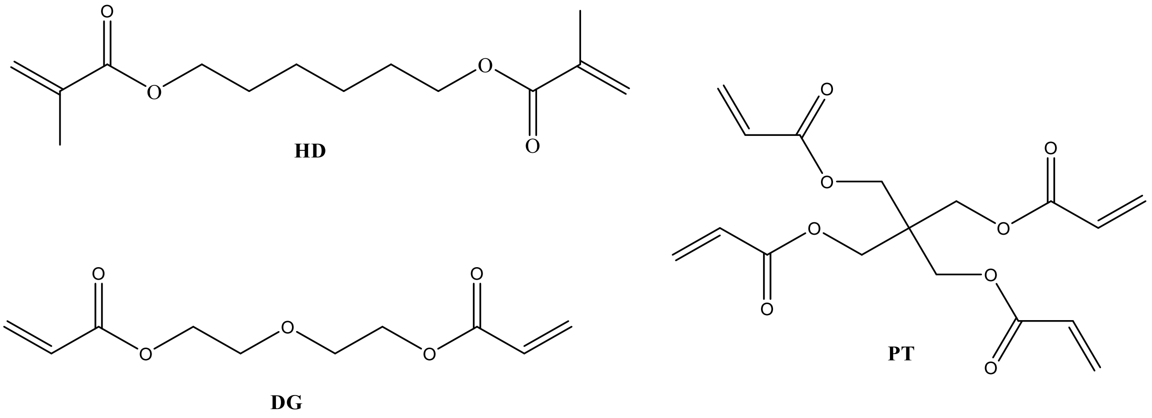


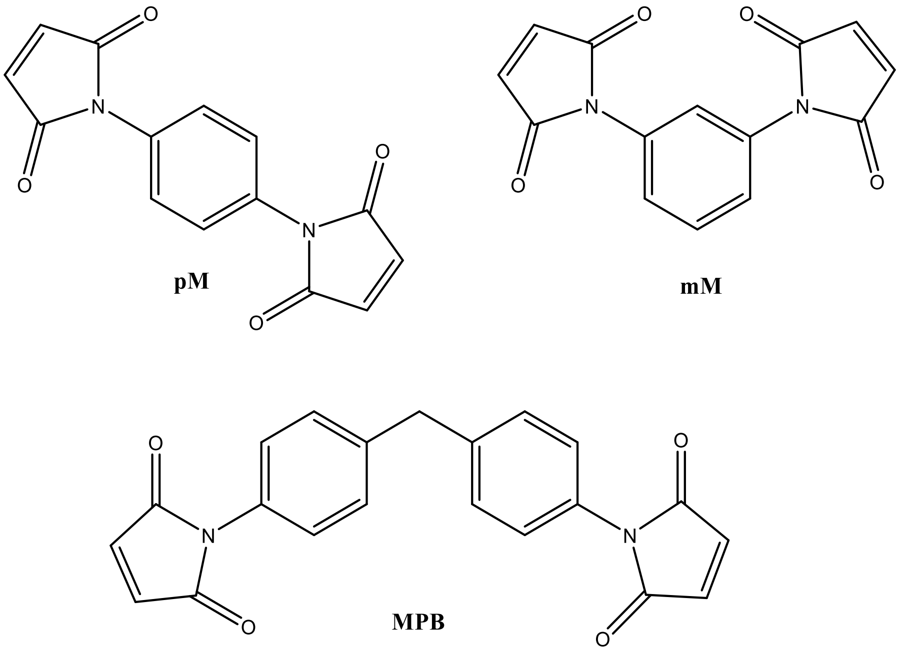
Figure 8: *pH of emulsion MHE-1 after storing at room temperature (RT) and 50 °C for t=0d, 7d, 14d, 21d and 28d.*

4.3.2 Crosslinkers

Over the course of the thesis, several different crosslinkers were tested, including acrylates 1,6-hexanediol diacrylate (HD), di(ethylene glycol)diacrylate (DG) and pentaerythritol tetraacrylate (PT) (**Scheme 16**). Dimaleimide crosslinkers were also employed in the reactions, including dimaleimides N,N'-(1,4-phenylene)dimaleimid (pM), N,N'-(1,3-phenylene)dimaleimid (mM) and 1,1'(methylenedi-4,1-phenylene)bismaleimide (MPB) (**Scheme 17**). The FTIR spectra are shown in Appendix **A.2**. Similar reactivity was expected for pM and mM due to the similarity in structure. Increased reactivity was expected for PT due to the presence of four functional groups compared to two functional groups in the other crosslinkers. The ^{1}H NMR spectra of the crosslinkers whose reactions were monitored through this method, including HD, DG and PT, are shown in Appendix **A.2**.



Scheme 16: *Acrylate crosslinkers, including 1,6-hexanediol diacrylate (HD), di(ethylene glycol)diacrylate (DG) and pentaerythritol tetraacrylate (PT).*



Scheme 17: *Maleimide crosslinkers, including N,N'(1-4-phenylene)dimaleimide (pM), N,N'-(1,3-phenylene)dimaleimide (mM) and 1,1'(methylenedi-4,1-phenylene)bismaleimide (MPB).*

4.4 Preliminary Reactions

The preliminary emulsion reactions were conducted by adding the crosslinker to the alkyd post-emulsification while the crosslinker was added post-emulsification in the preliminary alkyd reactions. The emulsion was used “as is” from Jotun AS and this series of reaction was conducted to acclimate ourselves with the reaction as well as explore viable ways to monitor its progress. The most powerful tool available to track a reaction in real time was FTIR. This series of experiments provided valuable experience in working with polymerization reactions, trained us in the use of characterization techniques and sharpened our problem solving skills in approaching an unknown area with limited hands-on knowledge in our arsenal. More importantly, it exposed some of the more serious obstacles we need to overcome such as proper real time characterization, residual chemicals in the starting material and possible side-reactions. The interested reader can find the entire characterization discussion and relevant FTIR/NMR/GPC spectra in Appendix **B**.

The observations in the preliminary emulsion reactions, including visual changes and FTIR, were attributed to evaporation of water which occurred more readily in small batches. The signal from water overlapped with the areas of interest in FTIR, restricting this method to reaction monitoring in the absence of water. Other characterization methods were employed for the further reactions. ^{1}H NMR was successfully employed to show a reduction in the vinylic crosslinker peaks in a reaction mixture consisting of emulsion and 1wt% HD after heating at 80 °C for t=24h. It also showed residual crosslinker in this mixture, indicating that the reaction time was not sufficient for a complete conversion of the crosslinker.

GPC was employed as a characterization method. Loss of solubility in THF at long reaction times (t>23h) for reaction mixture with 1 or 2wt% HD were observed, indicating that the crosslinking reactions were successful. While the molecular weight was improved by the addition of crosslinker (HD or pM) and heating in some experiments, the opposite was observed in others. Such contradicting trends were also observed regarding reaction time in reaction mixtures with the same crosslinker concentrations. The decreases in molecular weight could indicate competing reaction such as hydrolysis occurring (see Reaction **6**, **Scheme 11**). However, this could not be verified due to the incoherent trends. It could also be related to the solubility of the reaction mixtures, as high molecular weight fractions could be filtered out prior to measurements. There were, however, indications that increasing the reaction time to t>20 min was beneficial to obtain increased molecular weights. There was no clear correlation between the molecular weight and crosslinker concentration, although there are indications proving it beneficial to increase the concentration from 1wt% to 5 or 3wt%.

Prior to the GPC and NMR measurements, the emulsion reaction mixtures were dried, exposing the samples to oxygen which could result in the autoxidation reaction occurring. This would increase the molecular weight at could potentially “mask” the effects introduced by the crosslinker.

Conducting experiments with the alkyd prior to emulsification allowed for a facile reaction monitoring through FTIR using crosslinker PT. GPC confirmed an increase in molecular weight for the reaction mixture of alkyd and 10wt% PT after heating at 80 °C for t=16h. Gelation and loss of solubility was encountered in the reaction mixture with alkyd and 10wt% mM after heating at 80 °C for t=16h, indicating a higher crosslinking density and reactivity compared to the PT mixture. However, the solubility of mM proved challenging in the alkyd pre- and post-emulsification, and the reaction could not be monitored through FTIR. No significant changes were observed in FTIR as the pure alkyd was subjected to heating nor in the reaction mixtures of alkyd and PT or mM stored in room temperature (RT).

4.5 Crosslinker and Temperature Study

For the following study, the reactivity of the different crosslinkers including acrylates HD, DG and PT and dimaleimide pM were compared by using the model system with the alkyd. Equal amounts of reactive groups in the crosslinkers (50func%) were employed in the reactions (**Table 6**). Two temperatures were tested, 60 and 80 °C and the reaction mixtures were also monitored in RT.

__Table 6__: Amount of alkyd, conjugated fatty acid (cFA) and concentration (c) of crosslinkers 1,6-hexanediol diacrylate (HD), di(ethylene glycol)diacrylate (DG), pentaerythritol tetraacrylate (PT) and N,N'-(1,4-phenylene)dimaleimide (pM). Reaction time and temperature (T) are also presented.

		Alkyd		**Crosslinker**				
Exp.nr	**Weight (g)**	**Alkyd (mmol)**	**cFA (mmol)**	**Crosslinker (mmol)**	**Weight (g)**	**c (func%)**	**Reaction time (d)**	**T (°C)**
A03	10.017	4.1171	10.909	HD (5.476)	1.239	50.10	7	80
A04	10.004	4.1118	10.8949	DG (5.4393)	1.1652	49.96	7	80
A05	10.006	4.1126	10.8970	PT (2.756)	0.971	50.29	7	80
A06	9.990	4.1060	10.8796	pM (5.455)	1.463	50.07	7	80
A09	5.014	2.061	5.461	HD (2.889)	0.631	50.53	12	60
A10	4.998	2.054	5.443	DG (2.768)	0.593	50.42	7	60
A11	5.021	2.064	5.468	PT (1.362)	0.480	49.91	7	60
A12	2.498	1.027	2.720	pM (1.365)	0.366	50.08	7	60
A09*	5.014	2.061	5.461	HD (2.889)	0.631	50.53	14	RT
A10*	4.998	2.054	5.443	DG (2.768)	0.593	50.42	14	RT
A05*	10.006	4.1126	10.8970	PT (2.756)	0.971	50.29	21	RT
A06*	9.990	4.1060	10.8796	pM (5.455)	1.463	50.07	21	RT

*initial sample prior to heating was stored in room temperature (RT)

The initial alkyd reactions (**Section 4.4**) with crosslinker PT indicated that FTIR could be used to monitor the reaction progression, and this was extrapolated to the other acrylate crosslinkers. As mentioned previously, three parallels were analyzed with FTIR from different areas in the vial. Large variations were observed for some of the samples, indicating that the reaction mixtures were not homogeneous (see peak at 1406 cm^{-1} in **Figure 9**). As the mixtures were not stirred throughout the reaction, this could lead to local variations of the crosslinker concentration throughout the sample. This could result in the crosslinking reaction occurring to varying extents. For simplicity, only the first parallel is shown for each sample, as it is expected to give an indication of the reaction progression.

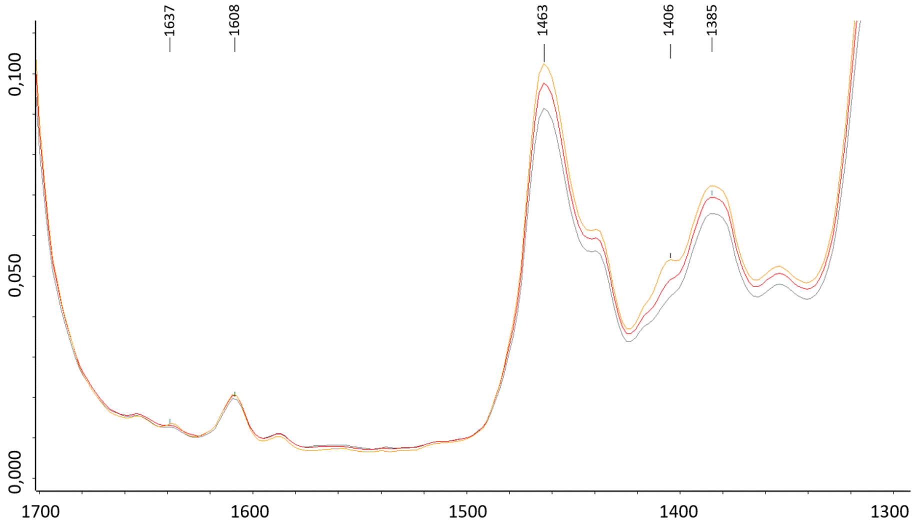


Figure 9:*FTIR spectra of three parallels of the reaction mixture of alkyd and 50func% di(ethylene glycol)diacrylate at t=7d.*

^{1}H NMR was run for selected samples to monitor the reactions and provide a quantitative method. For the 60 °C samples, NMR was measured immediately. For the 80 °C samples, NMR was run after storing the samples in room temperature for up to t=3 weeks. The reaction could have continued during this time, however, FTIR later indicated that the reaction did not occur, or occurred at a much slower rate in RT. NMR was not run for the initial mixtures before heating to 80 °C, but the initial mixtures prepared for the 60 °C mixtures were used as a reference points as the concentration should be the same. Since pM did not dissolve in any deuterated solvents, it was not possible to use the same method to monitor the progression of this crosslinker. The time required to obtain visual changes i.e. gelation time can also be used as an indication of the reaction progression although the visual observations are much less accurate as a method. The gelation time is estimated as the time prior to and after the visual changes were first observed.

The mixture with HD did not show any significant changes in FTIR in RT (**Figure 10**). The decrease in the acrylate peaks in FTIR occurs faster at the elevated temperature, indicating that the rate of the reaction is increased by heat (**Figure 11**). FTIR shows the presence of unreacted crosslinker after heating for t=1 week although smaller amounts are observed at the elevated temperature. The increase in reactivity is further demonstrated by NMR (**Figure 12**). Gelation occurred after t=46-60h at the highest temperature, and after t=7-12d at 60°C.

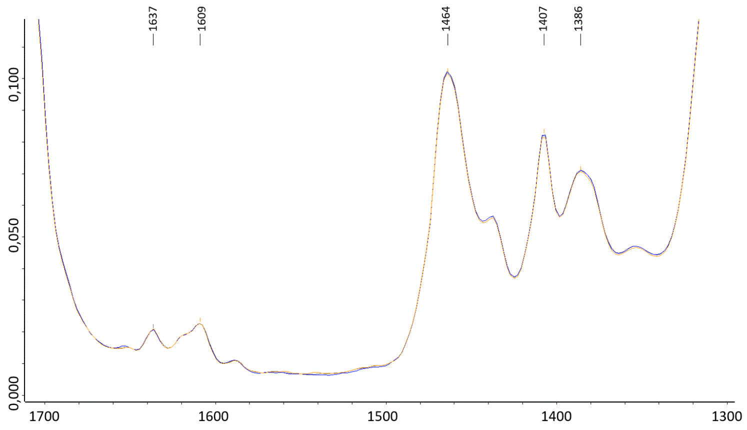


***Figure 10**: FTIR spectra of alkyd with 50func% 1,6-hexanediol diacrylate (HD) at t=0h, 1 week and 2 weeks in room temperature (RT).*

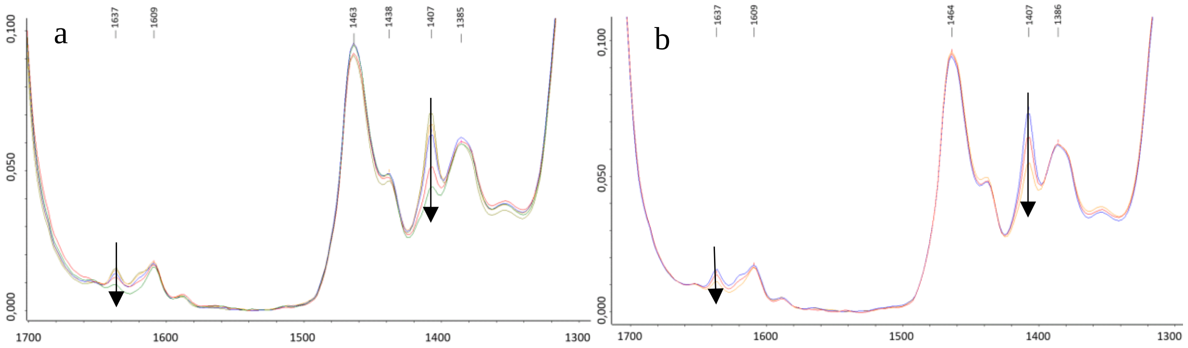


***Figure 11**: FTIR spectra of alkyd with 50func% 1,6-hexanediol diacrylate (HD) at **a)** 80 °C at t=0h, 27h, 46h, 3d and 7d and **b)** 60 °C at t=0h, 7d and 12d.*

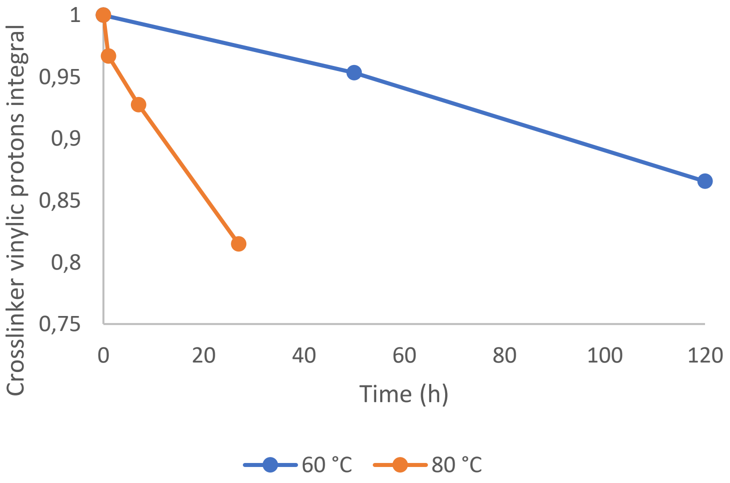


***Figure 12**: Decrease in the vinylic proton integral from the crosslinker in reaction mixture of alkyd with 50func% 1,6-hexanediol diacrylate (HD) after heating at 60 or 80 °C. Peak at 8.61 ppm was used to normalize the spectra integrals.*

FTIR showed no any indication of the reaction happening in RT in the DG reaction mixture (**Figure 13**). FTIR and NMR demonstrates the increased reactivity as the temperature was increased (**Figure 14** and **Figure 15**, respectively). FTIR indicated that most of the crosslinker had reacted within t=1 week at 80 °C (**Figure 14a**). Unlike the previous ^{1}H NMR plot, an increase in the integral between t=1h and t=7h is observed for the mixture heated at 80 °C (**Figure 15**). This could be due to the mixture being inhomogeneous, causing an uneven distribution of the crosslinker throughout the alkyd. Gelation was observed after heating for t=27-46h at 80 °C and after t=5-7d at 60 °C.

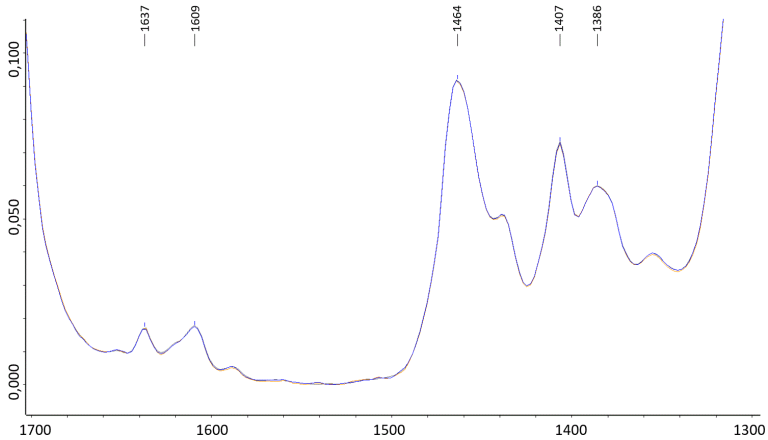


***Figure 13**: FTIR spectra of alkyd and 50func% di(ethylene glycol)diacrylate (DG) after t=0h, 1 week and 2 weeks at room temperature (RT).*

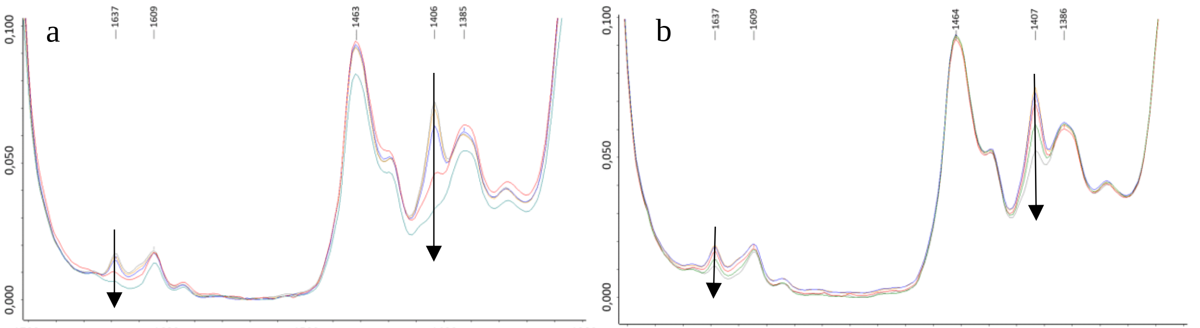


***Figure 14:** FTIR spectra of alkyd and 50func% di(ethylene glycol)diacrylate (DG) at **a)** 80 °C at t=0h, 5h, 22h, 3d and 7d and **b)** 60 °C at t=0h, 24h, 50h, 5d and 7d.*

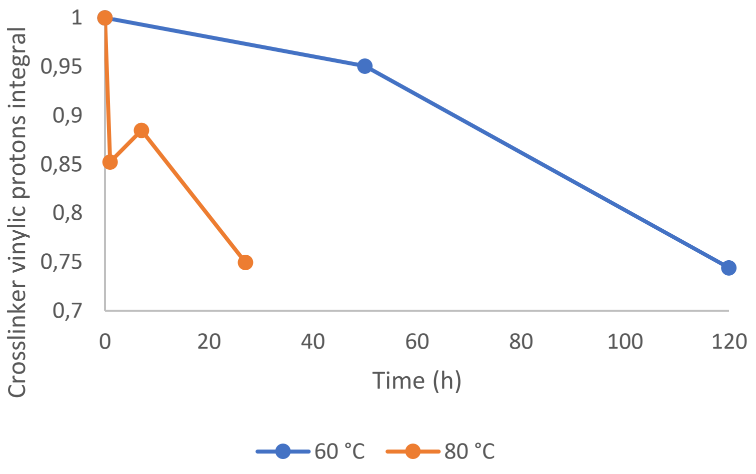


Figure 15: *Decrease in the vinylic proton integral from ^{1}H NMR for crosslinker di(ethylene glycol)diacrylate in the reaction mixture of alkyd and 50func% DG after heating at 60 or 80 °C. Peak at 8.61 ppm was used to normalize the spectra integrals.*

The PT mixture did not seem to react in RT (**Figure 16**). After heating for t=1 week at 80 °C, FTIR indicated that most of the crosslinker had reacted (**Figure 17a**), while there was still some unreacted crosslinker present at t=1 week at 60 °C (**Figure 17b**). NMR further demonstrates the increased rate observed as the temperature is increased (**Figure 18**). Gelation was observed after t=6-24h at 80 °C, and after t=32-53h at 60 °C.

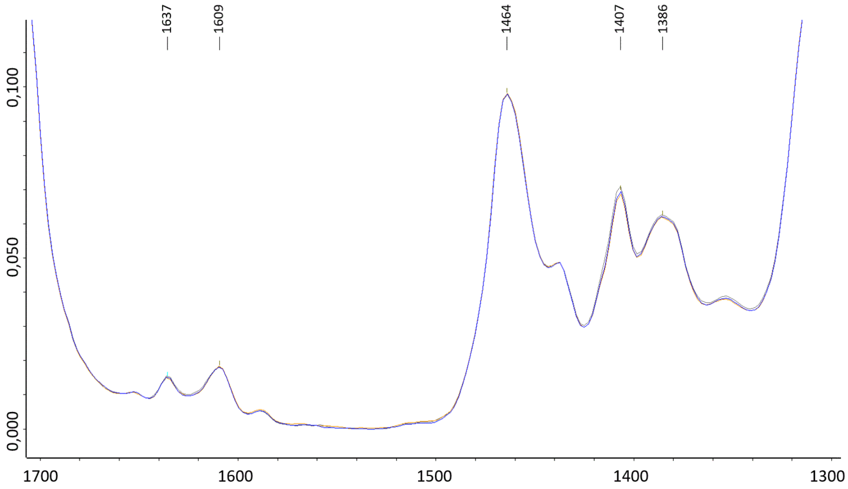


Figure 16*: FTIR spectra of alkyd and 50func% pentaerythritol tetraacrylate (PT) after t=0h, 1 week and 3 weeks at room temperature (RT).*

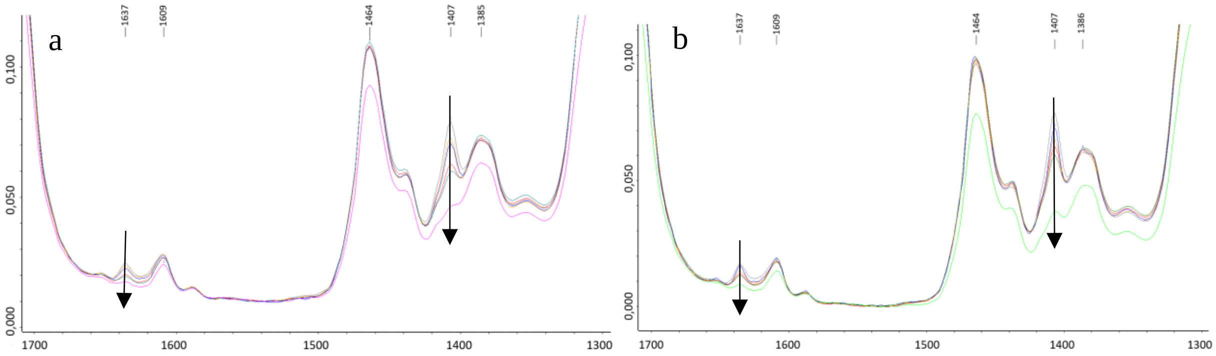


Figure 17*: FTIR spectra of alkyd and 50func% pentaerythritol tetraacrylate (PT) at* ***a)*** *80 °C at t=0h, 4h, 6h, 1d, 3d and 7d and* ***b)*** *60 °C at t=0h, 5,5h, 53h, 3d and 7d.*

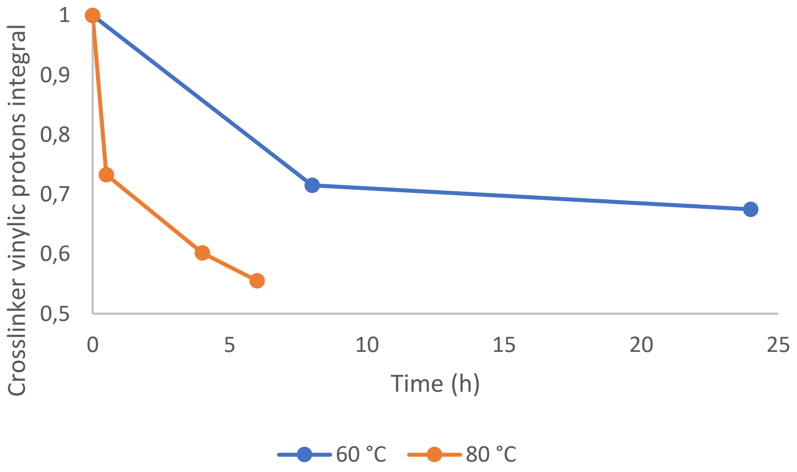


Figure 18: *Decrease in the vinylic proton integral from ^{1}H NMR for crosslinker pentaerythritol tetraacrylate (PT) in the reaction mixture of alkyd and 50func% PT after heating at 60 or 80 °C. Peak at 8.61 ppm was used to normalize the spectra integrals.*

In the previous experiments with alkyd and mM, no trends were observed in FTIR to indicate that the crosslinking reaction occurred. Instead, it seemed as characteristic crosslinker peaks appeared as the crosslinker became more soluble. As mentioned previously, pM was expected to show similar reactivity as mM, and therefore similar trends were expected in FTIR. In the 50func% pM mixture, peaks were observed at 1519, 1390 and 1375 cm^{-1} (**Figure 20a**). These peaks were expected to be due to the strong signals from the crosslinker (see FTIR spectra of pM in **Figure 173**) which do not overlap with the signals from the alkyd (see FTIR spectra in **Figure 165**). Simultaneously, a shift in the carbonyl peak was observed (**Figure 20b**), which was also expected to be due to the carbonyl peak from the crosslinker. The appearance of the characteristic crosslinker peaks indicates that the crosslinker became more soluble during the reaction time. The differences are more pronounced at 80 °C (**Figure 20**) compared to 60 °C (**Figure 21**), indicating that the crosslinker solubilizes faster at elevated temperatures. Small changes are observed at RT (**Figure 19**) although to a much smaller extent than at higher temperatures. Gelation occurred after t=20-44h at 80 °C, and after t=2-6d at 60 °C, indicating that a crosslinking reaction also occurs. Since FTIR provided no information about the crosslinking reaction progression, the only indication of any reaction occurring is achieved through viscosity changes.

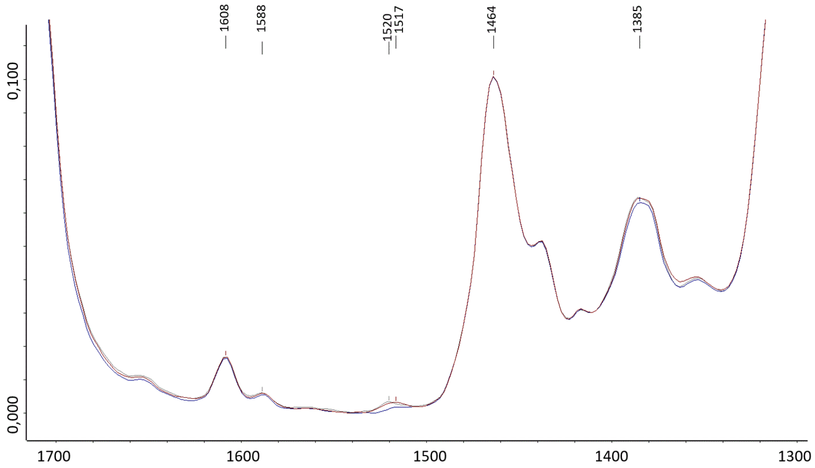


Figure 19: *FTIR spectra of 50func% N,N'-(1,4-phenylene)dimaleimide (pM) and alkyd after t=0h, 1 week and 3 weeks at room temperature (RT).*

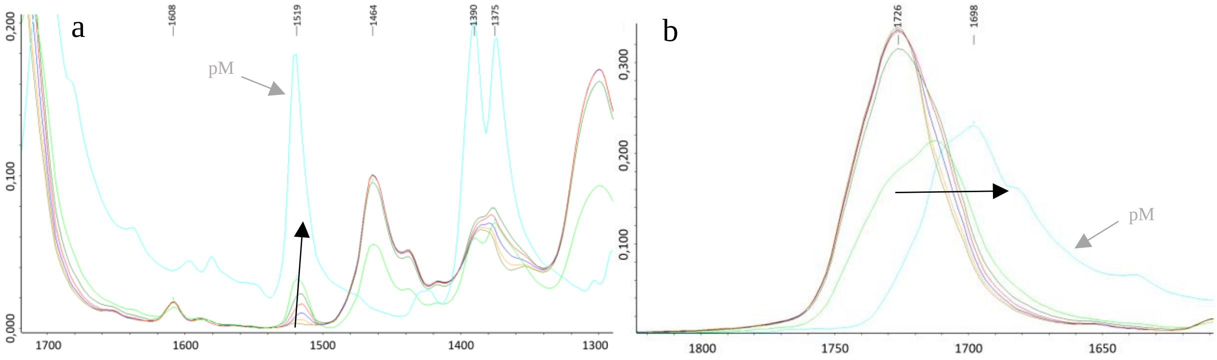


Figure 20*: FTIR spectra of N,N'-(1,4-phenylene)dimaleimide (pM) and 50func% pM and alkyd mixture after t=0h, 3h, 9h, 20h, 44h and 7d at 80 °C in the* ***a)*** *vinylic proton region and* ***b)*** *carbonyl region.*

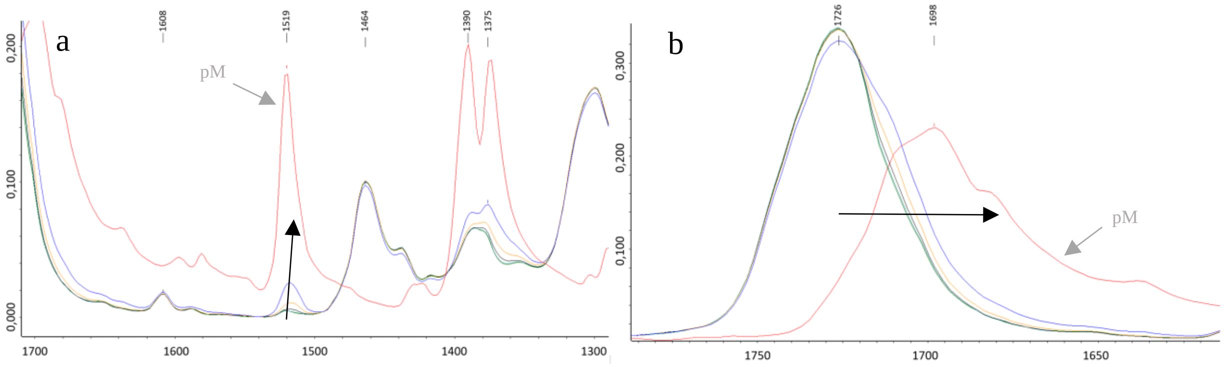


Figure 21: *FTIR spectra of N,N'-(1,4-phenylene)dimaleimide (pM) and 50func% pM and alkyd mixture after t=0h, 3h, 20h, 44h and 7d at 60 °C in the* ***a)*** *vinylic proton region and* ***b)*** *carbonyl region.*

^{1}H NMR indicates that there are still large amounts (50-80%) of residual crosslinker left in all the samples prior to the reaction mixtures becoming insoluble.

The reactivity of the crosslinkers can be compared through FTIR, NMR and estimated gelation time while comparisons with the pM mixture is limited to comparison of gelation time. The gelation time indicates that the highest reactivity is obtained by PT while the lowest reactivity is obtained by HD at both temperatures (**Figure 22**). The decrease in the vinylic peaks in FTIR and NMR further demonstrates the highest reactivity for PT, followed by DG, and, lastly, HD, at both temperatures.

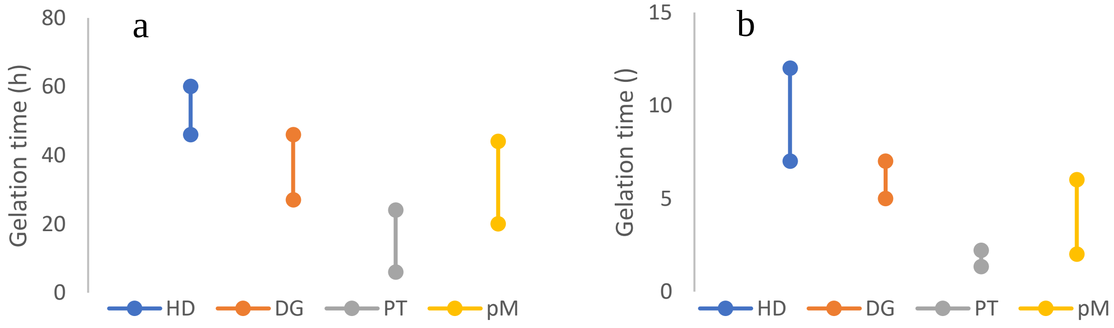


Figure 22*: Estimated gelation time for alkyd and 50func% 1,6-hexanediol diacrylate (HD), di(ethylene glycol)diacrylate (DG), pentaerythritol tetraacrylate (PT) or N,N'-(1,4-phenylene)dimaleimide (pM) when heated to* ***a)*** *80 °C and* ***b)*** *60 °C.*

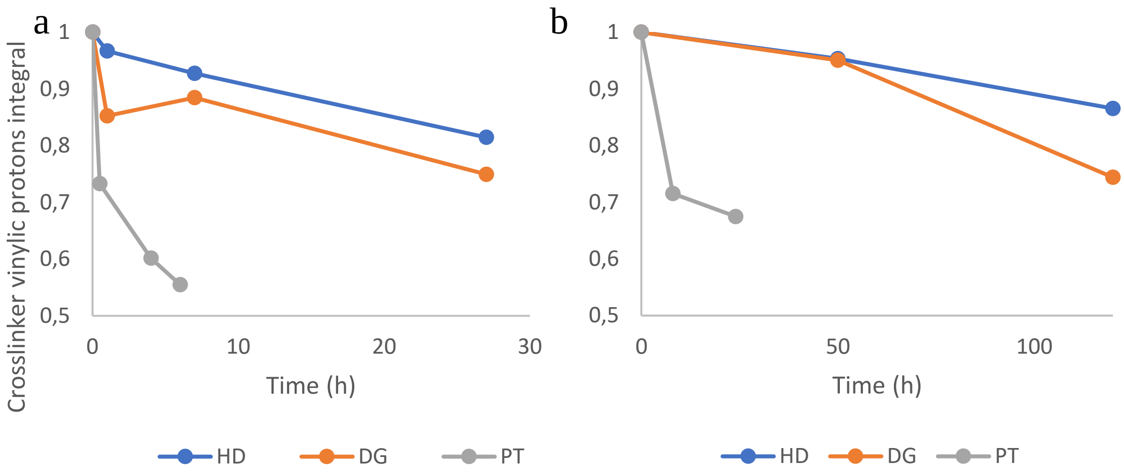


*Figure 23: Decrease in the vinylic proton integrals from ^{1}H NMR for crosslinkers 1,6-hexanediol diacrylate (HD), di(ethylene glycol)diacrylate (DG) and pentaerythritol tetraacrylate (PT) when heated to **a)** 80 °C and **b)** 60 °C. Peak at 8.61 ppm was used to normalize the spectra integrals.*

Selected samples were also analyzed by GPC. However, for the reaction mixture containing HD, the sample was left in RT for approximately one month prior to the measurement. The mixture might have reacted to some extent during this time. For the pM mixtures, a solid film had formed on the surfaces after being stored in RT prior to the measurements, and the reaction mixtures were no longer soluble. Therefore, the molecular weights of any pM mixtures could not be analyzed. This could be due to the reaction continuing at RT, autoxidation or due to the initial sample volume extracted for storing being too small.

Based on the gelation time, FTIR spectra and ^{1}H NMR plots, further analysis were conducted with DG and PT (Section **4.6**). These reaction mixtures were chosen for further GPC analysis. The conditions were identical to the conditions for HD but did not involve the long storage time. These reaction mixtures were expected to show a more accurate representation of the molecular weight.

As the crosslinking density was expected to increase with increasing reaction times, the samples with the longest reaction times which were still soluble in THF were chosen for the GPC analysis. This was expected to represent the largest molecular weight achieved for each crosslinker within the solubility limit. For the HD mixture this was at t=27h, for the DG mixture t=22h, and for PT t=13h. The loss of solubility after shorter reaction times, especially for the PT mixture, indicates a higher crosslinking density and hence higher reactivity.

Increases in molecular weight was observed for all the reaction mixtures, proving the crosslinking reaction successful (**Figure 24**). Since different reaction times were used, the crosslinkers could not be compared directly at constant reaction times. However, the plot combined with the loss of solubility could be used as an indication of reactivity. The M_n indicates similar reactivity for the HD and DG crosslinkers during t≤13h while a larger increase in the M_n is observed for PT. The M_n further increases for the HD crosslinker at t=27h while the reaction mixture with the DG crosslinker loses solubility after t=13h, indicating that a higher crosslinking density was achieved. Similar molecular weight is observed for DG at t=12h as for PT at t=8h, further confirming the trend observed by the other measurements, with the highest reactivity for PT, followed by DG and, lastly, HD.

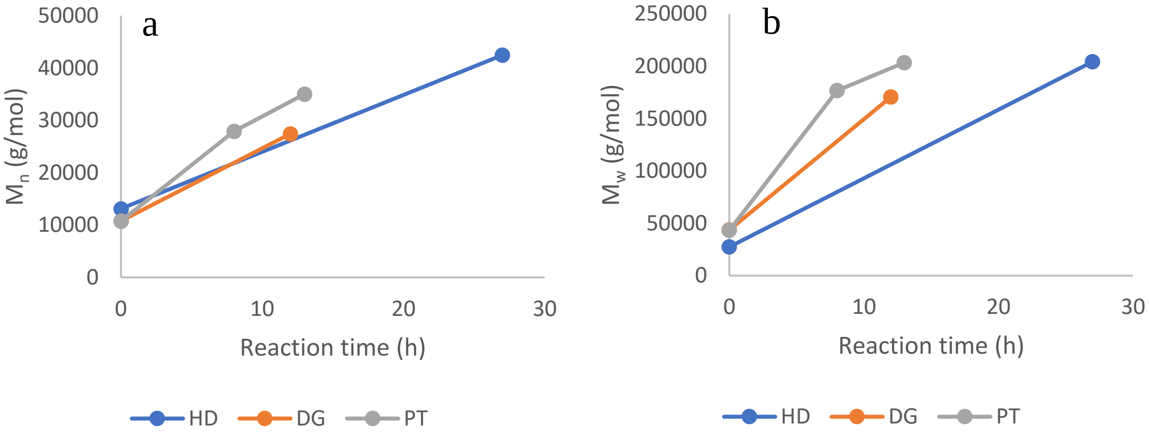


Figure 24: a) *Number average molecular weight (M_n) and* ***b)*** *weight average molecular weight (M_w) of emulsion with 50func% 1,6-hexanediol diacrylate (HD), di(ethylene glycol)diacrylate (DG) or pentaerythritol tetraacrylate (PT).*

The RT reactivity was further investigated with NMR. Since PT showed the highest reactivity among the crosslinkers, the reaction mixture tested was the mixture with 50func% PT. If the other crosslinkers were to react at RT, the decrease in the vinylic protons from the crosslinkers were expected to be smaller than for PT. Slight fluctuations in the amount of crosslinker are observed during t=3 weeks and is likely due to an uneven distribution of the crosslinker.

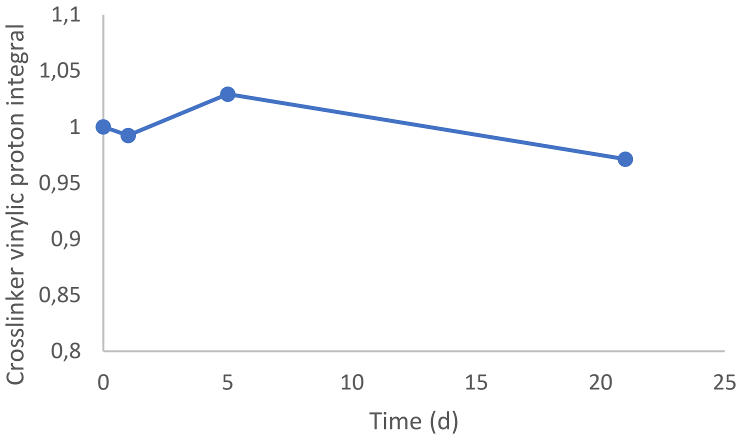


Figure 25: *Decrease in the vinylic proton integrals from ^{1}H NMR for alkyd with 50func% pentaerythritol tetraacrylate (PT) after storing the mixture in room temperature (RT) for t=0d, 1d, 5d and 3 weeks. Peak at 8.61 ppm was used to normalize the spectra integrals.*

4.6 Crosslinker Concentration Study

Based on the previous results, the conditions that resulted in the highest reaction rate was 80 °C using crosslinkers PT or DG. These conditions were therefore employed in further experiments, where the effect of the concentration was investigated. Three different concentrations (50, 33 and 20func%) of each crosslinker were tested based on the amount of reactive species (**Table 7**). The reactions were stopped when gelation occurred in the sample with the highest concentration. The reactions were tracked with FTIR and ^{1}H NMR, and GPC was run for some of the samples. It should be noted that the intensity of the peaks from the crosslinkers at lower concentrations, especially 20func%, are initially so weak that tracking the progression through FTIR does not provide sufficient information.

__Table 7__: Amount of alkyd, conjugated fatty acid (cFA) and concentration (c) of crosslinkers di(ethylene glycol)diacrylate (DG) and pentaerythritol tetraacrylate (PT), and reaction time.

		Alkyd			**Crosslinker**		
Exp.nr	**Weight (g)**	**Alkyd (mmol)**	**cFA (mmol)**	**Crosslinker (mmol)**	**Weight (g)**	**c (func%)**	**Reaction time (h)**
A13DG	11.935	4.9055	12.9978	DG (6.535)	1.400	50.14	31
A14DG	12.575	5.1685	13.6948	DG (3.384)	0.725	33.08	31
A15DG	13.181	5.4176	14.3548	DG (1.825)	0.391	20.27	31
A16PT	12.379	5.0880	13.4813	PT (3.292)	1.160	49.42	26
A17PT	12.668	5.2067	13.7961	PT (1.842)	0.649	34.81	26
A18PT	12.372	5.0851	13.4737	PT (0.826)	0.291	19.69	26

The sample with the highest concentration of DG was observed to solidify after t=22-31h. FTIR spectra (**Figure 26**) and NMR spectra (**Figure 27a**) show the decrease in the characteristic crosslinker peaks. In order to compare the reactivity of the different concentrations through NMR, the estimated amount in grams that has reacted is shown in **Figure 27b**. The functions show different trends; in the 20 and 33func% DG mixture, a more rapid reaction rate is observed for the first few hours before evening out, and then the rate is increased again. In the 50func% DG mixture, the rate appears more linear, except for the initial measurements where the plot indicates that the amount of crosslinker that has reacted decreases. The differences observed could be due to an uneven distribution of the crosslinker, especially since only one parallel was run for each mixture. The lowest reaction rate is achieved with 20func%. The data in this set of experiments might not be completely reliable due to the inhomogeneous mixtures. However, there are indications that increasing the concentration affects the reaction rate proportionally.

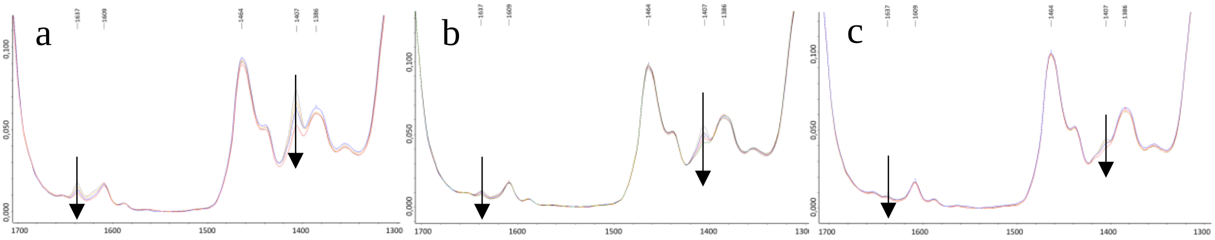


__Figure 26:__ FTIR spectra of alkyd with __a)__ 50func% di(ethylene glycol)diacrylate (DG) at t=0h, 12h, 22h and 31h, __b)__ 33func% DG at t=0h, 4h, 12h, 22h and 31h, and __c)__ 20func% DG at t=0h, 4h, 22h and 31h.

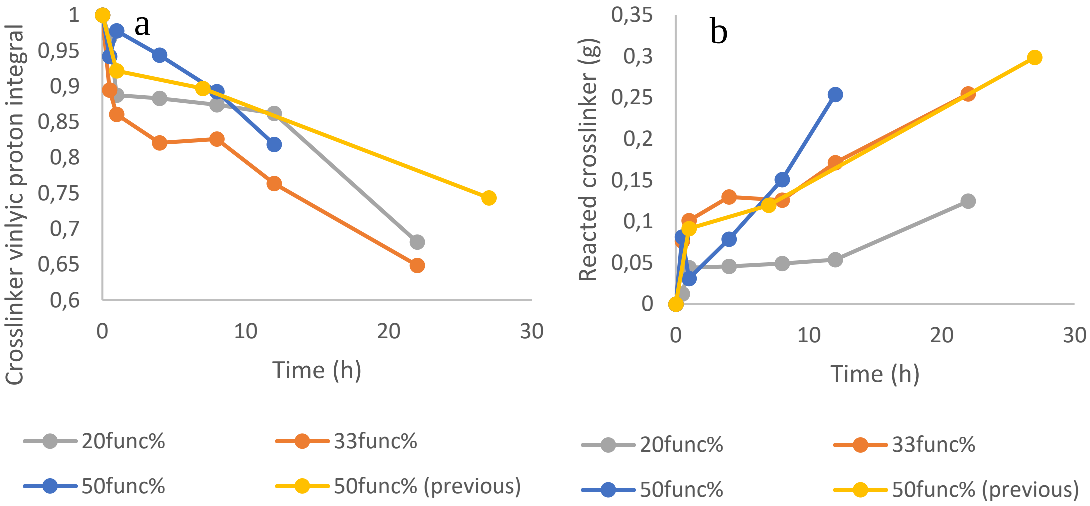


__Figure 27:__ Decrease in the vinylic proton integral for different concentrations of di(ethylene glycol)diacrylate (DG) from the __a)__ vinylic proton integral from ^{1}H NMR, and __b)__ amount in grams that has reacted based on initial amount and the decrease in the vinylic proton integral. Peak at 8.61 ppm was used to normalize the spectra integrals.

The M_n and M_w were calculated and are shown in **Figure 28**. Although the t=0h sample was not analyzed with GPC for the 33func% and 20func% DG, they are expected to be similar to the 50func% since the calculation exclude the low molecular weight of the crosslinker. The molecular weight increases proportionally to the reaction time and concentration. The 50func% DG mixture did not dissolve at t=22h, indicating a higher crosslinking density compared to the lower concentrations.

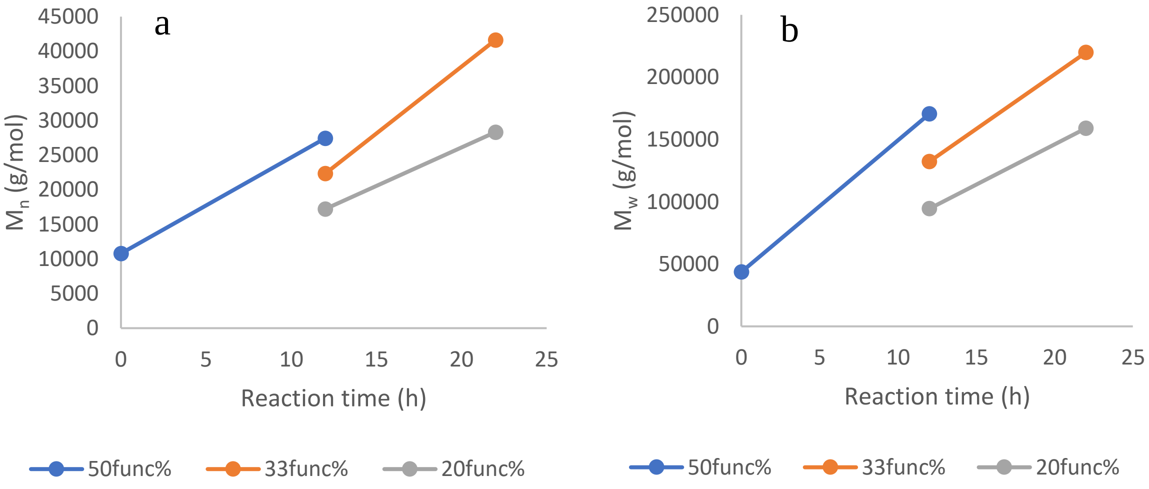


__Figure 28: a)__ Number average molecular weight (M_n) and __b)__ weight average molecular weight (M_w) after heating alkyd with 50func% di(ethylene glycol)diacrylate (DG) for t=0h and 12h, 33func% DG for t=12h and 22h and 20func% DG for t=12h and 22h at 80 °C.

The mixture with the highest concentration of PT solidified after t=13-26h. Decreases in the characteristic vinylic peaks were observed in FTIR (**Figure 29**) and NMR (**Figure 30**). **Figure 30b** shows the amount of crosslinker that has reacted (in grams) as a function of time for each of the mixtures. The lack of stirring could explain the behavior observed for the mixture containing 33func% PT, causing an uneven distribution of the crosslinker. For the other two concentrations, NMR indicated that the reaction rate was proportional to the concentration.

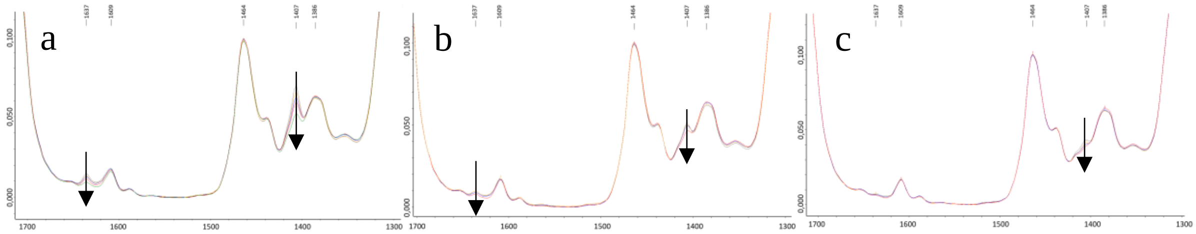


Figure 29: *FTIR spectra of alkyd and* ***a)*** *50func% pentaerythritol tetraacrylate (PT) at t=0h, 2h, 8h, 13h and 26h,* ***b)*** *33func% PT at t=0h, 8h, 13h, and 26h, and* ***c)*** *20func% PT at t=0h, 8h, 13h and 26h.*

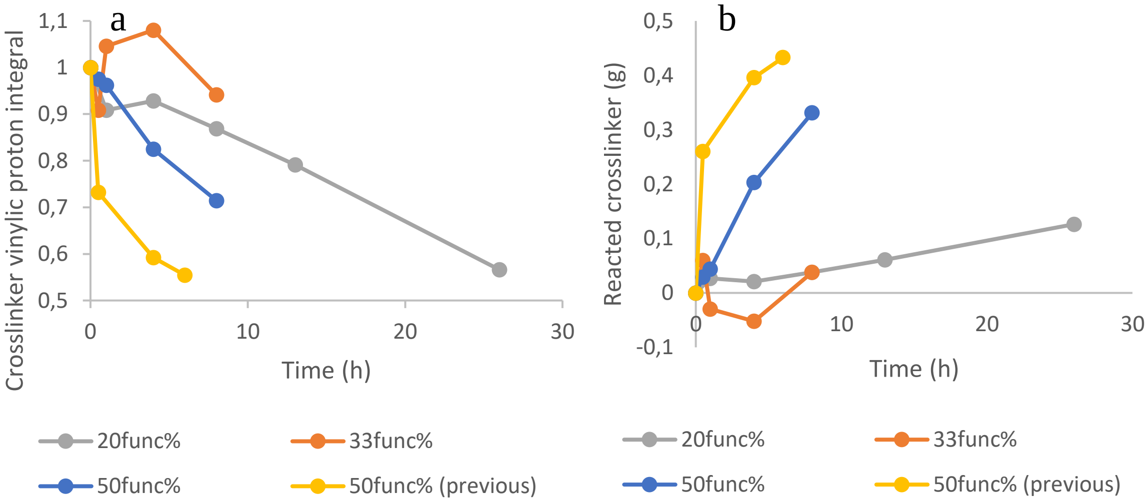


Figure 30: *Decrease in the vinylic proton integral for different concentrations of pentaerythritol tetraacrylate (PT) from the* ***a)*** *vinylic proton integral from ^{1}H NMR, and* ***b)*** *amount in grams that has reacted based on initial amount and the decrease in the vinylic proton integral. Peak at 8.61 ppm was used to normalize the spectra integrals.*

The M_n and M_w were calculated for all the samples (**Figure 31**). As with the DG reaction mixtures, the t=0h was only measured for the 50func% mixture but the lower concentrations are expected to initially have similar molecular weights. The molecular weight increased proportionally to the reaction time for all samples. The increase in molecular weight is smallest for the lowest crosslinker concentration. The higher concentrations, 33func% and

50func%, show similar M_n and M_w. However, the chromatograms (**Figure 32**) indicate that a larger share of high molecular weight polymer is formed at the highest concentration of crosslinker. The increased reactivity is further demonstrated by obtaining a larger molecular weight for the higher concentrations at lower reaction times (t=13h) compared to 20func% at longer reaction times (t=26h).

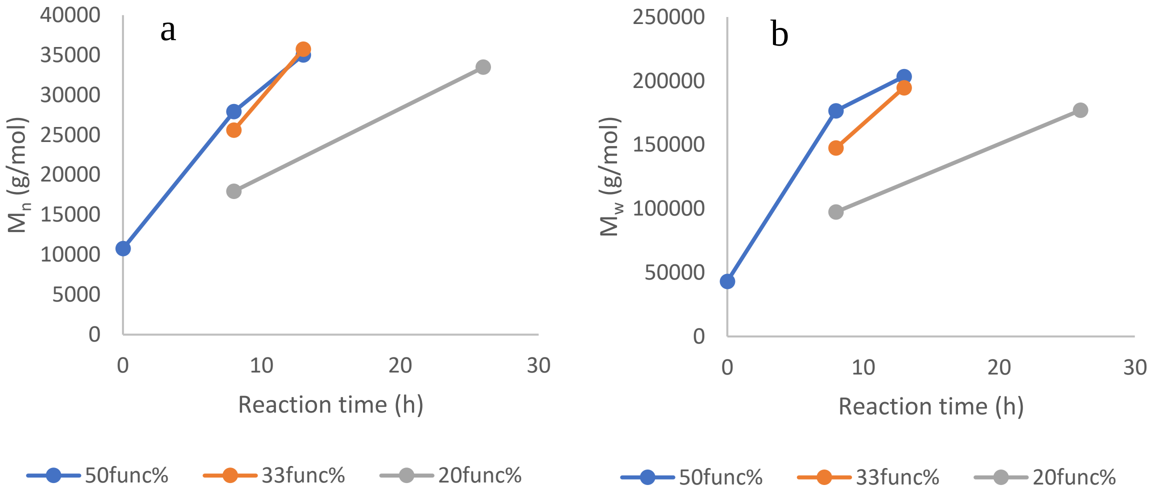


*Figure 31: **a)** Number average molecular weight (M_n) and **b)** weight average molecular weight (M_w) after heating alkyd with 50func% pentaerythritol tetraacrylate (PT) for t=0h, 8h and 13h, 33func% PT for t=8h and 13h and 20func% PT for t=8h and 26h at 80 °C.*

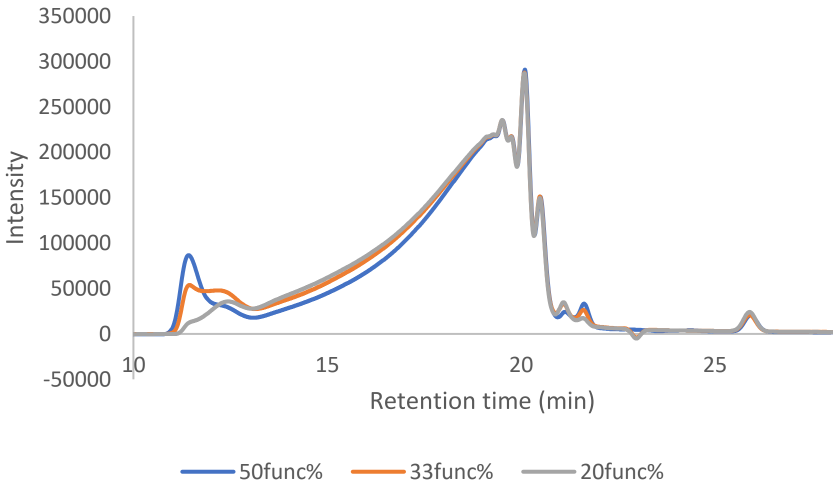


***Figure 32**: GPC chromatograms for alkyd and 50, 33 and 20func% pentaerythritol tetraacrylate (PT) at t=8h.*

The effect of increasing the concentration of either crosslinker is summarized in **Table 8**. FTIR was applied as a qualitative method and was limited to revealing whether the reaction occurred. The observations obtained from FTIR were in coherence with the results obtained from NMR. NMR has the additional benefit of providing a qualitative measurement of reactivity. Both methods were applied to monitor the reactivity of the crosslinker and are therefore limited by the inhomogeneous distribution of the crosslinker. For the following reactions, NMR and GPC were applied as the main methods for analysis while the FTIR measurements were discontinued.

Table 8: *Effect of increasing the concentration of di(ethylene glycol)diacrylate (DG) or pentaerythritol tetraacrylate (PT) based on methods FTIR, NMR, GPC and observed physical changes.*

	Increasing DG concentration	**Increasing PT concentration**
FTIR	Inconclusive	Inconclusive
NMR vinylic protons	↓*	Inconclusive
Molecular weight	↑	↑*
Physical changes	↑	↑

*evident for 50 and 33func% compared to 20func%

Comparing the results obtained from the ^{1}H NMR for the 50func% samples with the previously obtained results, it is evident that there is a low degree of repeatability. This could, as mentioned earlier, be due to the lack of stirring, allowing for non-uniformity in the reaction mixture. Another observation is that only small amounts of the crosslinker is reacting within the given time frame as was observed in the previous set of experiments (Section **4.5**). For the highest concentrations, only 18% of DG and 28% of PT has reacted before the mixture becomes insoluble. However, if the concentration is lowered, this would also affect the reaction rate (**Figure 27** and **Figure 30**) and molecular weight produced (**Figure 28** and **Figure 31**).

In the previous section (Section **4.5**), the gelation time, FTIR and ^{1}H NMR indicated that PT reacted faster than DG. For the crosslinker concentration study, ^{1}H NMR further confirms this trend for the 50func% (**Figure 33a**) mixtures while the 20func% mixtures show similar reactivities (**Figure 33b**). The reactivities of the 33func% mixtures (**Figure 33c**) cannot be stated with certainty due to the incoherent trend observed for PT.

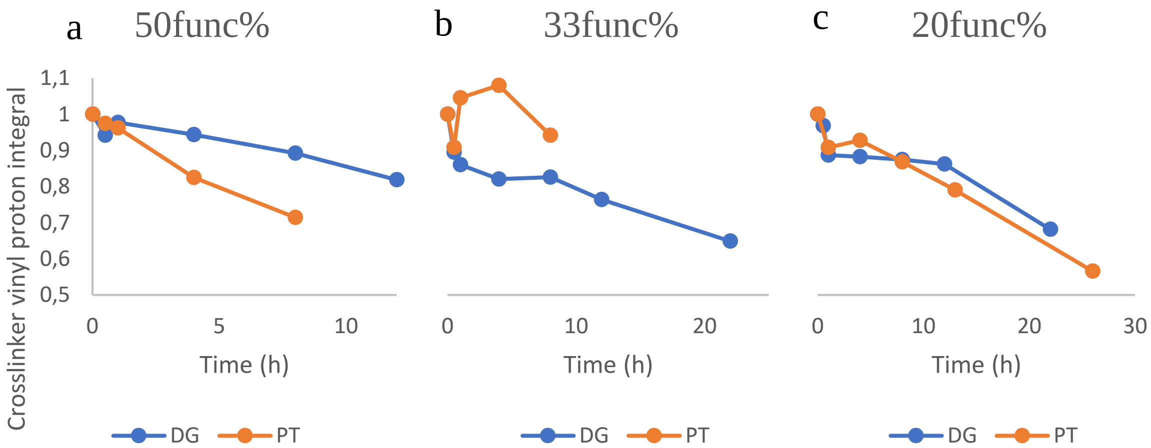


*Figure 33: Decrease in the ^{1}H NMR vinylic proton integral from crosslinkers di(ethylene glycol)diacrylate (DG) and pentaerythritol tetraacrylate (PT) using concentrations **a)** 50func%, **b)** 33func%, and **c)** 20func%. Peak at 8.61 ppm was used to normalize the spectra integrals.*

The molecular weight was only measured for a few of the reaction times which limits the accuracy of the molecular weight plots for comparison purposes. For the 50func% reaction mixtures, the largest molecular weight appears to be achieved using PT compared to DG (**Figure 34**). Increased reactivity for PT is further demonstrated for the 33func% and 20func% reaction mixture (**Figure 35** and **Figure 36**, respectively), where larger or similar molecular weights are achieved using the PT crosslinker for shorter reaction times (t=8h) than using DG (t=12h).

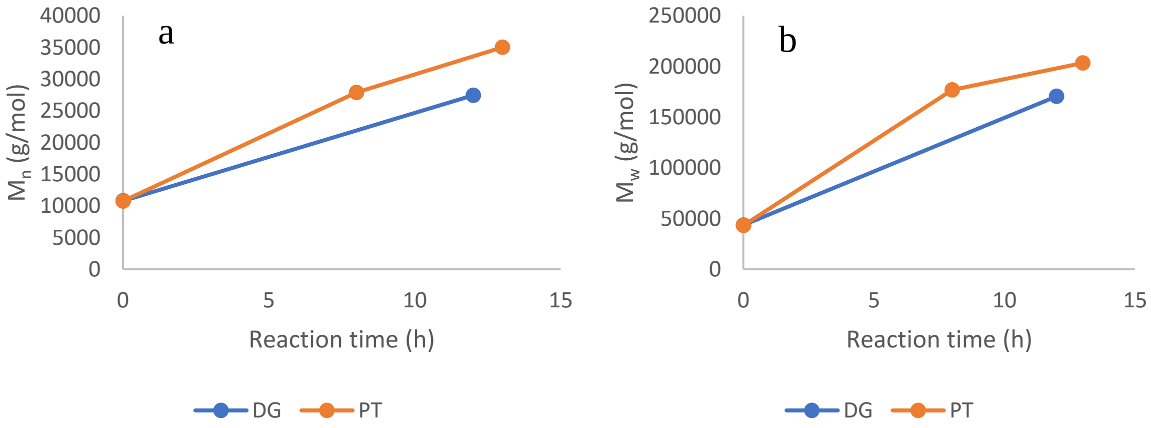


*Figure 34: **a)** Number average molecular weight (M_n) and **b)** weight average molecular weight (M_w) after heating alkyd with 50func% pentaerythritol tetraacrylate (PT) for t=0h, 8h and 13h or 50func% di(ethylene glycol)diacrylate (DG) for t=0h and 12h at 80 °C.*

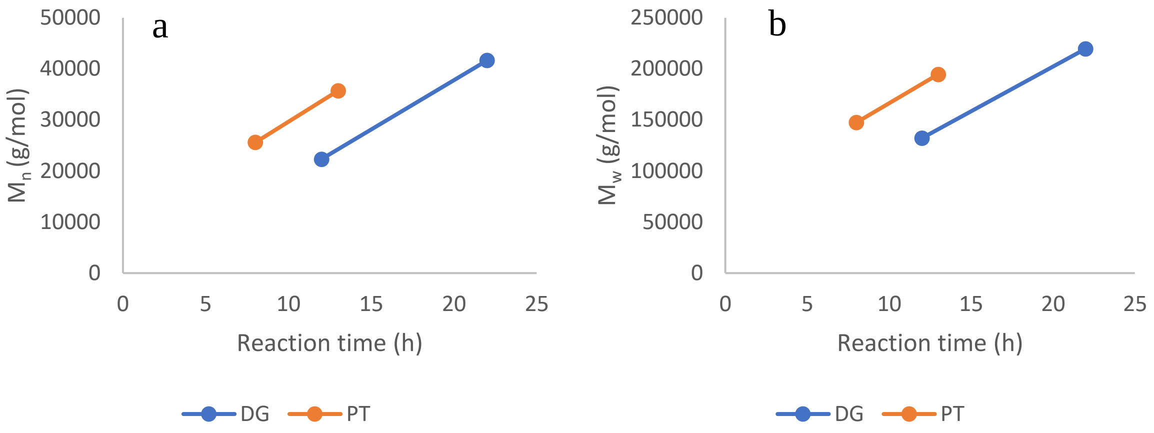


*Figure 35: a) Number average molecular weight (M_n) and **b)** weight average molecular weight (M_w) after heating alkyd with 33func% pentaerythritol tetraacrylate (PT) for t=8h and 13h or 33func% di(ethylene glycol)diacrylate (DG) for t=12h and 22h at 80 °C.*

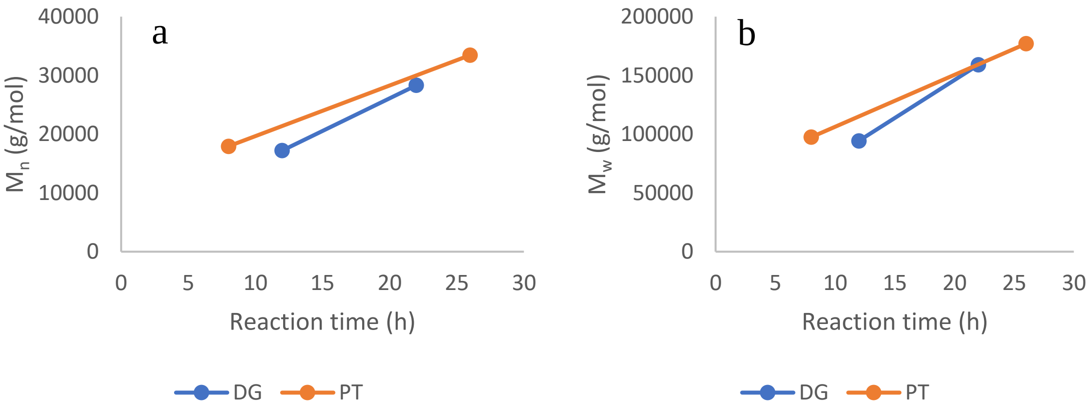


*Figure 36: a) Number average molecular weight (M_n) and **b)** weight average molecular weight (M_w) after heating alkyd with 33func% pentaerythritol tetraacrylate (PT) for t=8h and 26h or 33func% di(ethylene glycol)diacrylate (DG) for t=12h and 22h at 80 °C.*

4.7 Effect of Sonication/Stirring

Due to the incoherent trends observed, the effect of stirring was also investigated, using ^{1}H NMR as the characterization method of choice to probe the reaction kinetics. Each of the following samples contained 50func% PT (**Table 9**). All samples were thoroughly stirred prior to heating as this was believed to be one of the reasons for the differences in the plot, demonstrated in the entries marked as “previous” in **Figure 37**. Each of the samples were subjected to bath-sonication, mechanical stirring or no stirring during the reactions.

***Table 9**: Amount of alkyd, conjugated fatty acid (cFA) and concentration (c) of crosslinker pentaerythritol tetraacrylate (PT) in reactions subjected to no stirring, sonication and mechanical stirring.*

	Alkyd			**Crosslinker**			
Exp.	**Weight (g)**	**Alkyd (mmol)**	**cFA (mmol)**	**Crosslinker (mmol)**	**Weight (g)**	**c (func%)**	**Reaction time (h)**
Bath-sonicated	5.050	2.076	5.500	PT (1.416)	0.499	50.74	13
No stirring	5.013	2.060	5.459	PT (1.365)	0.481	50.01	12
Mechanical stirring (open system)	5.057	2.079	5.507	PT (1.331)	0.469	49.16	6
Mechanical stirring (N_2)	5.014	2.061	5.461	PT (1.340)	0.472	49.53	9
No stirring (open system)	4.999	2.055	5.444	PT (1.368)	0.482	50.13	8

Two experiments were run simultaneously to ensure identical reaction conditions. One of the samples was bath-sonicated for 45 seconds every half hour for the first t=3h, then hourly for t=12h. Samples for NMR were taken randomly from each vial. Perhaps contrary to expected results, NMR indicated that the sonication did not affect the reaction rate.

The effect of constant mechanical stirring was also investigated. However, NMR indicated that this lowered the reaction rate. In previous experiments, the system’s access to air was limited. It was suspected that the difference in reaction rate could be due to autoxidation reaction occurring (see Reaction **5**, **Scheme 11**) instead of the Diels-Alder reaction with the crosslinker. The reaction was repeated under inert atmosphere (N_2 “blanket-mode” gas). NMR still indicated a reduced reaction rate. The reaction was repeated with the same conditions, without stirring, and NMR indicated the same increased reaction rate as observed previously for the samples not subjected to stirring. Without stirring, the decrease in the proton integrals appear linear while a more uneven progression is observed with stirring.

Although the stirring-assisted series of experiments would be expected to yield some noticeable improvements in the reaction rate, this was not the case. All the reactions rates were decreased or remained unaffected. While this trend is extremely difficult to explain, it can be hypothesized that the heat introduced in the system *via* heating is enough to promote the reaction and disperse the crosslinker throughout the reaction volume. The kinetic energy *via* stirring evidently does not facilitate the specific monitored reaction.

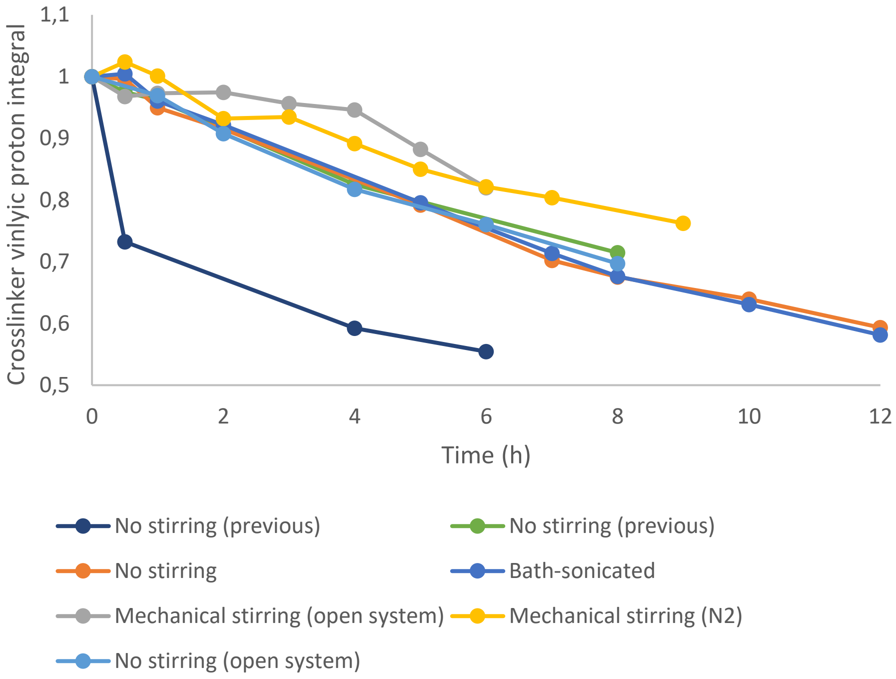


Figure 37: *^{1}H NMR plot for samples containing 50func% pentaerythritol tetraacrylate (PT) with various modifications to the reaction system. Peak at 8.61 ppm was used to normalize the spectra integrals.*

4.8 Emulsion and Alkyd Comparison

4.8.1 Emulsion with 50func% Pentaerythritol tetraacrylate (PT) and di(Ethylene glycol)diacrylate (DG)

Upon using our simplified alkyd mixtures pre-emulsification we were successful in developing a basic working model and verify that crosslinking reactions had occurred. These methods and conditions were further extrapolated into the alkyd post-emulsification. In the following reactions, emulsion and 50func% PT or DG were heated to 80 °C for t=12h (**Table 10**). The reactions were monitored with ^{1}H NMR after the removal of water.

***Table 10**: Amount of emulsion. alkyd. conjugated fatty acid (cFA) and concentration (c) of crosslinkers pentaerythritol tetraacrylate (PT) and di(ethylene glycol)diacrylate (DG).*

		Emulsion		**Crosslinker**		
Exp.nr	**Weight (g)**	**Alkyd (mmol)**	**cFA (mmol)**	**Crosslinker (mmol)**	**Weight (g)**	**c (func%)**
E01PT	15.038	3.1782	8.4211	PT (1.368)	0.482	48.59
E02DG	15.005	3.1712	8.4026	DG (4.262)	0.913	50.36

NMR showed a decrease in the vinylic protons from DG and PT, approximately 15% and 14% respectively (**Figure 38**) after heating for t=12h. The reactions seemed to occur at a faster rate initially and then reach a plateau after the first couple of hours. PT seemed to react slightly faster than DG, a trend also encountered for the alkyd reactions series of experiments (**Figure 23** and **Figure 33**).

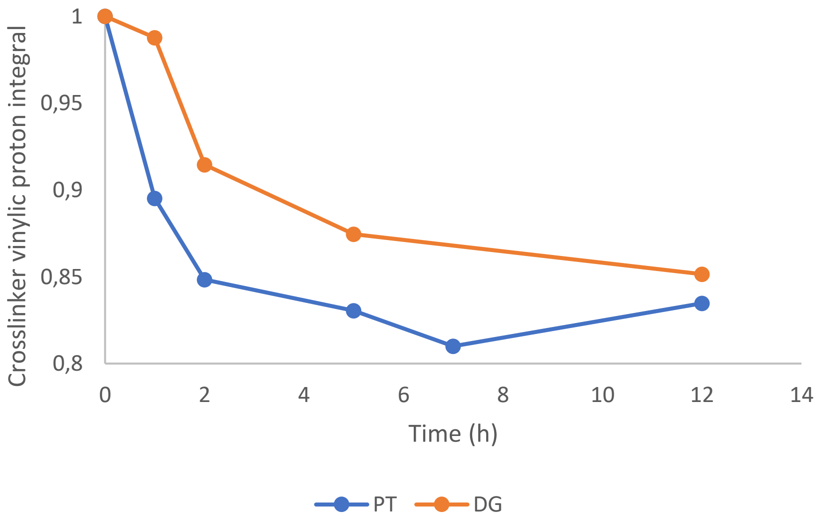


***Figure 38**: Decrease in vinylic crosslinker peaks from NMR for emulsion and 50func% pentaerythritol tetraacrylate (PT) or di(ethylene glycol)diacrylate (DG). Peak at 8.61 ppm was used to normalize the spectra integrals.*

The reaction mixtures were analyzed by GPC at t=0h, 5h and 12h. A relatively large difference in the retention time for the PS standards and the parallels for the analytes was observed. Therefore, two calibration curves were calculated, and the molecular weight of the analytes was calculated using both calibration curves. The average molecular weight is shown in **Figure 39**. At t=12h, the molecular weight is increased for both crosslinkers compared to the initial mixtures. At t=5h, the molecular weight is increased in the PT mixture while this is not observed for the DG mixture. The largest molecular weight at t=5h is therefore obtained by the PT mixture while at t=12h, DG produces a larger molecular weight.

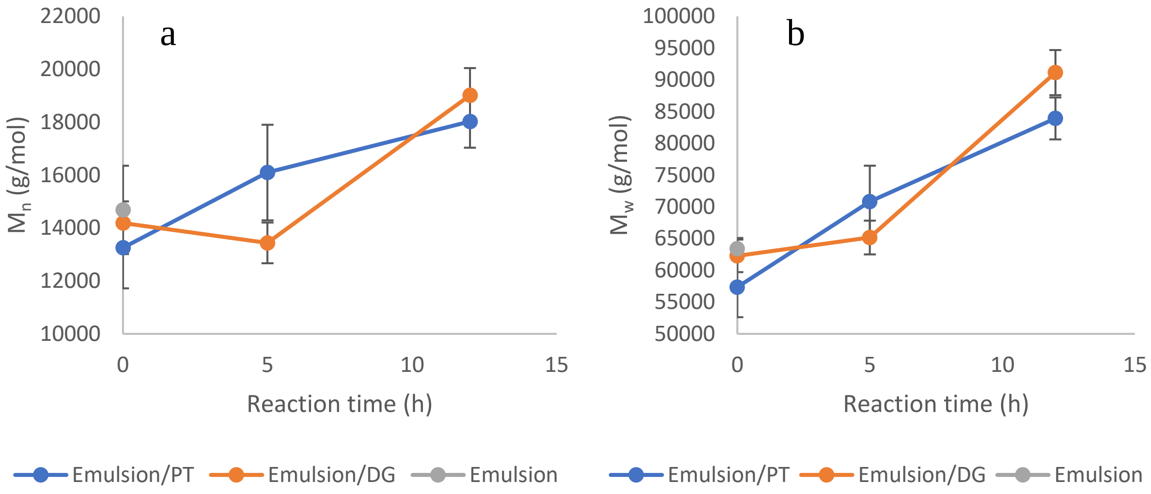


Figure 39: ***a)*** *Number average molecular weight (M_n) and* ***b)*** *weight average molecular weight (M_w) of emulsion, and emulsion with 50func% pentaerythritol tetraacrylate (PT) or di(ethylene glycol)diacrylate (DG) after heating for 80 °C for t=0h, 5h and 12h.*

There is no clear correlation between the decrease in the integral of the vinylic protons from NMR (**Figure 38**) and the increase in molecular weight (**Figure 39**). Initially, this could be explained by only one of the functional groups on the crosslinker reacting which would not increase the molecular weight significantly. The relative movement of the crosslinker might be restricted as one of the functional groups have reacted, given that small molecules are able to move more freely than larger polymers. This could explain the decrease in the rate observed in NMR. However, this was not observed in the alkyd reactions. Additionally, GPC indicates a large increase in molecular weight from t=5h to 12h while NMR does not show any significant decrease within this period. This is particularly pronounced for DG, as large variations are observed for the PT mixture at t=5h. Additionally, NMR indicates that PT reacts to a larger extent than DG at all reaction times, while the molecular weight shows the opposite at t=12h. This might indicate that there is no correlation between the decrease in the vinylic protons and the increased molecular weight, pointing to another reaction than Diels-Alder being responsible for the molecular weight increase.

The molecular weight of the reaction mixtures with crosslinker are initially lower compared to the pure emulsion. This might suggest that competing reactions such as hydrolysis is occurring (see Reaction **6**, **Scheme 11**). This could also explain the lack of coherency between NMR and GPC.

4.8.1.1 Comparison with Alkyd System

The emulsion reactions were also compared to the corresponding alkyd reactions under the same conditions. While the crosslinker integral seem to decrease linearly for the alkyd system, there seems to be a rapid decrease in the emulsion initially, before flattening out after t=2h (**Figure 40**). NMR indicated that the reaction progressed at a highest rate in the emulsion during t≤4h in the PT sample, then at the highest rate for the alkyd (**Figure 40a**). Similarly, for DG, the rate appears to be highest for the alkyd at t≤10h, and then for the emulsion (**Figure 40b**). However, the differences are quite small and possibly within experimental error.

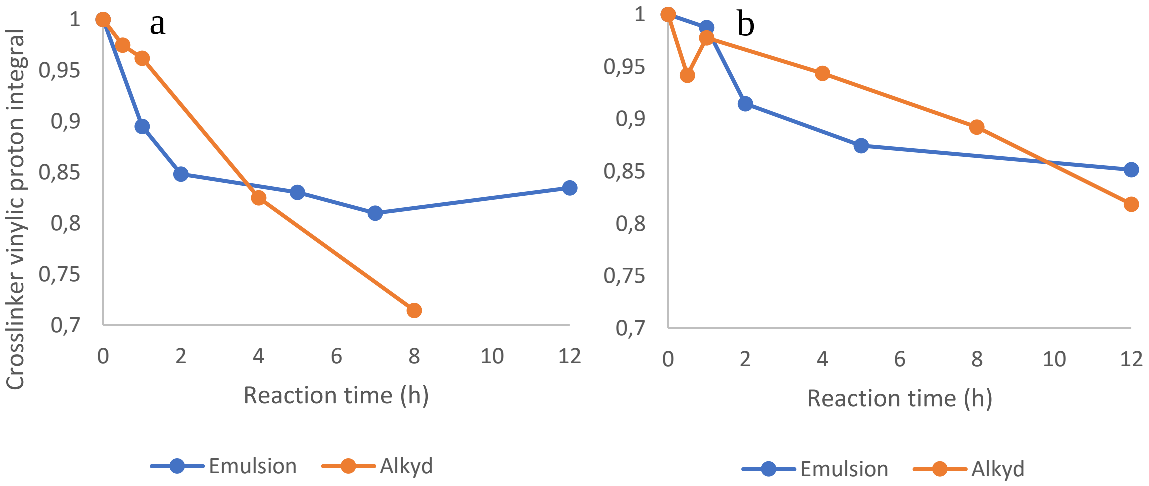


*Figure 40: Decrease in the ^{1}H NMR crosslinker vinylic proton integral for 50func% **a)** pentaerythritol tetraacrylate (PT) and **b)** di(ethylene glycol)diacrylate (DG) in emulsion and alkyd. Peak at 8.61 ppm was used to normalize the spectra integrals.*

The GPC calculations show that the increase in molecular weight for the alkyd is significantly larger than for the emulsion (**Figure 41** and **Figure 42**). Due to few measurements of molecular weight at various reaction times, this cannot be directly compared with the decrease in the vinylic protons. The molecular weight is initially larger for the emulsion mixtures compared to the alkyd mixtures which could indicate that the crosslinking reaction has occurred in the emulsions prior to the measurements. It may also be a result of the drying procedure, exposing the emulsion mixtures to oxygen and allowing the autoxidation reaction (see Reaction **5**, **Scheme 11**) to occur.

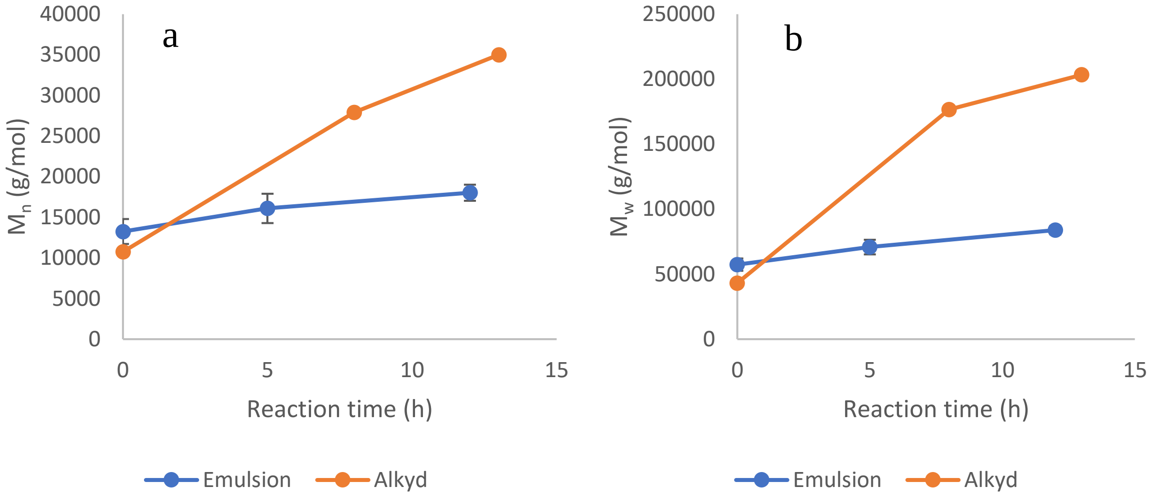


Figure 41: a) *Number average molecular weight (M_n) and* ***b)*** *weight average molecular weight (M_w) of emulsion and alkyd with 50func% pentaerythritol tetraacrylate (PT) after heating for 80 °C for t=0h, 5h and 12h and t=0h, 8h and 13h, respectively.*

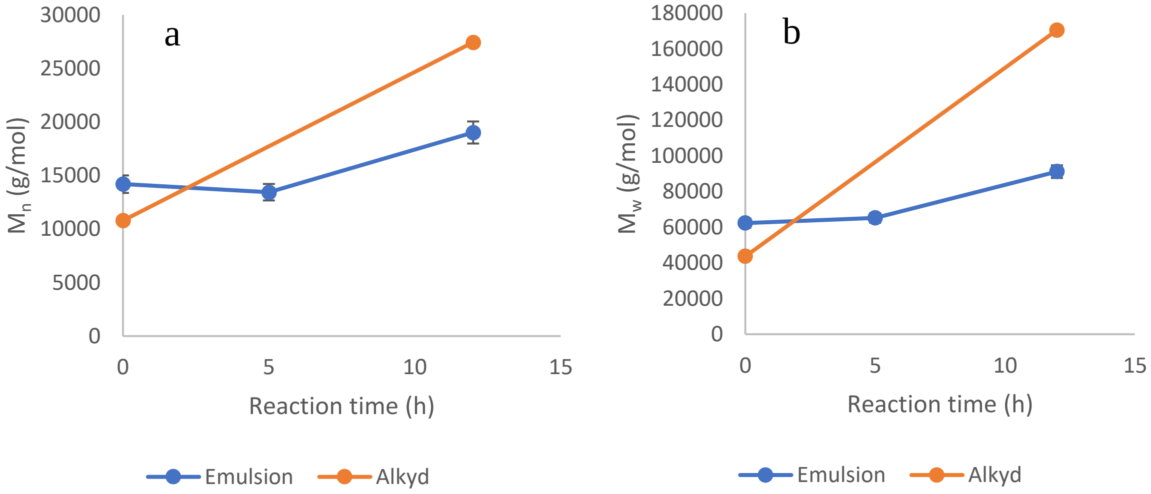


Figure 42: a) *Number average molecular weight (M_n) and* ***b)*** *weight average molecular weight (M_w) of emulsion and alkyd with 50func% di(ethylene glycol)diacrylate (DG) after heating for 80 °C for t=0h, 5h and 12h and t=0h and 12h, respectively.*

4.8.2 20func% Pentaerythritol tetraacrylate (PT) and di(Ethylene glycol)diacrylate (DG)

The crosslinking reaction had proved successful in the post-emulsification system (Section **4.8.1**) as well as in the pre-emulsification system (Sections **4.5** and **4.6**), although a higher degree of crosslinking could be achieved in the pre-emulsification system. For this set of experiment, practical application tests (pendulum hardness) and stability of the emulsions were also tested. One of the concerns regarding the previous set of experiments was that the molecular weights obtained in the alkyd system may be too large and prevent the formation of a smooth film. Therefore, lower concentrations of the crosslinkers were incorporated (20func%) as this had previously been proven to lower the crosslinking density in the alkyd reactions (see **Figure 28**). Reaction mixtures of this concentration were synthesized for both the alkyd and emulsion system. For a comparison of the performance of higher concentrations, a reaction mixture with alkyd and 50func% PT was also synthesized. This reaction mixture had previously shown to provide the largest increase in molecular weight. While this reaction mixture was heated for t=8h to ensure complete solubility, samples from the lower concentration mixtures were extracted at t=12h and 22h. All reaction mixtures were heated to 80 °C.

The reaction mixtures were analyzed by NMR and GPC. Additional tests were conducted by Jotun AS, including solid content, pendulum hardness and GPC, using the conventional and absolute method. Additional analysis including pH, drop size and PDI of the emulsion mixtures were also conducted by Jotun AS. The results are summarized for the alkyd reactions and emulsion reactions in

Table 12 and **Table 13**, respectively.

***Table 11**: Amount of emulsion (when applicable), alkyd, conjugated fatty acid (cFA) and concentration (c) of crosslinkers pentaerythritol tetraacrylate (PT) and di(ethylene glycol)diacrylate (DG). Total reaction time is also given.*

	Emulsion/alkyd			**Crosslinker**			
Exp.nr	**Weight (g)**	**Alkyd (mmol)**	**cFA (mmol)**	**Crosslinker (mmol)**	**Weight (g)**	**c (func%)**	**Reaction time (h)**
E03PT	170.233*	35.9777	95.3287	PT (6.045)	2.130	20.23	22
E04DG	170.464*	36.0265	95.4580	DG (12.04)	2.579	20.14	22
A24PT	33.007	13.5664	35.9463	PT (2.319)	0.817	20.51	0
A24PT	32.918	13.5298	35.8493	PT (2.313)	0.815	20.51	12
A24PT	33.032	13.5767	35.9735	PT (2.313)	0.815	20.46	22
A25DG	32.978	13.5545	35.9147	DG (4.528)	0.970	20.14	0
A25DG	32.957	13.5458	35.8918	DG (4.472)	0.958	19.95	12
A25DG	33.023	13.5730	35.9637	DG (4.528)	0.970	20.12	22
A26PT	33.040	13.5799	35.9822	PT (9.000)	3.171	50.01	0
A26PT	32.951	13.5434	35.8853	PT (9.034)	3.183	50.17	8

*initial weight of emulsion

4.8.2.1 Alkyd reactions

As seen previously, NMR shows that the vinylic proton integral from the crosslinker decreases linearly as the reaction progresses (**Figure 43**) and the highest rate is obtained for PT. The molecular weight increases proportionally to the reaction time for both crosslinkers (**Figure 44**). The PT crosslinker produces a higher molecular weight product compared to DG, in accordance with results from previous alkyd reactions (Sections **4.5** and **4.6**). Larger molecular weights are also produced by the addition of crosslinker compared to subjecting the pure alkyd to heating (Section **4.9.2**).

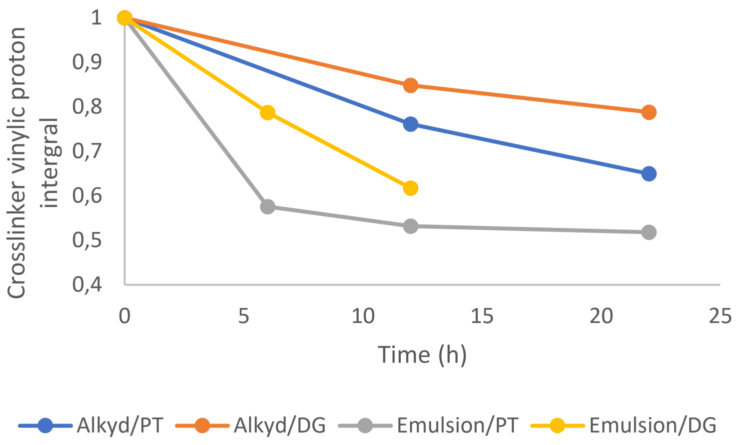


Figure 43: *Decrease in crosslinker vinylic protons, estimated from ^{1}H NMR, for 20func% pentaerythritol tetraacrylate (PT) and di(ethylene glycol)diacrylate (DG) in emulsion and alkyd. Peak at 8.61 ppm was used to normalize the spectra integrals.*

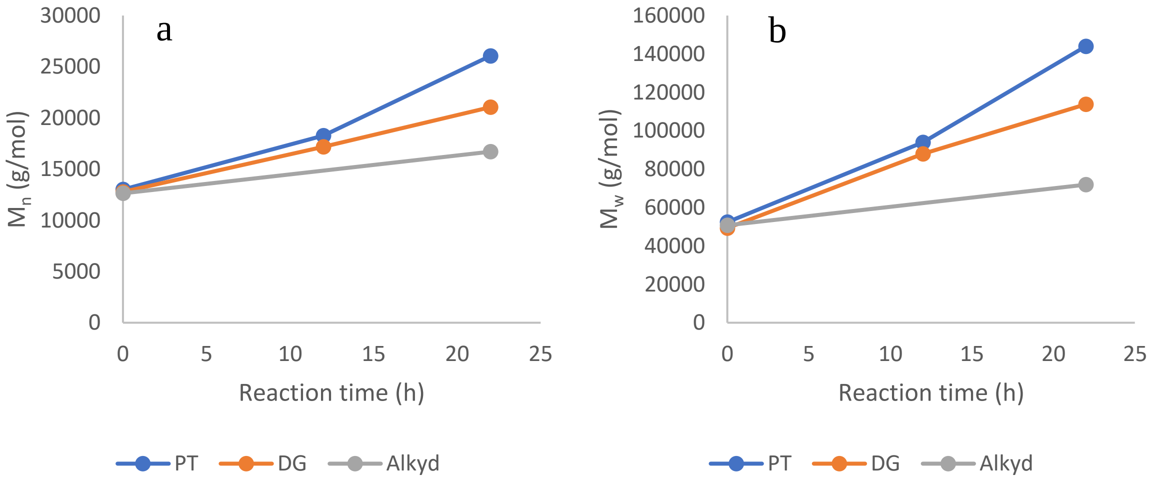


Figure 44: a) *Number average molecular weight (M_n) and* ***b)*** *weight average molecular weight (M_w) of alkyd, and alkyd with 20func% pentaerythritol tetraacrylate (PT) or di(ethylene glycol)diacrylate (DG) after heating at 80 °C for t=0h, 12h and 22h.*

The GPC results conducted by Jotun AS further confirmed that the molecular weight is proportional to the reaction time for all the samples, and that larger molecular weights are formed by the PT crosslinker compared to DG (**Figure 45** and **Figure 46**). As expected from previous experiments, the molecular weight is also further increased by increasing the concentration of PT from 20func% to 50func% (**Figure 45** and **Figure 47**). The molecular weight prior to heating is much larger for the 50func% PT mixture compared to the lower concentration (**Figure 45b-c** and **Figure 47b-c**), indicate that the crosslinking reaction might have occurred at a larger extent at RT prior to the measurements, despite prior observations (see **Figure 25**).

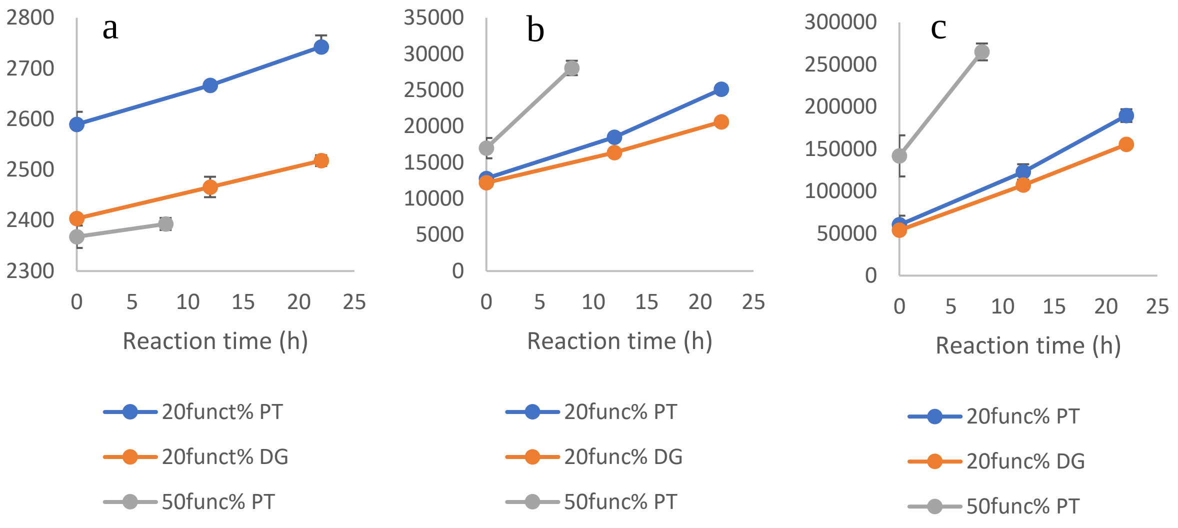


Figure 45: ***a)*** *Number average molecular weight (M_n),* ***b)*** *weight average molecular weight (M_w), and* ***c)*** *z-average molecular weight (M_z) of alkyd samples with 20 func% pentaerythritol tetraacrylate (PT) or 20func% di(ethylene glycol)diacrylate (DG) at t=0h, 12h and 22h, or 50func% PT at t=0h and 8h, using the conventional method.*

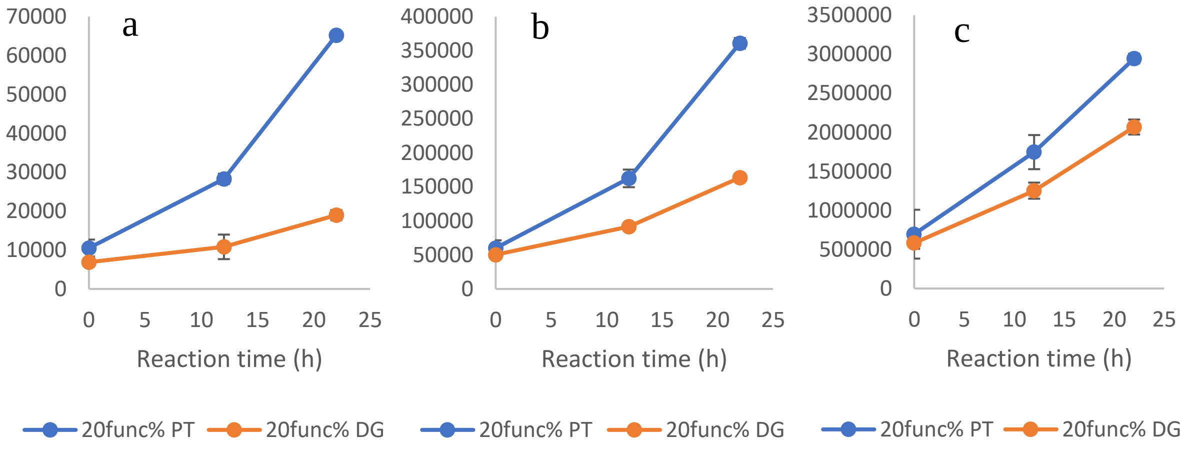


Figure 46: ***a)*** *Number average molecular weight (M_n),* ***b)*** *weight average molecular weight (M_w), and* ***c)*** *Z-average molecular weight (M_z) of alkyd samples with 20 func% pentaerythritol tetraacrylate (PT) or 20func% di(ethylene glycol)diacrylate (DG) at t=0h, 12h and 22h, using the absolute method.*

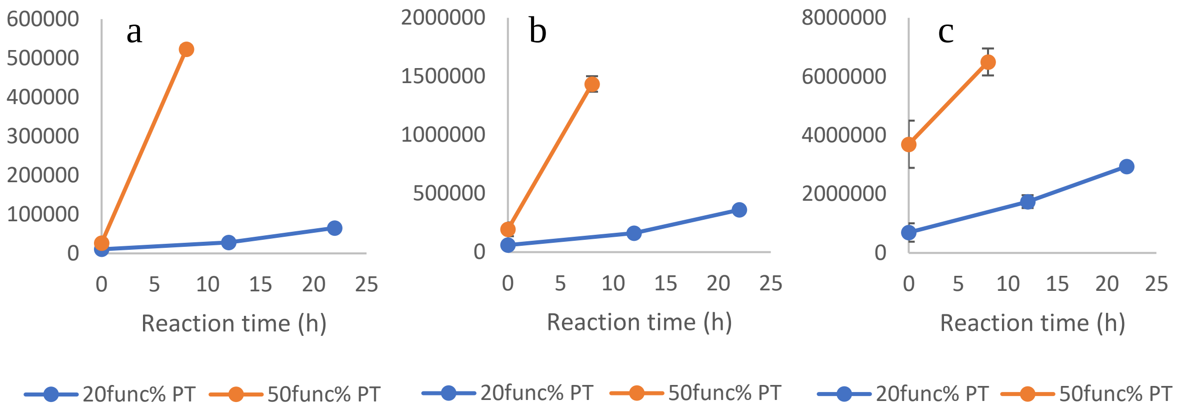


Figure 47: ***a)*** *Number average molecular weight (M_n),* ***b)*** *weight average molecular weight (M_w), and* ***c)*** *Z-average molecular weight (M_z) of alkyd samples with 20 func% pentaerythritol tetraacrylate (PT) at t=0h, 12h and 22h or 50func% PT at t=0h and 8h, using the absolute method.*

The solid contents for the alkyd samples are relatively high (**Figure 48**). The solid content is slightly reduced with the DG which might be due to impurities.

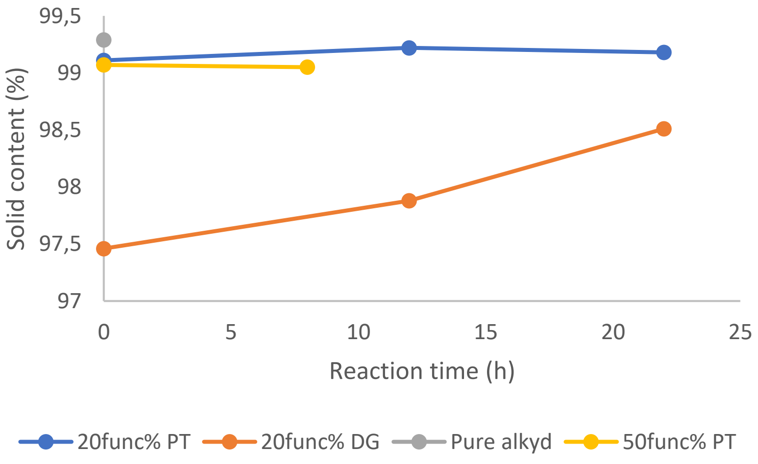


Figure 48: Solid content for pure alkyd, and alkyd mixtures with 20func% pentaerythritol tetraacrylate (PT) and 20func% di(ethylene glycol)diacrylate (DG) at t=0h, 12h and 22h, and 50func% PT at t=0h and 8h.

The addition of crosslinkers result in harder films (evidenced by the pendulum hardness) for all of the alkyd samples, regardless of crosslinker, concentration or reaction time (**Figure 49**, **Figure 50** and **Figure 51**). The reaction mixtures at t=0h form harder films compared to the pure emulsion which could be caused by the crosslinking reaction occurring at RT prior to measurements or that the crosslinker contributes to the autoxidation reaction through its reactive unsaturated bonds.

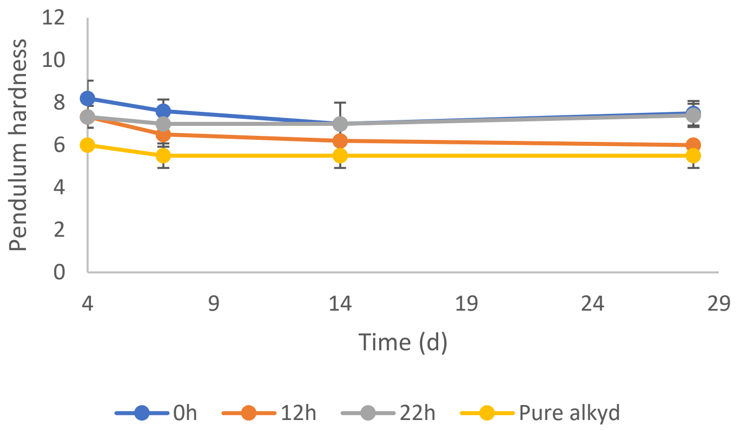


***Figure 49:** Pendulum hardness for films formed by pure alkyd and alkyd with 20func% pentaerythritol tetraacrylate (PT) at t=0h, 12h and 22h.*

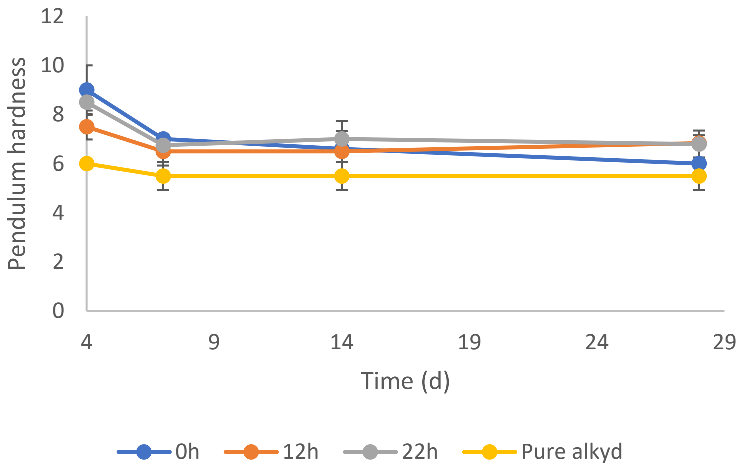


***Figure 50:** Pendulum hardness for films formed by pure alkyd and alkyd with 20func% di(ethylene glycol)diacrylate (DG) at t=0h, 12h and 22h.*

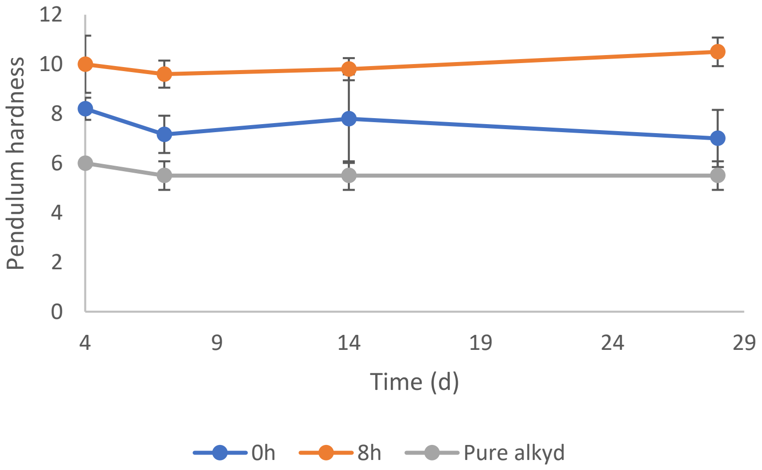


***Figure 51**: Pendulum hardness for films formed by pure alkyd and alkyd with 50func% pentaerythritol tetraacrylate (PT) at t=0h and 8h.*

Table 12: *Summary of results for the alkyd experiments.*

	Increasing reaction time	**Increasing concentration of PT**
NMR vinylic protons	↓	N/A
Molecular weight	↑	N/A
Molecular weight*	↑	↑
Pendulum hardness	Inconclusive	Inconclusive

*conducted by Jotun AS, includes conventional and absolute method

4.8.2.2 Emulsion reactions

The properties of the emulsion reaction mixtures containing 20func% PT or DG were subjected to the same tests as the alkyd mixtures. The ^{1}H NMR plot indicates that the reaction rate is highest initially (t≤6h) for the PT mixture before flattening out (**Figure 43**), similar to previous experiments (see **Figure 38**). For DG, the decrease in the vinylic protons seems to follow a linear trend for t≤12 after which the mixture was no longer soluble. This is a strong indication that the crosslinking reaction has progressed further than in the PT mixture. For t≤12h, however, NMR indicates that the reaction rate is higher for PT than DG.

A slight increase in the molecular weight is observed for both reaction mixtures containing crosslinkers after t=12h while a much larger increase is observed after t=22h (**Figure 52**). Contrary to the alkyd reactions, the largest molecular weight is obtained using the DG crosslinker compared to PT, especially at t=22h. This could be related to the water solubility of the crosslinkers. The molecular weights of the reaction mixtures prior to heating are slightly lower than of the pure emulsion, in accordance with previous observations (see **Figure 39**).

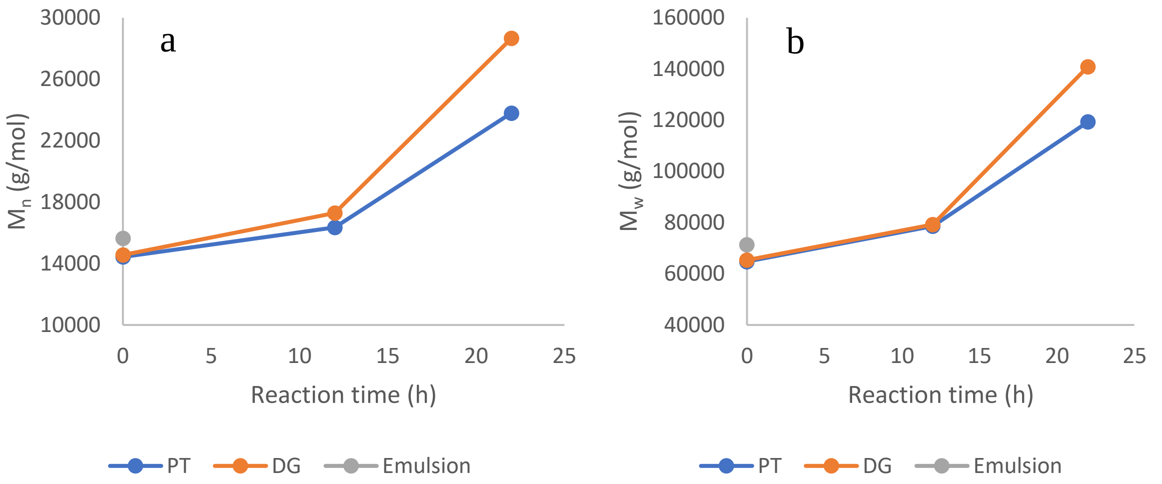


Figure 52: ***a)*** *Number average molecular weight (M_n) and* ***b)*** *weight average molecular weight (M_w) of emulsion, and emulsion with 20func% pentaerythritol tetraacrylate (PT) or di(ethylene glycol)diacrylate (DG) after heating for 80 °C for t=0h, 12h and 22h.*

The GPC analysis was also conducted at Jotun AS, using both the conventional and absolute method. The conventional and absolute method further confirms the trends regarding the M_n (**Figure 53**) and M_w (**Figure 54**), as well as the increased molecular weight with DG compared to PT (**Figure 53-Figure 55**). At t=12h, decreases are observed in the M_z (**Figure 55**) for both reaction mixtures which might indicate that hydrolysis is occurring simultaneously as the incorporating of crosslinker into the alkyd. The hydrolysis can split the alkyd backbone, hence significantly reduce the molecular weight. At t=22h, the M_z is significantly increased, indicating that the crosslinking reaction is the dominant reaction.

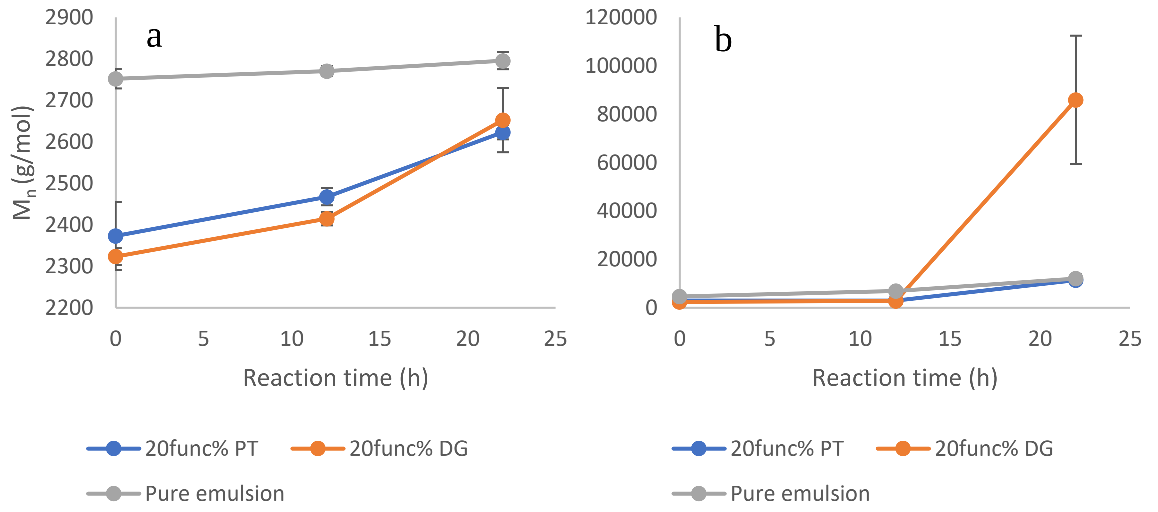


Figure 53: *Number average molecular weight (M_n) of pure emulsion and emulsion with 20func% pentaerythritol tetraacrylate (PT) or 20func% di(ethylene glycol)diacrylate (DG) at t=0h, 12h and 22h of heating at 80°C, using the* ***a)*** *conventional method, and* ***b)*** *absolute method.*

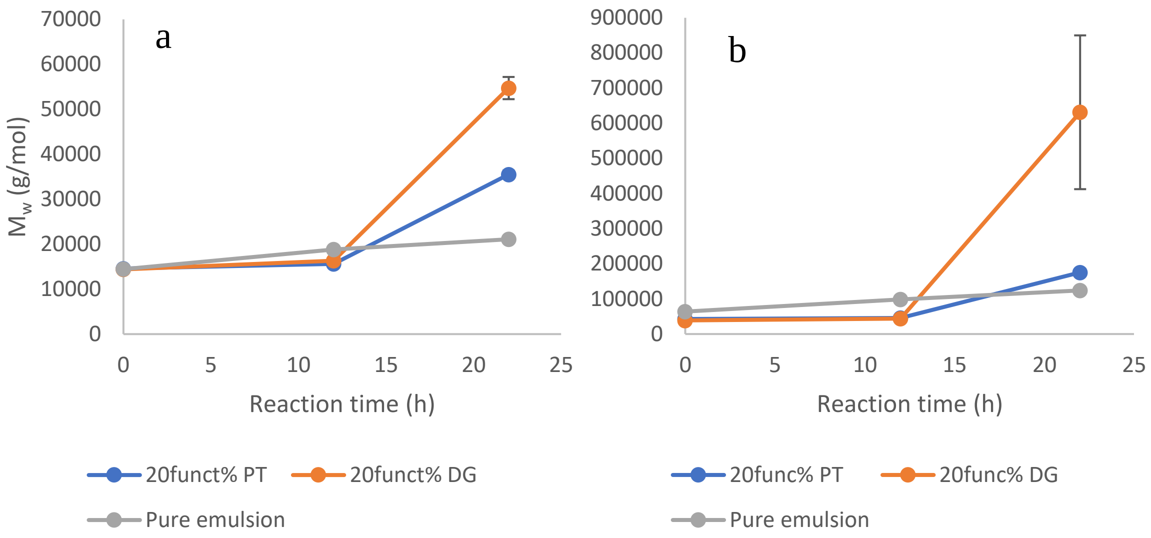


__Figure 54:__ Weight average molecular weight (M_w) of pure emulsion and emulsion with 20func% pentaerythritol tetraacrylate (PT) or 20func% di(ethylene glycol)diacrylate (DG) at t=0h, 12h and 22h of heating at 80°C, using the __a)__ conventional method, and __b)__ absolute method.

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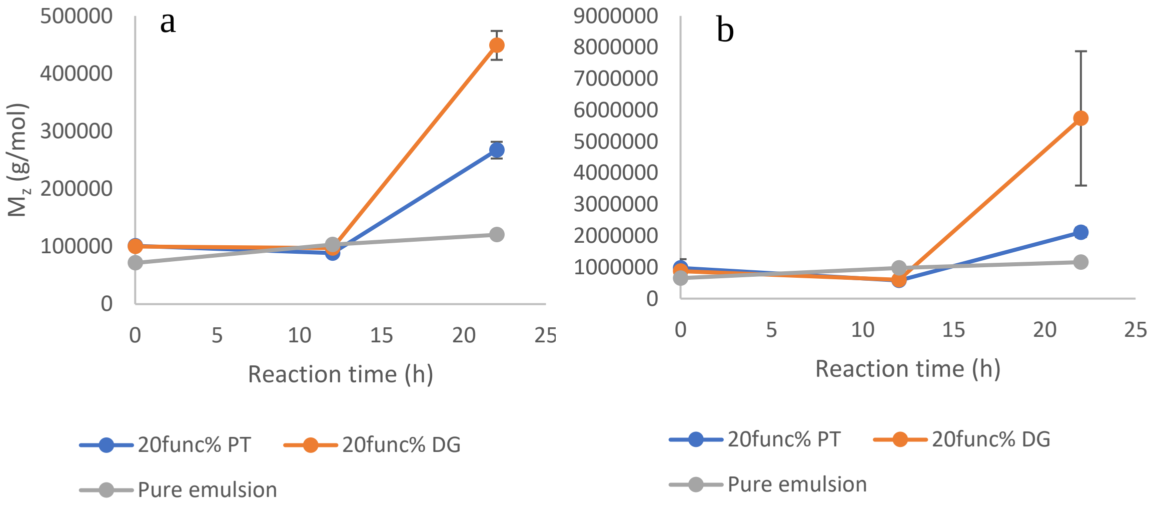


__Figure 55:__ Z-average molecular weight (M_z) of pure emulsion and emulsion with 20func% pentaerythritol tetraacrylate (PT) or 20func% di(ethylene glycol)diacrylate (DG) at t=0h, 12h and 22h of heating at 80°C, using the __a)__ conventional method, and __b)__ absolute method.

The reaction mixtures were also compared to the pure emulsion after subjected to heat under similar conditions (Section **4.9.1**). The decrease in the M_z (**Figure 55**) at t=12h is not observed in the pure emulsion. It can therefore seem as the addition of the crosslinker can be the cause of the reduced molecular weight. It can also be observed that although the molecular weight is also increased in the pure emulsion, the increase is larger for the mixtures containing crosslinker at t=22h (**Figure 54** and **Figure 55**).

The preliminary emulsion experiments showed that water evaporated during the reaction, especially for small batch sizes (Section **4.4**). The solid content was therefore measured for each of the emulsion samples to get an estimate of the extent that this occurs for increased batch sizes. The solid content increases for all of the emulsion samples as the reaction time increases, indicating that some of the water evaporates (0,40-1,80wt%) (**Figure 56**).

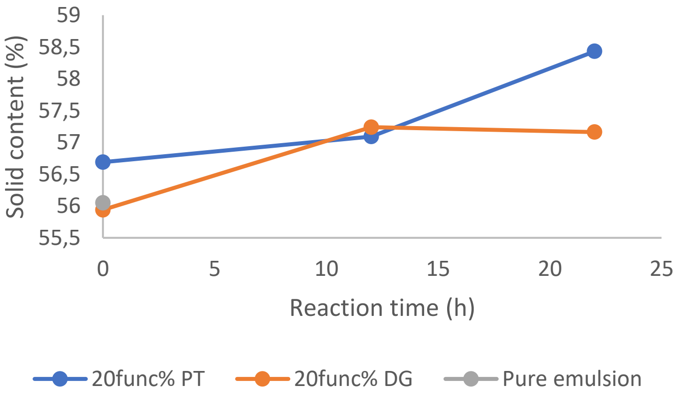


Figure 56: *Solid content in pure emulsion and in emulsion samples containing 20func% pentaerythritol tetraacrylate (PT) or di(ethylene glycol)diacrylate (DG) at t=0h, 12h and 22h.*

pH was measured (**Figure 57**a) as a possible indicator for hydrolysis of the ester bondage which would result in a decreased pH. The pH decreases with the addition of crosslinker, and inversely proportional to the reaction time. The pH was not measured at t=22h for the DG mixture before the addition of driers; therefore, the pH was also measured for all of the samples after the driers were added (**Figure 57b**). However, the pH does not seem to be affected by the driers, and the same trends regarding crosslinker addition and reaction time are observed. The pH is initially lower for DG than PT but decreases in a similar rate for both samples.

The decrease in pH could indicate that hydrolysis of the ester bondage occurs as a competing reaction as the emulsion is heated (see Reaction **6**, **Scheme 11**). This would also explain the decrease observed in the M_z at t=12h (**Figure 55**). While the pH shows a linear decrease throughout the reaction, the molecular weight is only increased at t=22h. This could suggest that only one of the functional groups in the crosslinker is reacting initially, which would not increase the molecular weight significantly. This results in the hydrolysis side-reaction having the largest effect on the resulting molecular weight. The crosslinking reaction might be slowed down due to the limited movement of the chain as the size is increased. At longer reaction times, it may be hypothesized that more than one of the functional groups in the crosslinker reacts, resulting in the increased molecular weight. The crosslinking reaction appear to be the more dominant pathway at long reaction times compared to hydrolysis. This could also explain why the decrease in the vinylic proton integral is largest in the beginning of the reaction, at least for PT (see **Figure 43**). It can also explain the lack of correlation between the vinylic crosslinker protons and the molecular weight encountered in both section **4.8.1** and **4.8.2**.

The decrease in pH is not observed as pure emulsion is subjected to heating (**Figure 57**), indicating that the decrease is attributed to the addition of crosslinker. If hydrolysis is the cause for the decrease in pH, it appears to be catalyzed by the addition of crosslinker.

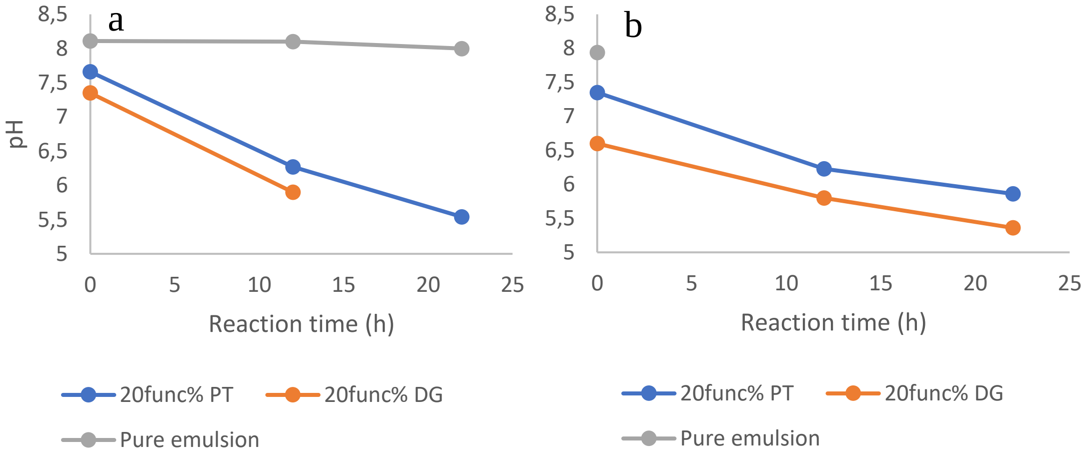


Figure 57: *pH for pure emulsion and 20func% pentaerythritol tetraacrylate (PT) or di(ethylene glycol)diacrylate (DG) at t=0h, 12h and 22h* ***a)*** *without driers and* ***b)*** *with driers.*

The scope of the thesis is to achieve crosslinking within the emulsion droplets. Therefore, large changes in the original drop size is not desirable. The drop size (**Figure 58a**) seems to decrease slightly as either crosslinker is added to the emulsion. Opposite trends are observed as the reaction mixtures as heated; for DG, the drop size is initially reduced and increases as the reaction time increases. For PT, the drop size is similar in size to the pure emulsion but decreases with time. This could be related to the solubility of the crosslinkers. The changes are relatively small. The lack of a clear correlation between reaction time and drop size could indicate that coalescence might not be an issue. The polydispersity index (PDI), indicating the distribution of the drop sizes, of the 20func% PT is similar to the pure emulsion while it is slightly lower for the reaction mixture with DG (**Figure 58b**). The PDI does not seem to be affected by increased reaction time for the emulsion with crosslinker, while it decreases slightly for the pure emulsion.

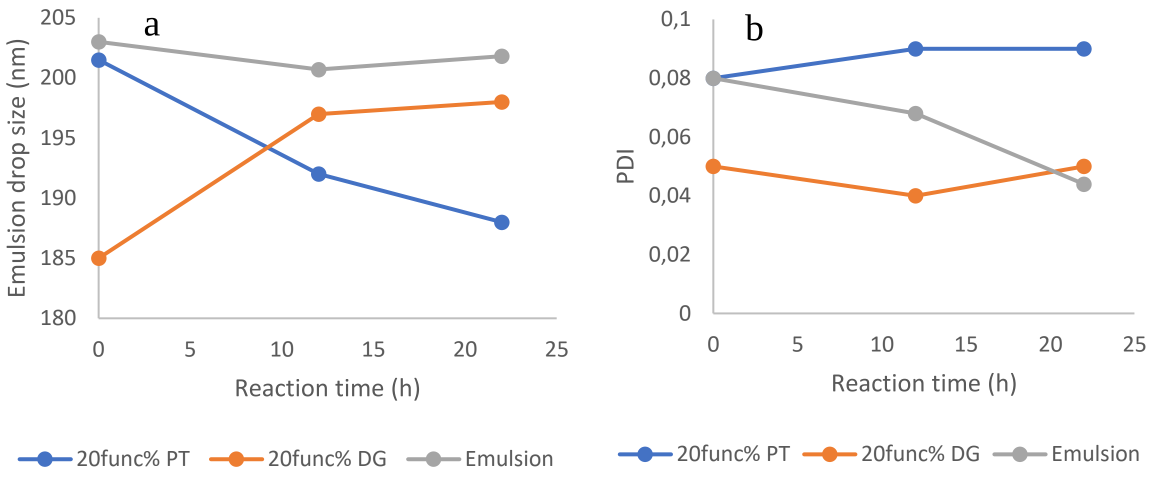


Figure 58: a) Emulsion drop size and b) PDI of pure emulsion and emulsion with 20func% pentaerythritol tetraacrylate (PT) or di(ethylene glycol)diacrylate (DG) at t=0h, 12h and 22h.

For both reaction mixtures, the hardest films are formed by the pure emulsion while the softest film is formed by the reaction mixtures heated for t=12h (**Figure 59** and **Figure 60**). This could be linked to the decreased M_z evident for both mixtures, possibly linked to hydrolysis. However, the film formed by the PT mixture at t=22h show similar hardness, despite the significant increase in the M_z. The softness of the films might be related to the loss of unsaturated bonds during the reaction progression, limiting the ability to undergo the autoxidation reaction. The hardness of the films formed by the pure emulsion after heating generally increases with increasing reaction time (**Figure 76** and **Figure 77**). This further confirms that a competing reaction occurs in the emulsion samples attributed to the addition of crosslinkers.

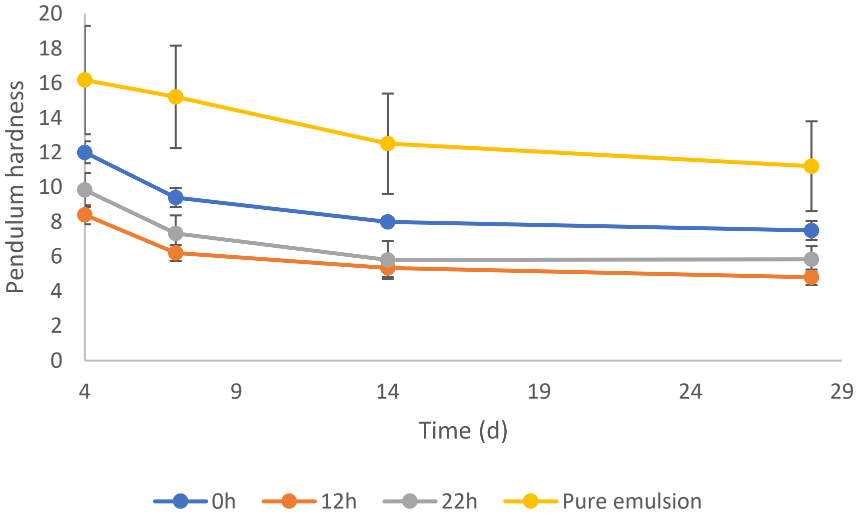


Figure 59: Pendulum hardness for films formed by pure emulsion and emulsion with 20func% pentaerythritol tetraacrylate (PT) at t=0h, 12h and 22h.

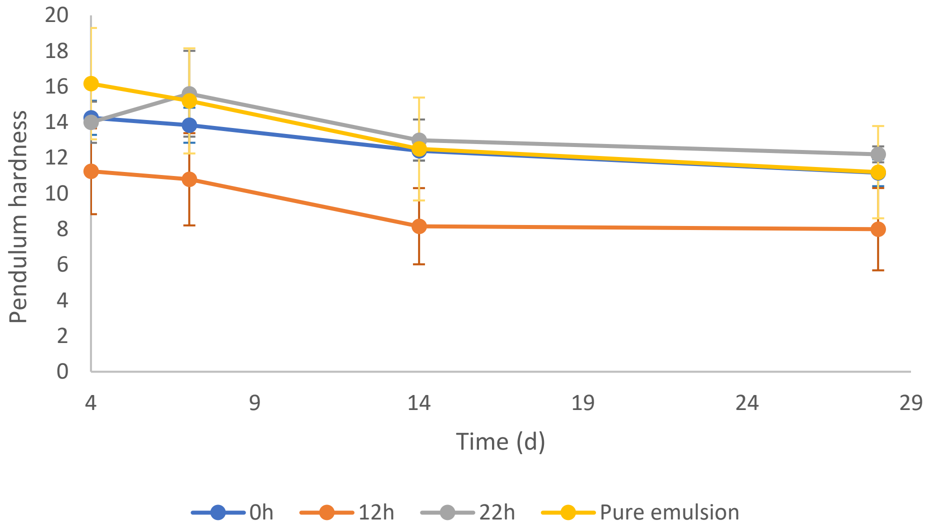


Figure 60: *Pendulum hardness for films formed by pure emulsion and emulsion with 20func% di(ethylene glycol)diacrylate (DG) at t=0h, 12h and 22h.*

Table 13: *Summary of results obtained for emulsion reaction mixtures with 20func% pentaerythritol tetraacrylate (PT) or di(ethylene glycol)diacrylate (DG). No changes are denoted by 0.*

	Increased reaction time
NMR vinylic protons	↓
Molecular weight	↑
Molecular weight*	↑**
Solid content	↑
pH	↓
Drop size	Inconclusive
PDI	0
Pendulum hardness	↓

*analyzed by Jotun AS, including the conventional and absolute method
**except for M_z at t=12h

4.8.2.3 Reactivity of the alkyd and emulsion system

The properties of the reactions conducted with 20func% PT or DG were compared for the alkyd and emulsion system. NMR indicates that the reaction progresses faster for the emulsions than for the alkyds (**Figure 43**).

As observed in the 50func% crosslinker in alkyd or emulsion (Section 4.8.1), the molecular weight of the alkyd mixtures are initially lower than for the emulsion mixtures (**Figure 61** and **Figure 62**). Despite this, the molecular weight obtained for the alkyd mixture with PT is larger than for the emulsion mixture at t=12h and 22h, contradicting the observations from NMR. For the DG mixtures, similar molecular weights are obtained for the alkyd and emulsion containing DG at t=12h. However, at t=22h, the molecular weight obtained for the emulsion mixture is significantly larger than for the alkyd, in contrast to the PT mixture. This may be attributed to the solubility of the crosslinkers. While the molecular weight appears to increase linearly in the alkyd reaction mixture, the emulsion reaction mixture shows an initially lower reaction rate at t≤12h compared to at t>12h.

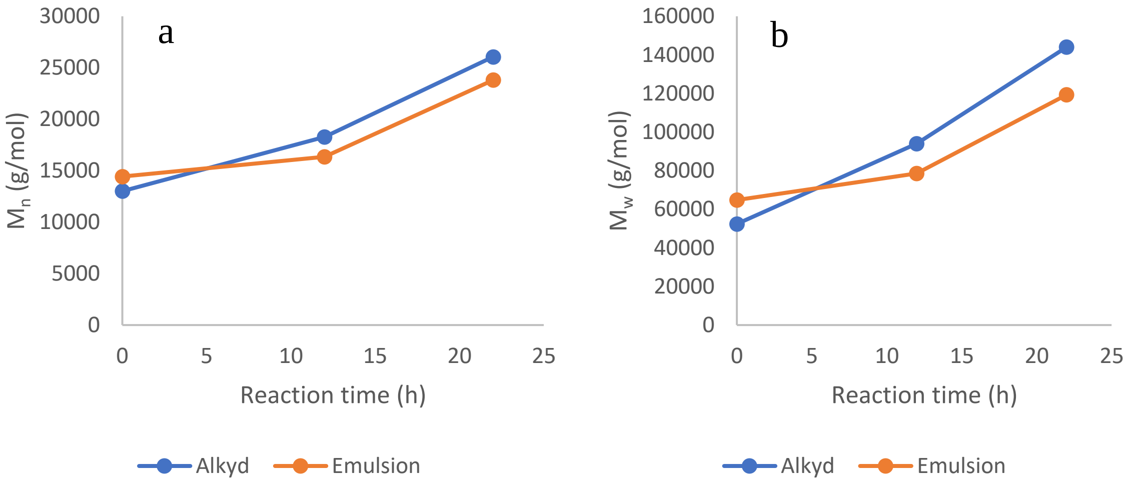


Figure 61: a) *Number average molecular weight (M_n) and* ***b)*** *weight average molecular weight (M_w) of alkyd or emulsion with 20func% pentaerythritol tetraacrylate (PT) at t=0h, 12h and 22h.*

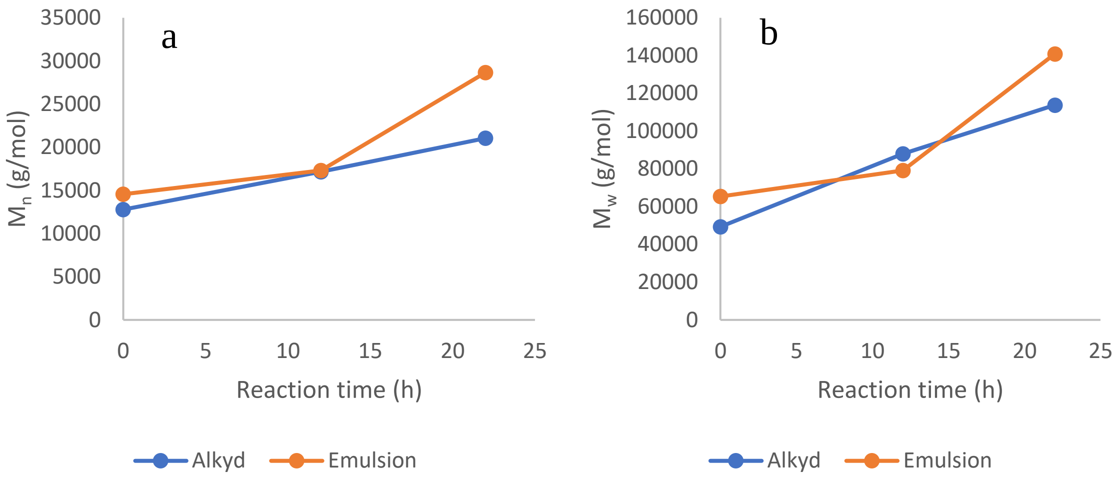


*Figure 62: **a)** Number average molecular weight (M_n) and **b)** weight average molecular weight (M_w) of alkyd or emulsion with 20func% di(ethylene glycol)diacrylate (DG) at t=0h, 12h and 22h.*

The GPC analysis were also conducted by Jotun AS. Generally, the M_n is affected by the presence of surfactants and other low molecular weight molecules (**Figure 63** and **Figure 64**). In accordance with the analysis conducted at NTNU, the M_w and M_z are initially larger for the emulsion compared to the alkyd and different rates in the increase of the molecular weight are observed (**Figure 63-Figure 68**).

The increased molecular weight for DG in the emulsion system compared to the alkyd system, especially at t=22h, is further evident in the conventional and absolute method (**Figure 64**, **Figure 66** and **Figure 68**). For PT, the absolute method further confirms the increased reactivity in the alkyd system compared to the emulsion system (**Figure 65b** and **Figure 67b**). The conventional method, however, indicates that larger molecular weight are formed in the emulsion system compared to the alkyd system at t=22h (**Figure 65a** and **Figure 67a**). The contradicting trends regarding PT fails to provide definite answers regarding the reaction system.

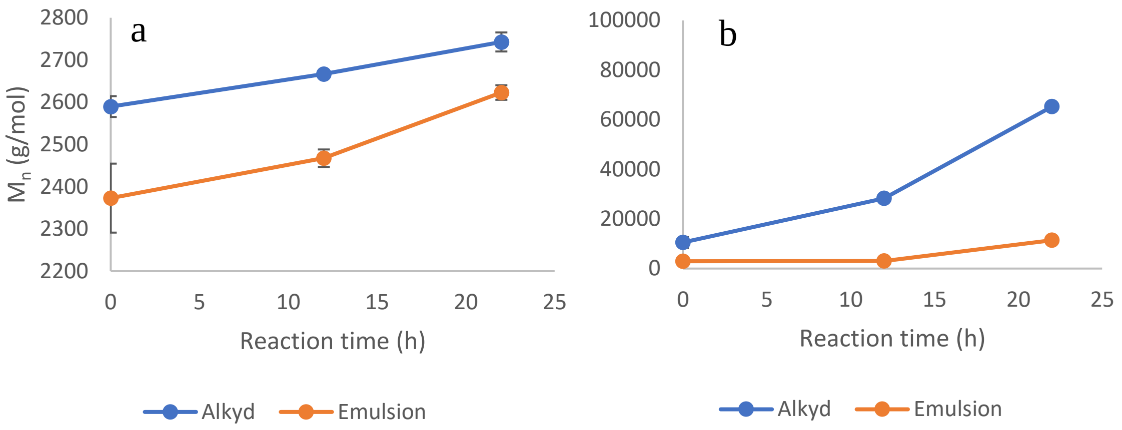


Figure 63: *Number average molecular weight (M_n) of 20func% pentaerythritol tetraacrylate (PT) in alkyd or emulsion at t=0h, 12h and 22h, using the **a)** conventional method, and **b)** absolute method.*

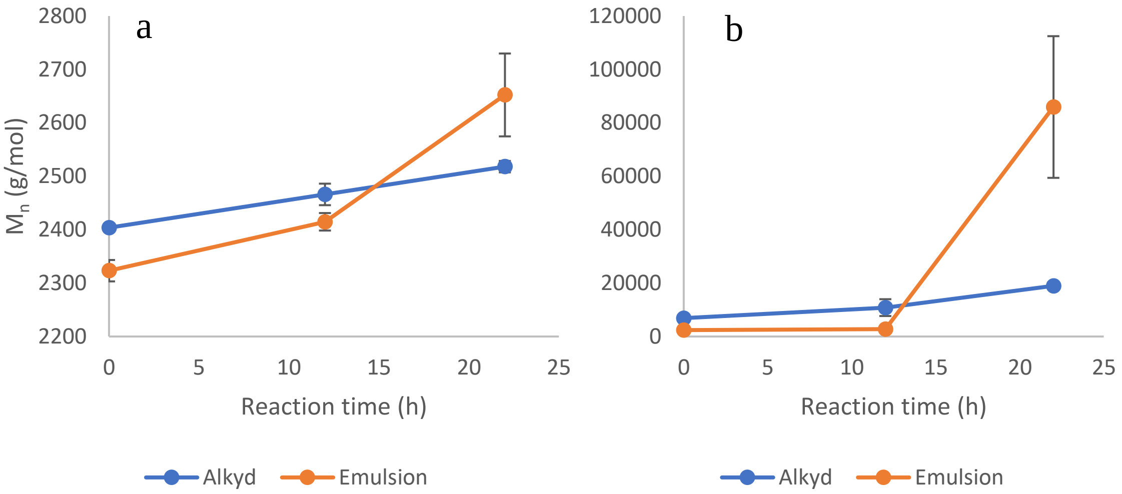


Figure 64: *Number average molecular weight (M_n) of 20func% di(ethylene glycol)diacrylate (DG) in alkyd or emulsion at t=0h, 12h and 22h, using the **a)** conventional method, and **b)** absolute method.*

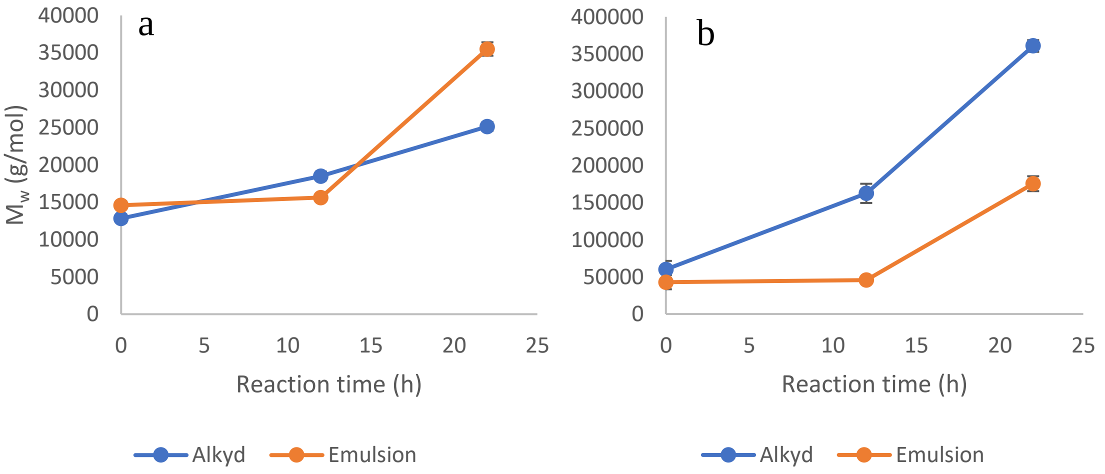


Figure 65: *Weight average molecular weight (M_w) of 20func% pentaerythritol tetraacrylate (PT) in alkyd or emulsion at t=0h, 12h and 22h, using the **a)** conventional method, and **b)** absolute method.*

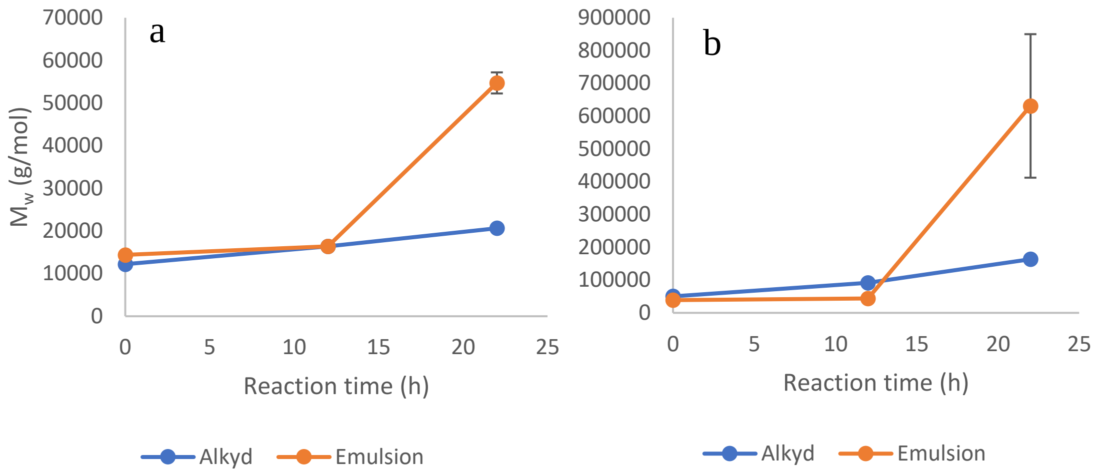


Figure 66: *Weight average molecular weight (M_w) of 20func% di(ethylene glycol)diacrylate (DG) in alkyd or emulsion at t=0h, 12h and 22h, using the **a)** conventional method, and **b)** absolute method.*

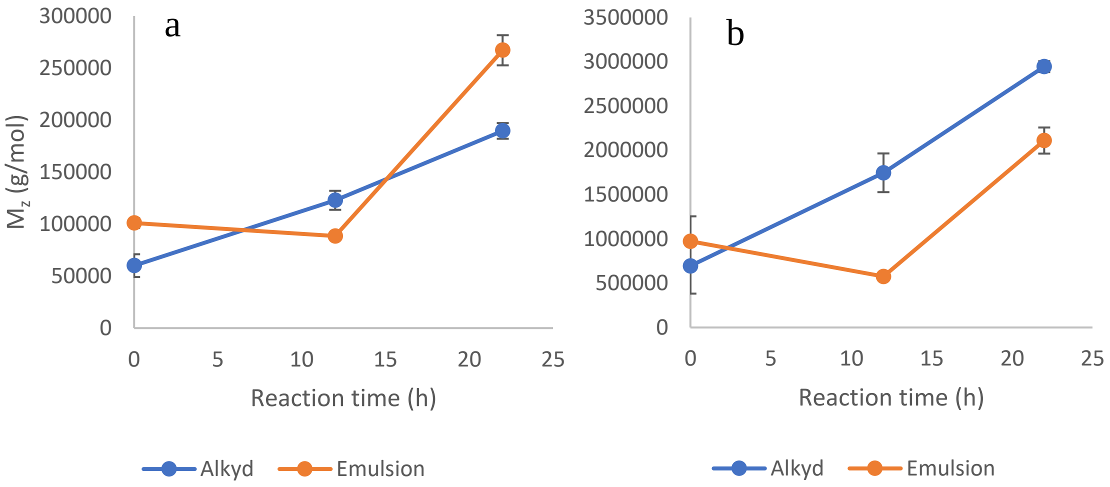


Figure 67*: Z-average molecular weight (M_z) of 20func% pentaerythritol tetraacrylate (PT) in alkyd or emulsion at t=0h, 12h and 22h, using the **a)** conventional method, and **b)** absolute method.*

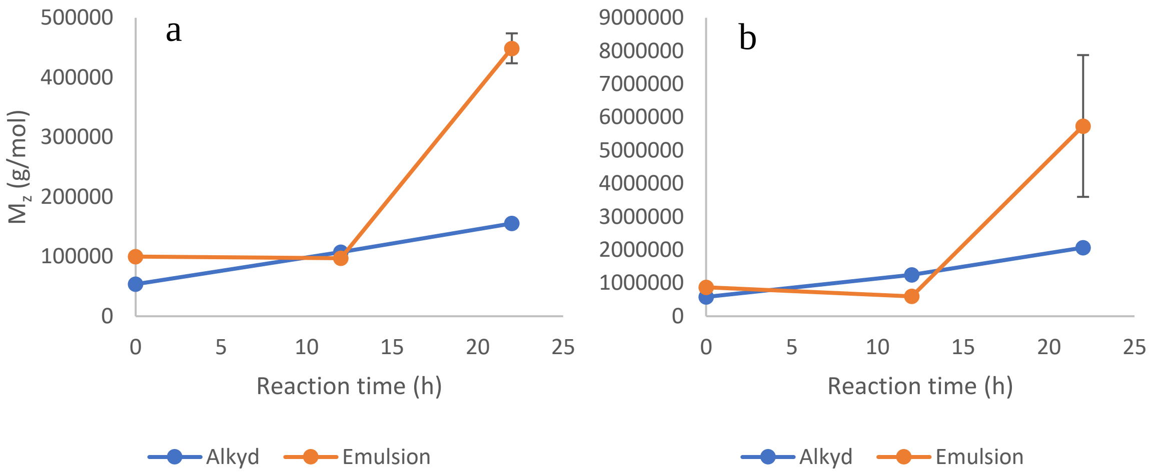


*Figure 68: Z-average molecular weight (M_z) of 20func% di(ethylene glycol)diacrylate (DG) in alkyd or emulsion at t=0h, 12h and 22h, using the **a)** conventional method, and **b)** absolute method.*

For the pendulum hardness, the emulsion samples generally exhibit a higher hardness compared to the alkyd samples. This is observed for the pure alkyd and emulsion and is therefore not expected attributes to the crosslinkers. This could be due to the efficiency of the driers in the two systems. While the hardness of the alkyd films increases with the addition of crosslinker and heating (**Figure 49** and **Figure 50**), this is not the case for the emulsion films (**Figure 59** and **Figure 60**). This further indicates that competing reaction might be occurring in the emulsions.

The differences observed in NMR, GPC and pendulum hardness, combined with the decreased pH, makes it likely that a competing reaction or possibly a different reaction is occurring in the emulsion system. This might be hydrolysis as a competing reaction with the crosslinking reaction. It may also be due to the drying procedure resulting in autoxidation reaction; however, it would not explain the decreased molecular weights or decrease in pH. For this set of experiments, it is evident that longer reaction times are required for the emulsion systems to obtain increased molecular weights.

4.9 Study of Starting Reagents

In order to identify basic reaction pathways (see Reaction **2**, **4** and **5**, **Scheme 11**) and hydrolysis (see Reaction **6**, **Scheme 11**) which might occur within the alkyd, the starting reagent were subjected to reaction condition in the absence of a crosslinker. The emulsion and alkyd prior to emulsification were subjected to heating under the same conditions (**Table 14**) as the previous experiments to reveal which of the results were due to heating and which could be attributed to the crosslinker.

Table 14: *Amount of emulsion/alkyd, reaction time and temperature.*

Exp.nr	Reagent	Weight (g)	Alkyd (mmol)	Temperature (°C)	Reaction time (h)
A27	Alkyd	2.768	1.138	80	22
E05	Emulsion	130.00	27.475	80	22
E06	Emulsion	120.81	25.533	60	22

4.9.1 Emulsion

It was suspected that the decrease in pH, pendulum hardness and M_z as the reaction time increased could be due to hydrolysis occurring as the emulsion was heated. Therefore, pure emulsion was investigated under the same conditions as the previous samples. Additionally, a lower temperature of 60 °C was investigated, to reveal whether the potential hydrolysis would occur at a lower rate.

Water evaporated from the emulsions at both temperatures (0.6-0.8wt%) (**Figure 69**). The pH is not significantly decreased as the emulsion is heated (**Figure 70**). A slight decrease in the drop size (**Figure 71a**) is observed for the emulsion heated at 60 °C, and small decreases in the PDI for the emulsions at both temperatures (**Figure 71b**).

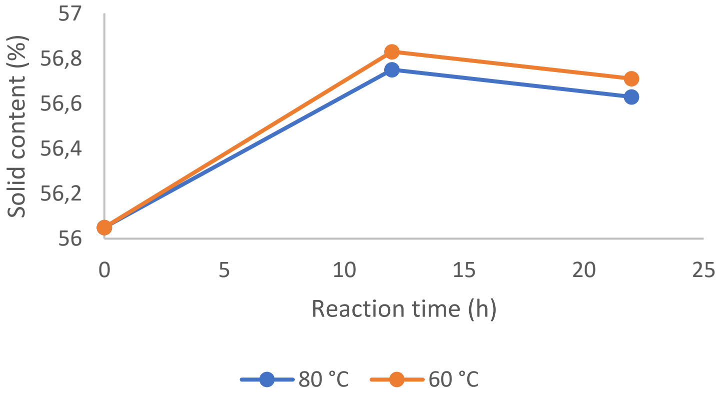


Figure 69: *Solid content of pure emulsion when heated for t=0h, 12h and 22h at 60 and 80 °C.*

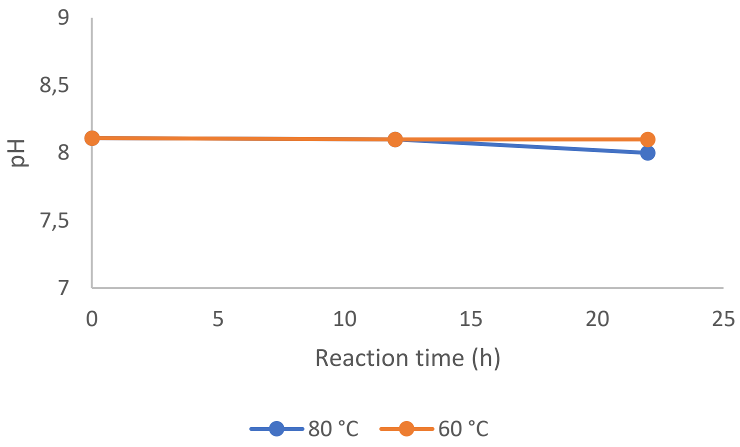


Figure 70: pH for pure emulsion after heating at 60 and 80 °C for t=12h and 22h.

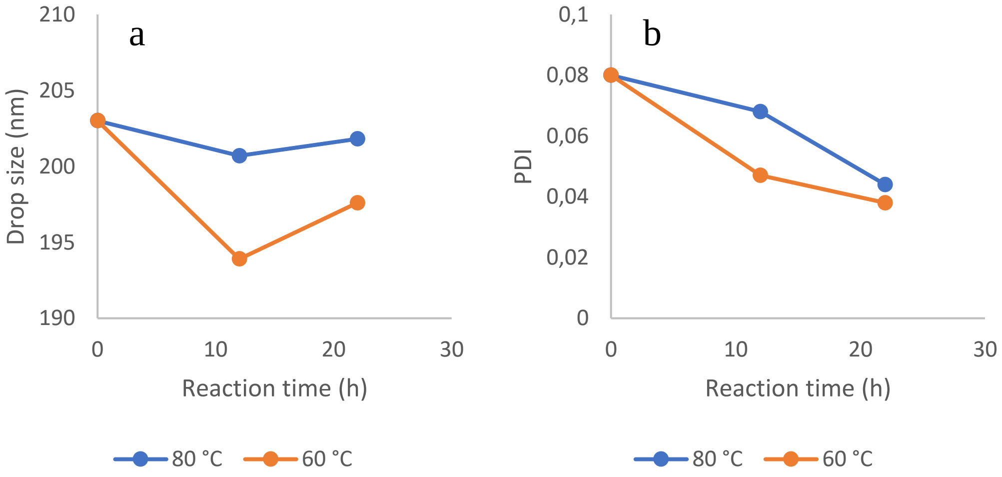


*Figure 71: **a)** Drop size and **b)** PDI of emulsion heated to 80 and 60 °C for t=0h, 12h and 22h.*

The emulsion mixture at t=0h showed a superior molecular weight compared to what had previously been measured for the emulsion (**Figure 72**). Prior to the GPC measurements for this set of experiments, the emulsions were dried in a similar matter as the previous samples. However, a small quantity was set aside after drying and stored in closed vials for approximately 2 months prior to the GPC measurements. This could have exposed the samples to oxygen and may have resulted in the autoxidation reaction occurring at a larger extent than for the previous samples. The same applies to all emulsion samples in this set of experiments. The increase in molecular weight could also be caused by changes in the emulsion after storage as small changes could occur during storing (see **Figure 6**).

Solid aggregated were observed in the samples which had been heated at 80 °C for t=12h and 22h and at 60 °C for t=22h (**Figure 72**). The insolubility was believed to be caused by autoxidation reactions during the storage time. Due to the formation of aggregates, the molecular weights given are not representative.

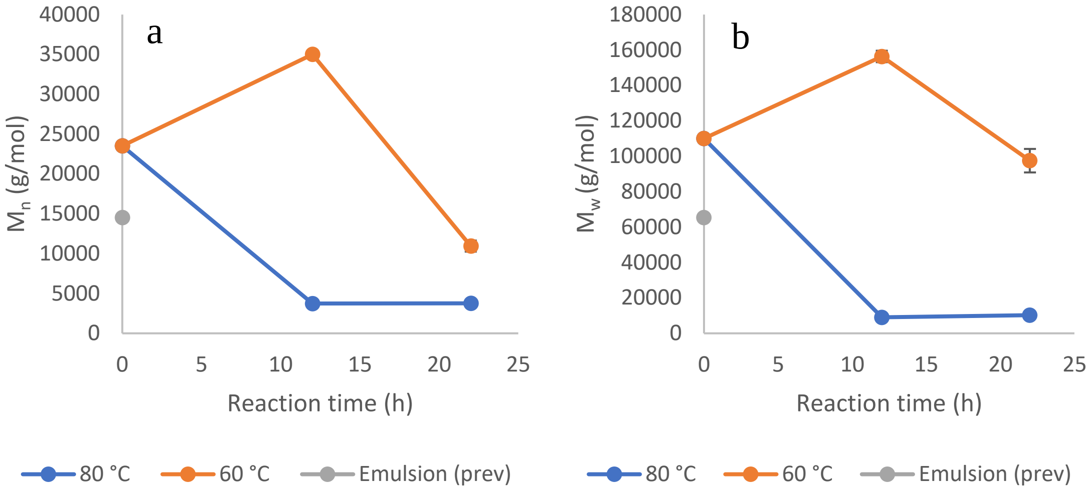


*Figure 72: **a)** Number average molecular weight (M_n) and **b)** weight average molecular weight (M_w) for emulsion heated at 80 or 60 °C for t=0h, 12h and 22h.*

The molecular weight was also analyzed by Jotun AS (**Figure 73-Figure 75**). Unlike the previous molecular weight measurements (**Figure 72**), the vials contained larger quantities of dried emulsion and were stored for a shorter period, both of which are expected to reduce the probability of the alkyd reacting with oxygen in the atmosphere. These measurements are therefore expected to provide an accurate representation of the molecular weight.

The molecular weight is increased, nearly linearly, as the pure emulsion is heated (**Figure 73**, **Figure 74** and **Figure 75**), especially at 80 °C. Combined with the absence of a decrease in pH, this indicated that hydrolysis does not occur in the pure emulsion.

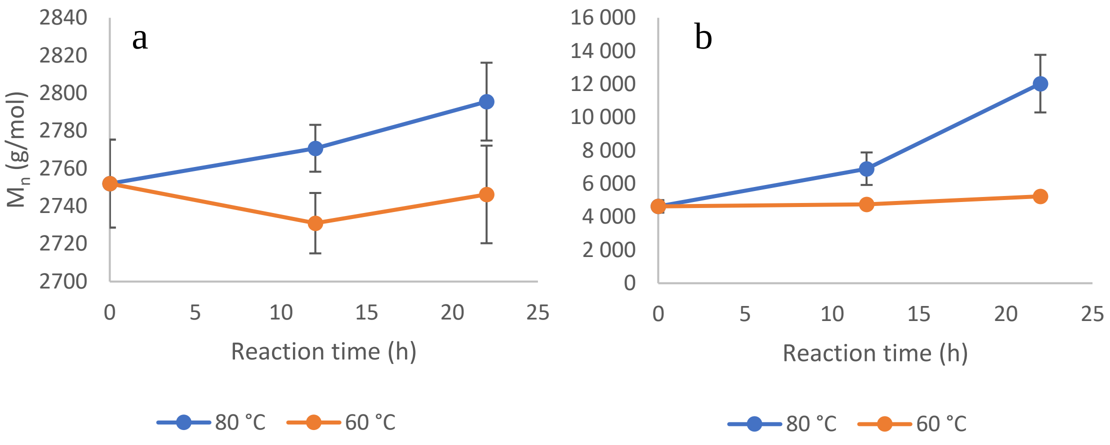


*Figure 73: Number average molecular weight (M_n) of pure emulsion heated to 80 and 60 °C at t=0h, 12h and 22h using **a)** the conventional method, and **b)** the absolute method.*

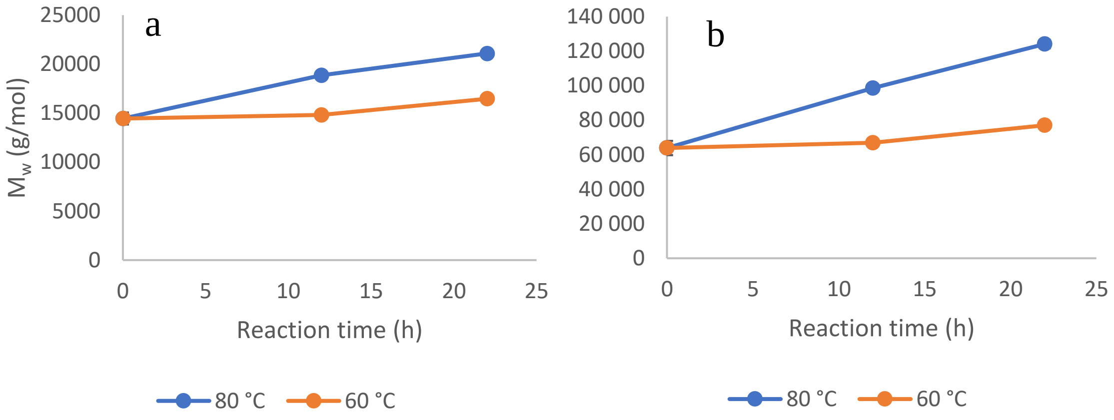


***Figure 74:** Weight average molecular weight (M_w) of pure emulsion heated to 80 and 60 °C at t=0h, 12h and 22h using **a)** the conventional method, and **b)** the absolute method.*

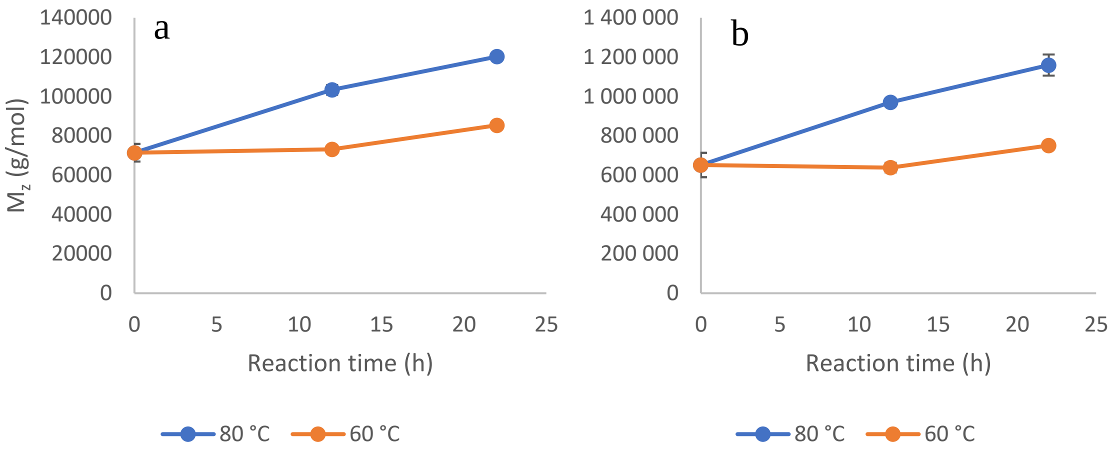


Figure 75: *Z-average molecular weight (M_z) of pure emulsion heated to 80 and 60 °C at t=0h, 12h and 22h using* ***a)*** *the conventional method, and* ***b)*** *the absolute method.*

The pendulum hardness (**Figure 76** and **Figure 77**) shows that the hardness is increased as the reaction times is increased, especially at 80 °C. The hardness also seems to slightly increase as the temperature is increased although the differences are small. This is also an indication against the hydrolysis side-reaction, as the hydrolysis is expected to soften the films due to the decreased molecular weight.

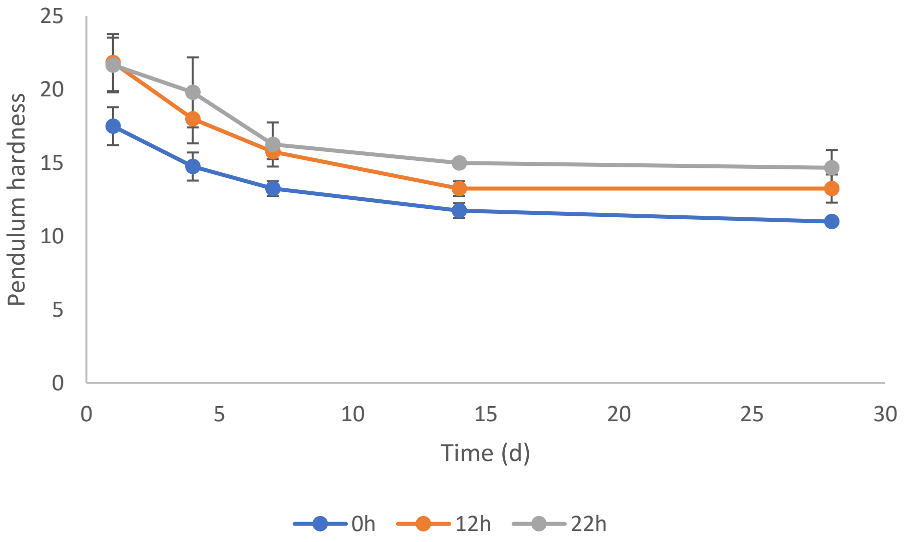


Figure 76: *Pendulum hardness for pure emulsion prior to heating, and after heating at 80 °C for t=12h and 22h.*

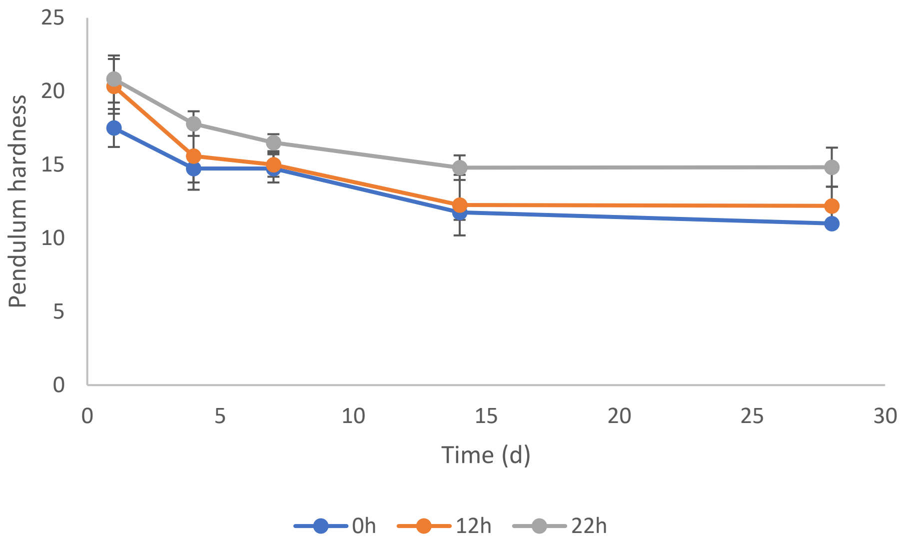


Figure 77: Pendulum hardness for pure emulsion prior to heating, and after heating at 60 °C for t=12h and 22h.

4.9.2 Alkyd

The alkyd was not expected to change significantly after heating based on the initial investigations (Section **4.4**) combined with the low temperature (≤80 °C) compared to the polymerization temperature. However, the reaction times (t=22h) are much longer which could allow for changes. Although the initial investigations showed no changes in the alkyd, this was based solely on changes observable in FTIR. As with the emulsion (Section **4.9.1**), no significant changes could be observed in ^{1}H NMR. An increase in molecular weight was observed after heating for t=22h (**Figure 78**). Due to the loss of solubility for the emulsion samples, a comparison of the molecular weights obtained for the two systems could not be established.

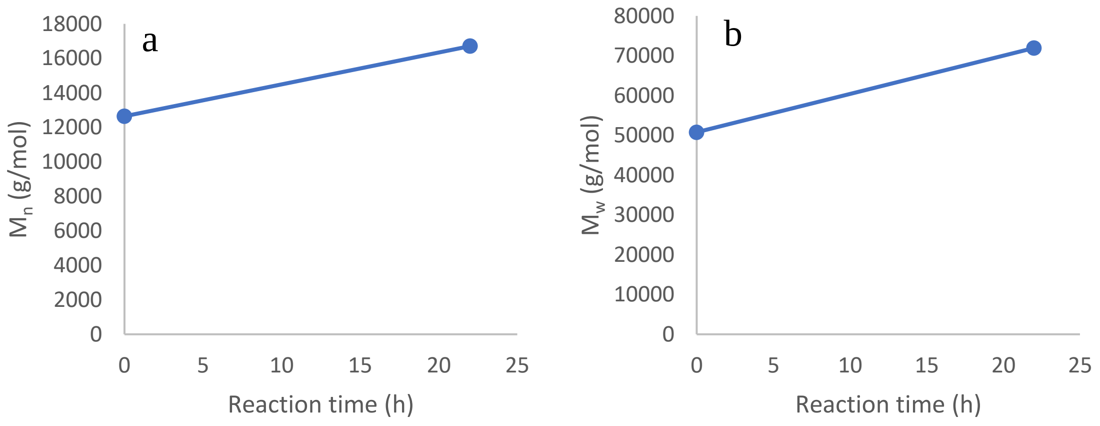


*Figure 78: a) Number average molecular weight (M_n) and **b)** weight average molecular weight (M_w) of alkyd prior to heating and after heating at 80 °C for t=22h.*

4.10 Repeatability

Although most reactions were run several times over the course of this master thesis, several factor might cause repeatability issues. This includes variations in the master batches prepared, differences observed in the characterization methods, the commercial composition of our reaction mixtures, as well as the absence of stirring (Section **4.7**).

4.10.1 Alkyd Reactions

A high degree of repeatability had previously been observed in ^{1}H NMR for a reaction mixture with alkyd with 50func% PT when the reaction was carried out without stirring (Section **4.7**). Investigations of reaction mixtures consisting of alkyd and 20func% PT (A18PT and A24PT, **Table 7** and **Table 11**, respectively) or 20func% DG (A15DG and A25DG, **Table 7** and **Table 11**, respectively) had been conducted twice and analyzed by ^{1}H NMR and GPC. All conditions were the same except for batch sizes. Due to the difference in reaction times, only the main trends may be compared. NMR shows a relatively high degree of repeatability for the PT mixture (**Figure 79**) and for the DG mixtures at t=12h (**Figure 80**). For the DG mixtures at t=22h, larger differences are observed.

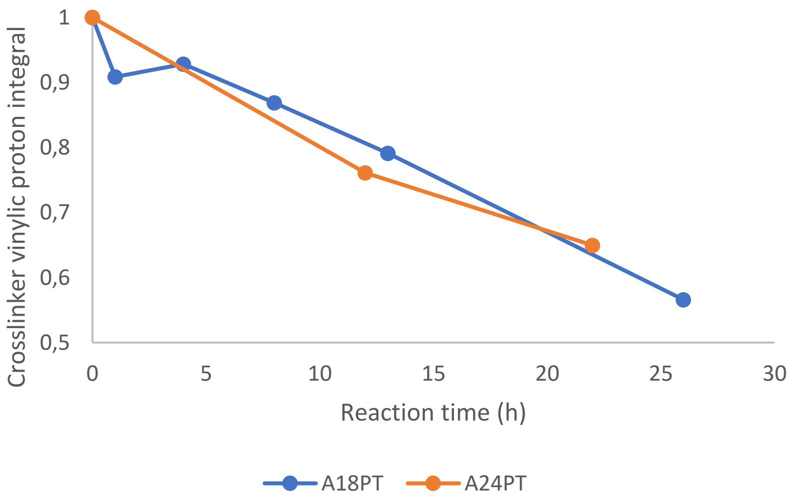


Figure 79: ^{1}*H NMR plot for two mixtures containing alkyd with 20func% pentaerythritol tetraacrylate (PT). Peak at 8.61 ppm was used to normalize the spectra integrals.*

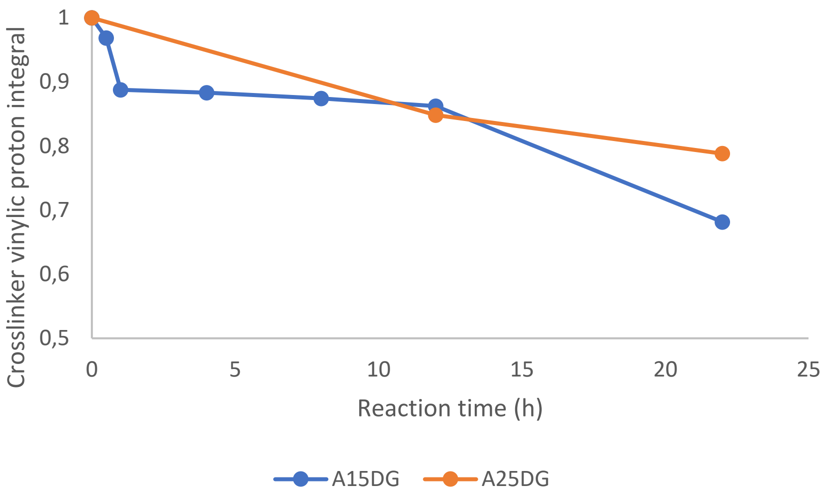


Figure 80: ^{1}H NMR plot for two mixtures containing alkyd with 20func% di(ethylene glycol)diacrylate (DG). Peak at 8.61 ppm was used to normalize the spectra integrals.

Despite the different reaction times, the overall trends in the plots for the PT mixture indicated relatively good repeatability (**Figure 81**). For the DG reaction mixtures, the molecular weight is similar in both parallels at t=12h while relatively large differences are observed at t=22h which is in accordance with NMR observations (**Figure 82**). The difference in molecular weight could be due to poor distribution of the crosslinker in the reaction mixture, resulting in a varying extent of the crosslinking reaction. The differences might also be a result of the accuracy of the GPC instrument and the calculations of the molecular weight (Section **3.1.3**).

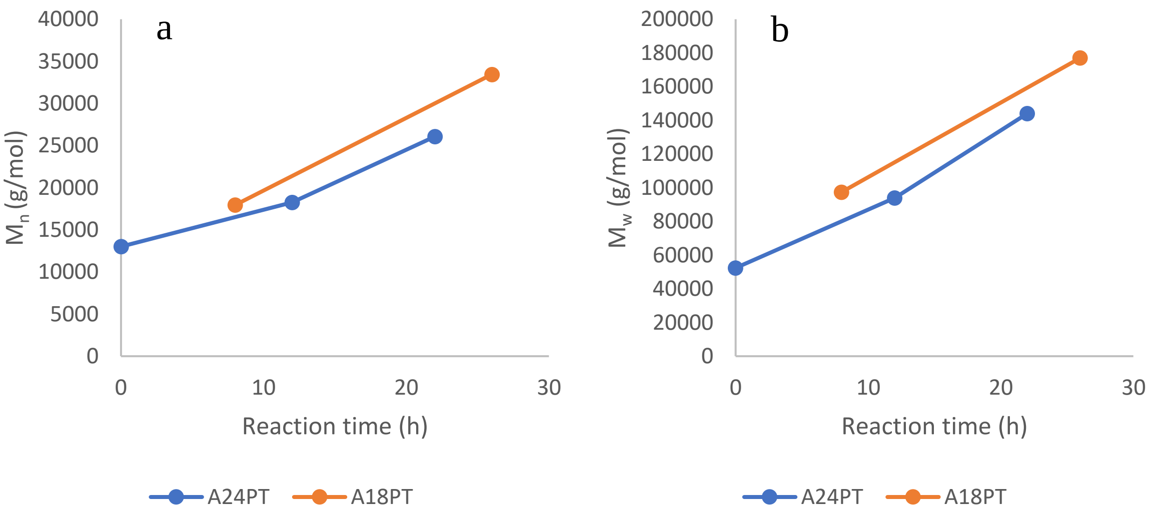


***Figure 81: a)** Number average molecular weight (M_n) and **b)** weight average molecular weight (M_w) of two experiments conducted with alkyd with 20func% pentaerythritol tetraacrylate (PT) after heating at 80 °C.*

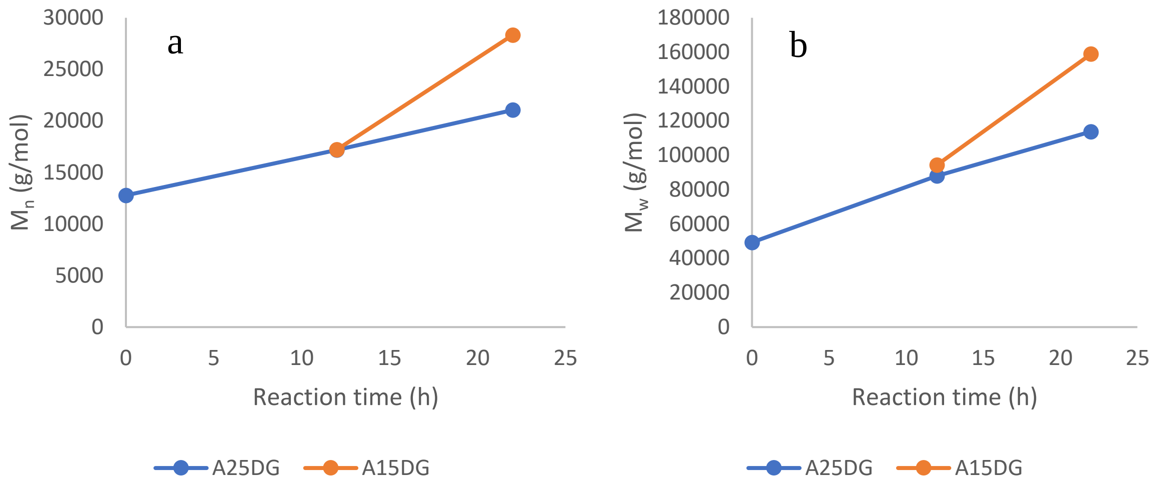


***Figure 82:* a)** *Number average molecular weight (M_n) and* **b)** *weight average molecular weight (M_w) of two experiments conducted with alkyd with 20func% di(ethylene glycol)diacrylate (DG) after heating at 80 °C.*

4.10.2 Emulsion Reactions

The repeatability for the emulsion mixtures were also tested by preparing a sample with 20func% PT which was compared to the previously analyzed E07PT (**Table 15**). Both reaction mixtures were heated at 80 °C for t=22h and were analyzed with NMR, GPC, solid content, pH, drop size, PDI and pendulum hardness.

Table 15: *Amount of emulsion, alkyd, conjugated fatty acid (cFA) and concentration (c) of crosslinker pentaerythritol tetraacrylate (PT).*

	Emulsion			**Crosslinker PT**		
Exp.nr	**Weight (g)**	**Alkyd (mmol)**	**cFA (mmol)**	**Crosslinker (mmol)**	**Weight (g)**	**c (func%)**
E03PT	170.233	35.9777	95.3287	6.045	2.130	20.23
E07PT	179.978	38.0373	100.786	6.108	2.152	19.51

Differences in the two parallels are observed in NMR (**Figure 83**), the solid content (**Figure 84**), drop size (**Figure 85a**), PDI (**Figure 85b**) and pH (**Figure 86**). Some of the differences, such as NMR, might be due to an uneven distribution of the crosslinker while others might be due to the measurements being conducted at different temperatures, such as pH.

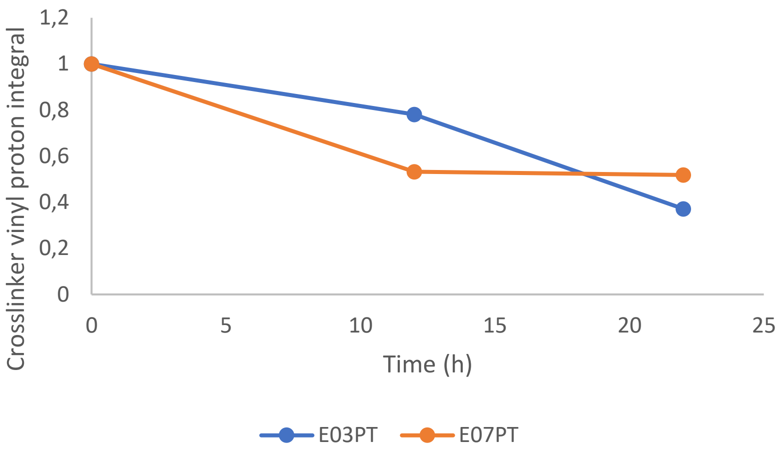


Figure 83: *Decrease in the crosslinker vinyl proton integral from ^{1}H NMR for two parallels of emulsion and 20func% pentaerythritol tetraacrylate (PT). Peak at 8.61 ppm was used to normalize the spectra integrals.*

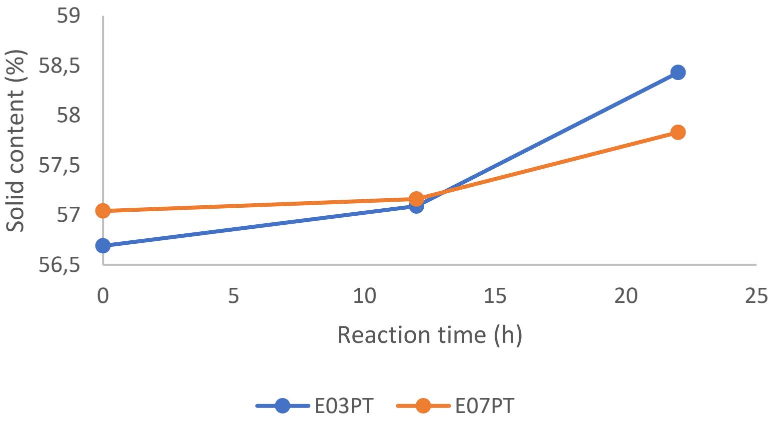


Figure 84*: Solid content for two parallels of emulsion with 20func% pentaerythritol tetraacrylate (PT).*

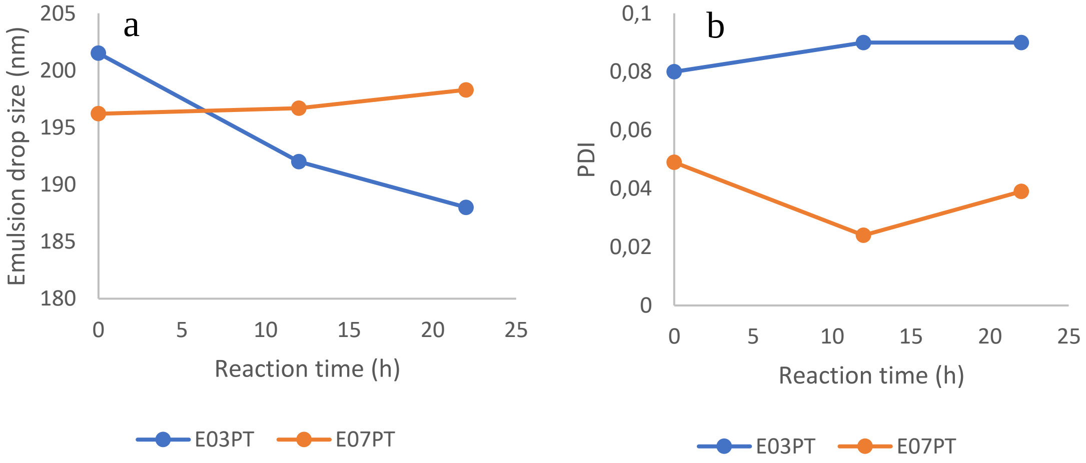


Figure 85: a) *Drop size and* ***b)*** *PDI of two parallels of emulsion with 20func% pentaerythritol tetraacrylate (PT).*

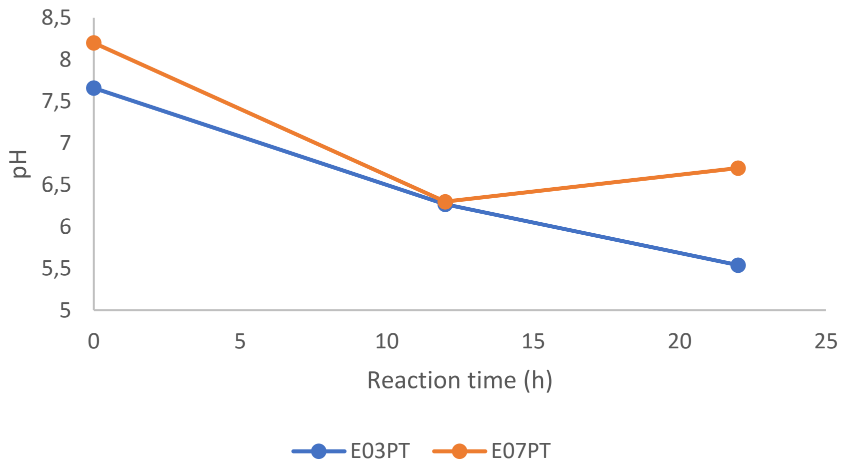


***Figure 86:** pH for two parallels of 20func% pentaerythritol tetraacrylate (PT) in emulsion.*

The molecular weight was calculated for both parallels (**Figure 87**). While the first parallel show an increase in molecular weight from t=12h to 22h, a decrease is observed for the second parallel. All samples were analyzed twice to verify the trends. The decrease in molecular weight had not been previously observed, neither for the alkyd nor emulsion samples. While the decrease in molecular weight is extremely difficult to explain, it may be related to the prolonged drying times for this parallel, causing the autoxidation reaction to occur. However, both samples t=12h and 22h for the second parallel were subjected to the same drying time. While this causes large differences in molecular weight for the two parallels at t=12h, the two parallels show a high degree of repeatability for the t=22h reaction mixtures, despite being subjected to different drying times.

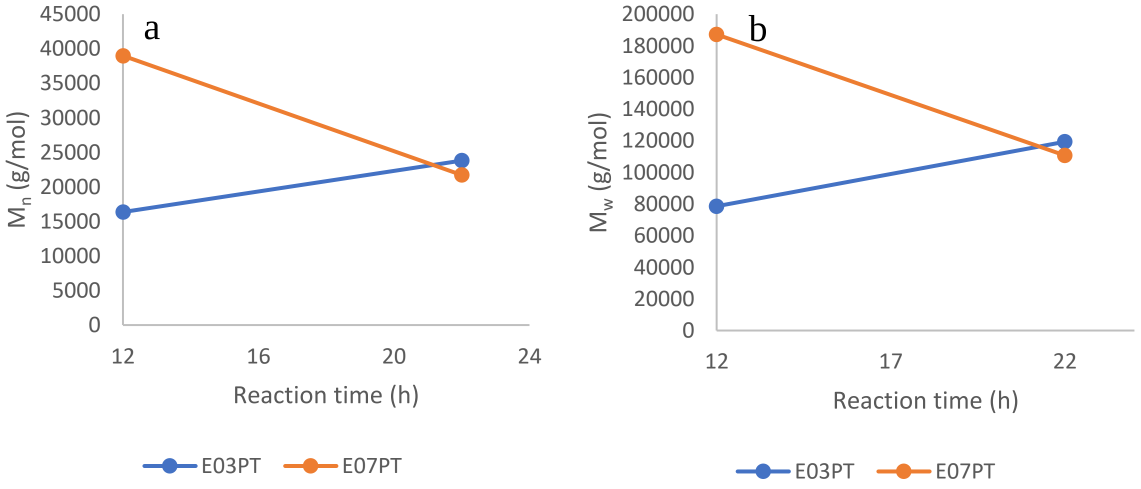


***Figure 87:** **a)** Number average molecular weight (M_n) and **b)** weight average molecular weight (M_w) of two parallels of emulsion with 20func% pentaerythritol tetraacrylate (PT).*

Differences are also observed for the two parallels for the pendulum hardness tests. For both parallels, the softest films are formed by the reaction mixtures after heating for t=12 or 22h while the reaction mixture prior to heating forms the hardest films (**Figure 59** and **Figure 88**).

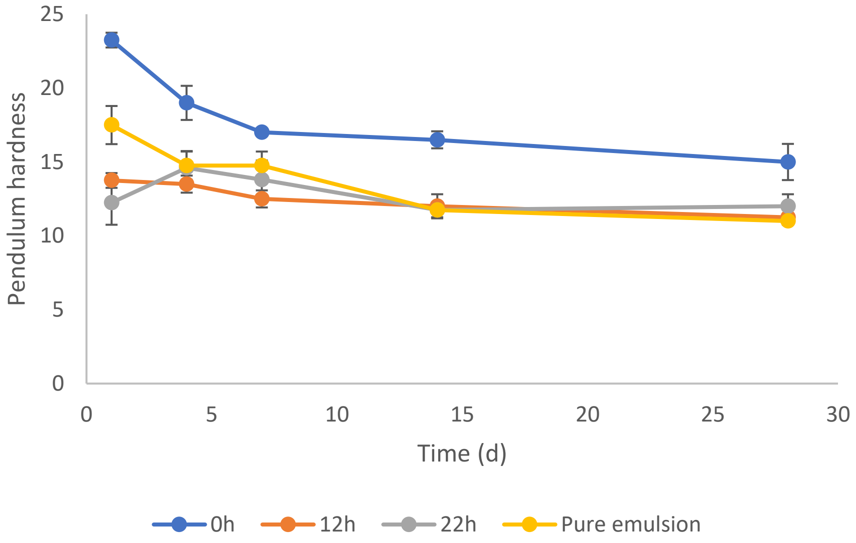


Figure 88: *Pendulum hardness for pure emulsion and emulsion with 20func% pentaeryhritol tetraacrylate (PT) after heating at 80 °C for t=0h, 12h and 22h.*

4.11 Concentration Study in Emulsions

Up to this point, the effect of concentration had only been investigated for the alkyd reaction mixtures, prior to emulsification. 50func% and 20func% had previously been analyzed (E01PT, **Table 10** and E03PT, **Table 11**, respectively). Lower concentrations of crosslinker PT in emulsion were further synthesized under the same conditions as for the previous experiments (**Table 16**), including heating at 80 °C for t=0h, 12h and 22h.

Table 16: *Amount of emulsion, alkyd, conjugated fatty acid (cFA) and concentration (c) of crosslinker PT.*

	Emulsion			**Crosslinker PT**		
Exp.nr	**Weight (g)**	**Alkyd (mmol)**	**cFA (mmol)**	**PT (mmol)**	**Weight (g)**	**c (func%)**
E08PT	181.30	38.317	101.53	3.037	1.070	10.69
E09PT	180.39	38.124	101.02	1.55	0.546	5.78
E10PT	179.19	37.872	100.35	0.786	0.277	3.04

^{1}H NMR shows that the crosslinker vinyl proton integral decreases with time for reaction mixtures 50, 20 and 11func% (**Figure 89a**) and the amount of crosslinker which has reacted relative to the batch size is shown in **Figure 89b**. At t=12h, similar amounts of the crosslinker has reacted in the 50 and 20func% reaction mixtures. Significantly less of the crosslinker has reacted in the 11func% reaction mixture. This is also demonstrated in the 20 and 11func% reaction mixtures at t=22h. This could be due to an increased probability of the reaction occurring as the concentration is increased. For the lower concentrations (6func% and 3func%), the initial intensity of the signal from the vinylic crosslinker protons were not significantly pronounced and could therefore not be accurately monitored through NMR. This indicates that NMR is an unsuitable characterization method for too low concentrations of the crosslinker.

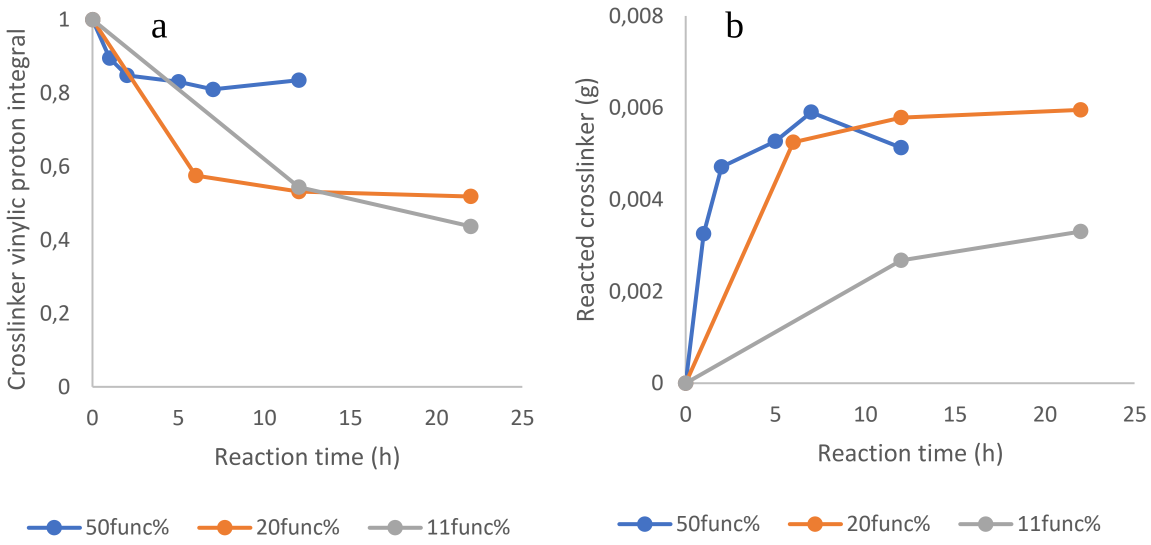


*Figure 89: **a)** Decrease in the crosslinker vinyl proton integral and **b)** amount of crosslinker (g) reacted relative to batch size from ^{1}H NMR for emulsion with 50, 20 or 11func% pentaerythritol tetraacrylate (PT). Peak at 8.61 ppm was used to normalize the spectra integrals.*

The molecular weight of all of the different concentrations of PT added to emulsion are summarized in **Figure 90**. The higher concentration reaction mixtures show similar initial molecular weight. Although the initial molecular weights at t=0h of the lower concentration mixtures were not analyzed, all reaction mixtures are expected to show similar molecular weights as the calculations were carried out to exclude the molecular weight of the residual crosslinker.

The molecular weight of the 11func% PT reaction mixture is superior to the other concentrations at t=12h and 22h. It had been previously observed that the molecular weight in the emulsion samples did not increase significantly during the first 12 hours (see **Figure 52**, **Figure 53**, **Figure 54** and **Figure 55**), possibly due to hydrolysis occurring. This is could explain the relatively small differences and lack of coherence regarding concentration observed in molecular weights between the different concentrations (**Figure 90**). However, this is not observed for the 11func% PT mixture.

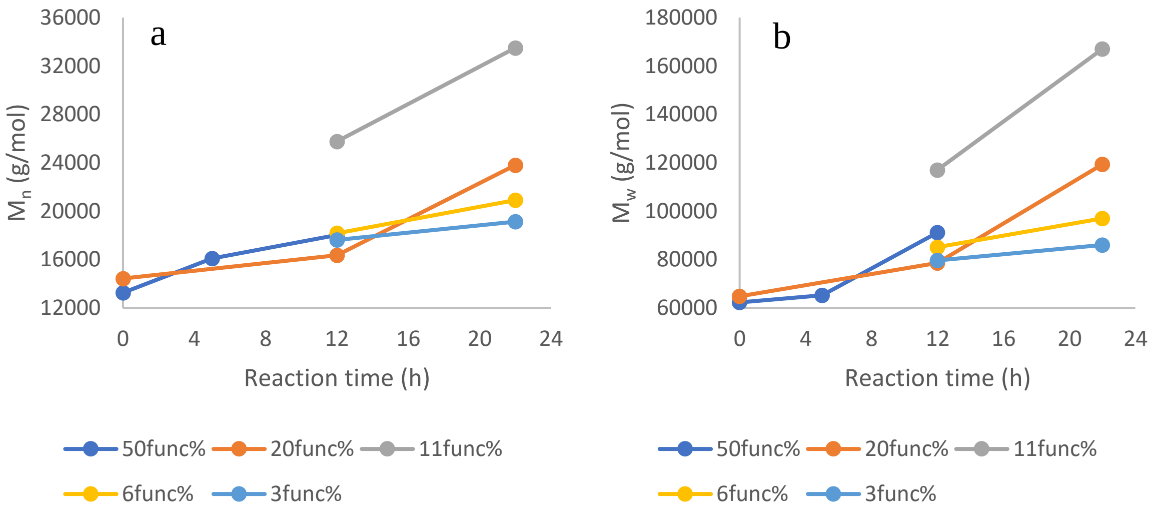


Figure 90: ***a)*** *Number average molecular weight (M_n) and* ***b)*** *weight average molecular weight (M_w) of emulsion with different concentrations of pentaerythritol tetraacrylate (PT) including 50, 20, 11, 6 and 3func% after heating at 80 °C.*

Larger differences between the molecular weights of the different concentrations are observed at t=22h, coherent with the previous experiments (see **Figure 52-Figure 55**). At t=22h, the molecular weight is proportional to the crosslinker concentration (**Figure 90**) except for the 11func% PT mixture. The molecular weight of the 50func% reaction mixture was not measured and could therefore not be compared.

The unreacted crosslinker is expected to be able to move more freely than a crosslinker which has reacted with the polymer as this will affect the relative size and hence movement of the molecule. If the crosslinker concentration is too high, the probability of a reaction between an unreacted crosslinker molecule and the unsaturated alkyd bond might be more likely to occur than with a crosslinker already attached to the alkyd. As more double bonds react, the concentration of available double bonds decreases, further decreasing the probability of the reaction. This may result in the crosslinker being linked with only one alkyd chain which will not lead to an increased molecular weight. By decreasing the crosslinker concentration, fewer freely moving small crosslinker molecules are present which may increase the probability of the reaction to occur between a crosslinker molecule already attached to the alkyd polymer. This could explain the superior molecular weight of the 11func% PT mixture. However, the superior molecular weight could also be a result of the prolonged drying time of the particular samples. The reaction mixture was dried for almost two months while other samples such as the 6 and 3func% were only dried for one week. The prolonged drying may have resulted in the autoxidation reaction occurring.

In order to properly compare the effect of the crosslinker concentration, the samples discussed should have been exposed to the same drying conditions. For this set of experiments, the changes observed in molecular weight may reflect the effect of concentration, the drying procedure or a combination of both.

Further analysis was conducted on the 20func% and 11func% reaction mixture by Jotun AS, including solid content (**Figure 91**), drop size (**Figure 92a**) and PDI (**Figure 92b**), all indicating small differences. The pH is inversely proportional to the reaction time for both samples but the decrease also appears dependent on the concentration (**Figure 93**). The pendulum hardness for both concentrations show that the softest film is formed by the reaction mixtures at t=12h (**Figure 94**).

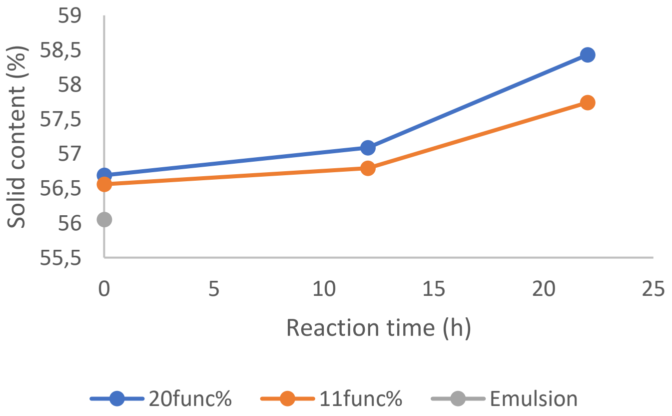


Figure 91: Solid content of emulsion and emulsion with 20 or 11func% pentaerythritol tetraacrylate (PT) after heating at 80 °C for t=0h, 12h and 22h.

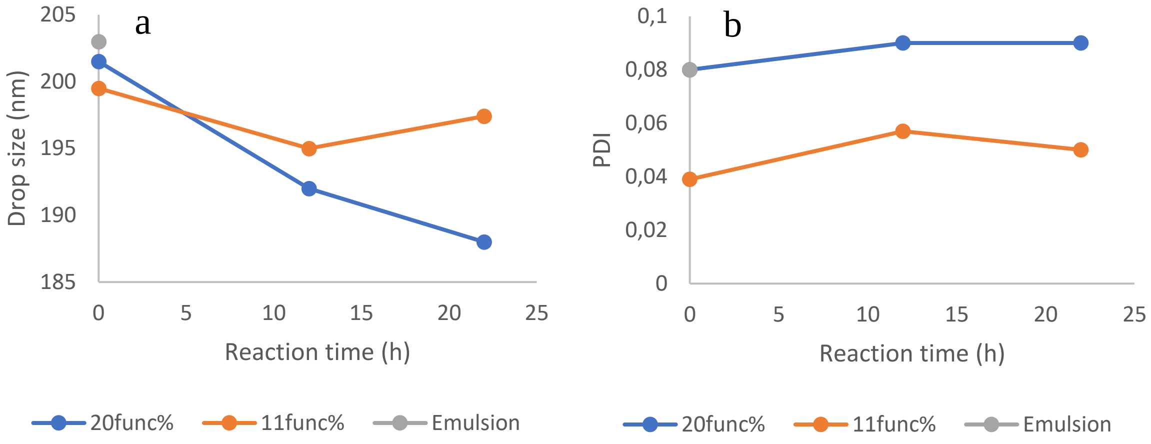


Figure 92: *a)* Drop size and *b)* PDI of emulsion and emulsion with 20 or 11func% pentaerythritol tetraacrylate (PT) after heating at 80 °C for t=0h, 12h and 22h.

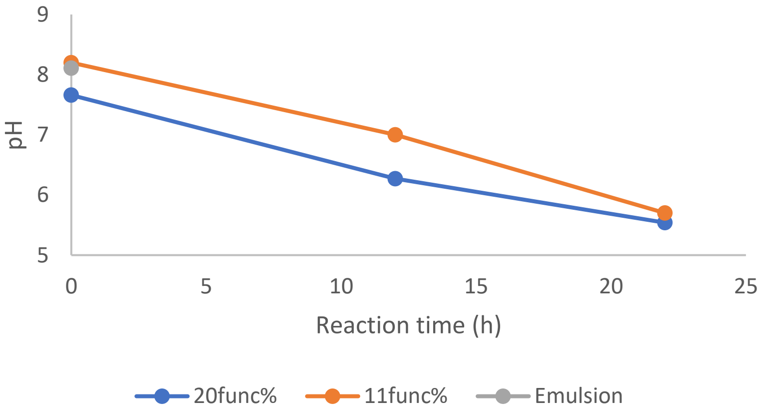


Figure 93: pH of emulsion and emulsion with 20 or 11func% pentaerythritol tetraacrylate (PT) after heating at 80 °C for t=0h, 12h and 22h.

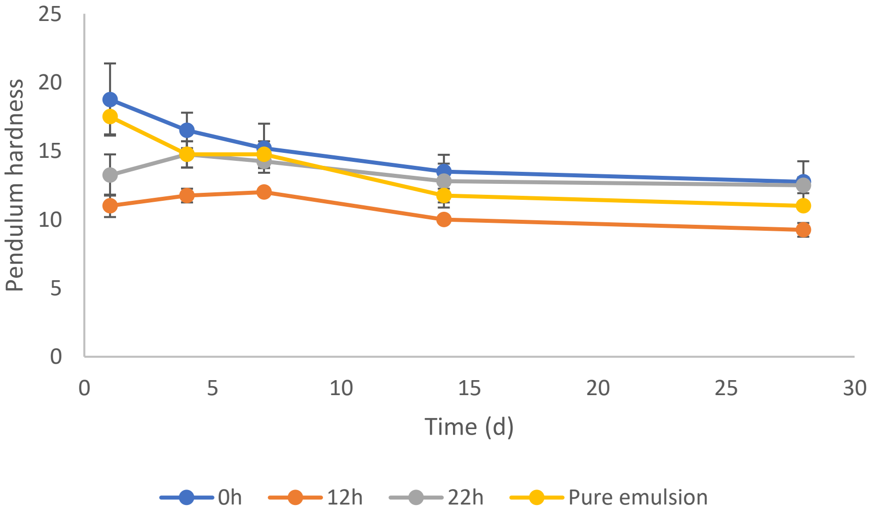


Figure 94: Pendulum hardness for pure emulsion and emulsion containing 11func% pentaerythritol tetraacrylate (PT) at t=0h, 12h and 22h.

4.12 Addition of Crosslinker to Alkyd Prior to Emulsification

In this set of experiments, the crosslinker was added to the alkyd mixture prior to emulsification (CPE). Due to the relatively low temperature and reaction time, the crosslinking reaction was not expected to occur to a significant extent during the emulsification (Section **4.5**). A new alkyd (MH-5e) and emulsion (MHE-5e) were synthesized for this set of reaction and its properties compared to the previous are given in **Table 4** and **Table 5**. 20func% PT or MPB were added to the alkyd (**Table 17**). The mixtures, including emulsion without crosslinker, were then subjected to heating at 80 or 60 °C for t=3h, 6h, 9h and 24h.

Adding the crosslinker prior to emulsification is expected to facilitate the reaction by distributing the crosslinker in the alkyd droplets and limits the need for the crosslinker to travel through the water phase to enter the micelles.

The storage stability of the reaction mixtures was analyzed through pH, drop size and PDI, as this is an important factor the industrial use of the final products. The product is intended for commercial use and changes in these properties can affect production timelines as well as the actual "shelf-life". The measurements were conducted after the preparation of samples and after storing the samples in RT for t=1.5 months. The drop size and PDI analysis were only conducted for the reaction mixtures after being subjected to heating at 80 °C for t=0h and 24h, as these are expected to be the maximum values of the reactions.

Table 17: *Amount of alkyd, conjugated fatty acid (cFA) and concentration (c) of crosslinkers pentaerythritol tetraacrylate (PT) and 1,1' (Methylenedi-4,1-phenylene) (MPB).*

	Emulsion			Crosslinker		
Exp.nr	**Weight alkyd (g)**	**Alkyd (mmol)**	**cFA (mmol)**	**Crosslinker (mmol)**	**Weight (g)**	**c (func%)**
J24	904.82	371.89	985.39		N/A	
J25	802.20	329.71	873.63	PT (54.88)	19.34	20.08
J26	913.76	375.57	995.13	MPB (128.58)	46.08	20.54

4.12.1 Emulsion Without Crosslinker

4.12.1.1 Reaction Time

From previous experiments, increased molecular weights and hardness were obtained when the emulsion was heated, indicating that a reaction occurred within the pure emulsion heated (Section **4.9.1**). The emulsion without crosslinker was therefore also heated and samples were tested more frequently (t=3h, 6h, 9h and 24h) to further establish this.

For the emulsion heated to 60 °C, the pH remains constant at ≤9h (**Figure 95**) after which a slight decrease in pH is observed. A slightly larger decrease in pH is observed for the emulsion heated at 80 °C, in accordance with previous results. Small increases are observed in the drop size and PDI at t≥6h (**Figure 96**), especially for the emulsion heated at 80 °C, contrary to the previous observations.

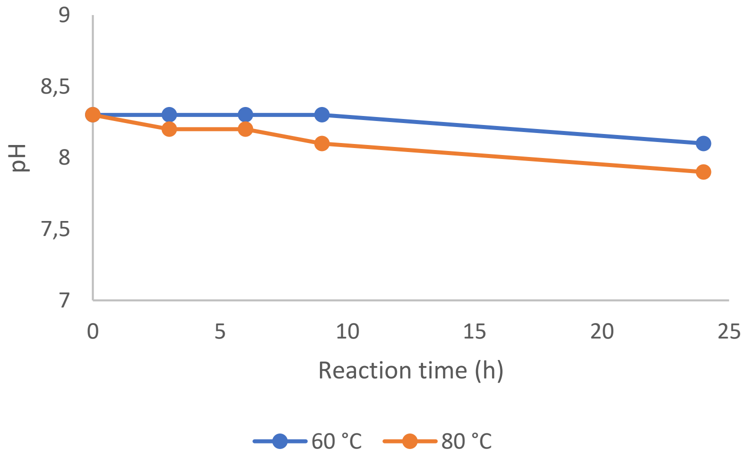


Figure 95: *pH of emulsion heated to 60 or 80 °C for t=0h, 3h, 6h, 9h and 24h.*

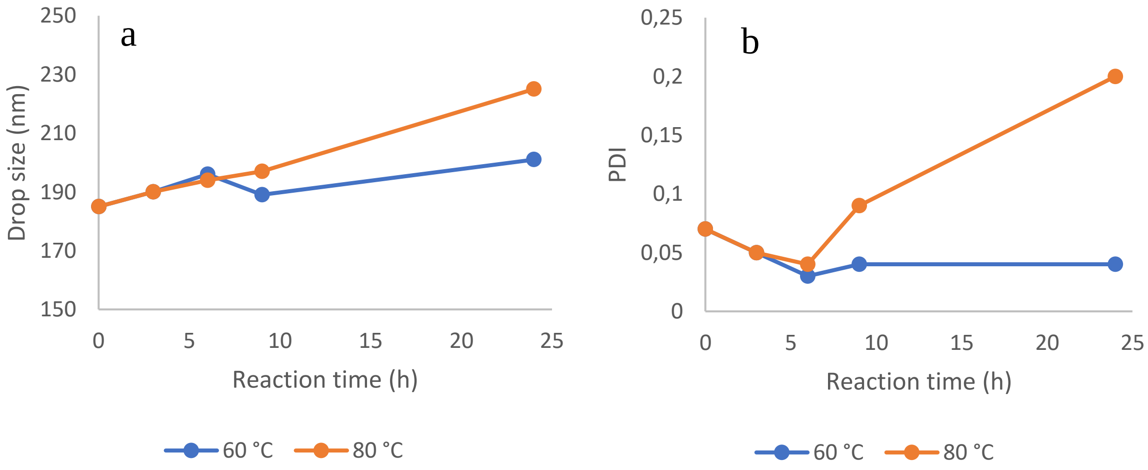


Figure 96: a) *Drop size and* ***b)*** *PDI of emulsion heated to 60 or 80 °C for t=0h, 3h, 6h, 9h and 24h.*

The GPC calculations shows a slight decrease in the molecular weight at t=3h for the emulsion heated at 60 °C (**Figure 97**), after which a slight increase is observed. For the emulsion heated at 80 °C, the molecular weight increases gradually during the first 9 hours after which the molecular weights remain constant.

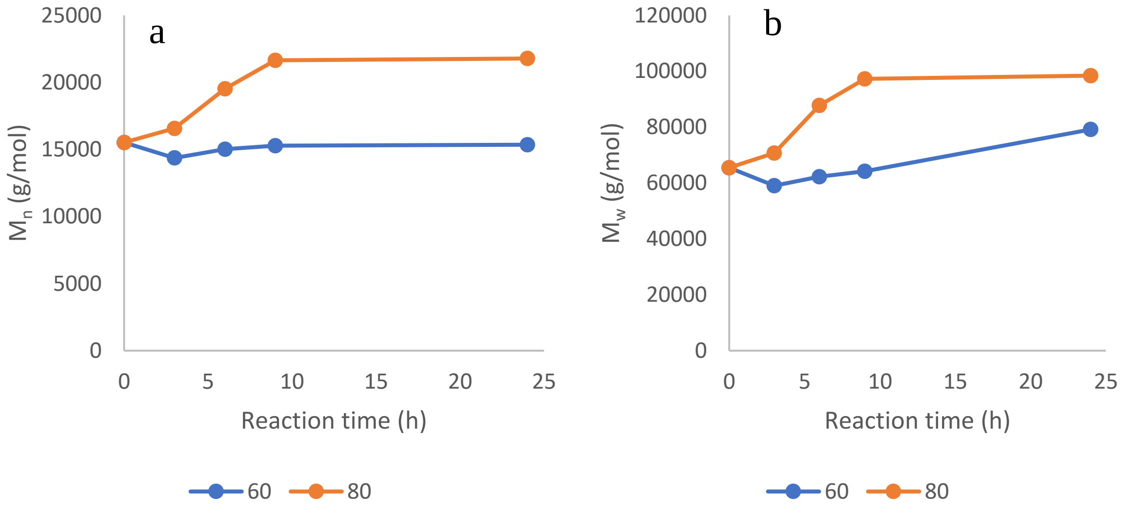


Figure 97: ***a)*** *Number average molecular weight (M_n) and* ***b****) weight average molecular weight (*M_w*) of emulsion heated at 60 or 80 °C for t=0h, 3h, 6h, 9h and 24h.*

For the GPC analysis conducted by Jotun AS, the conventional method shows no significant change in the M_n at either temperature (**Figure 98a**). The initial decrease in molecular weight at t=3h is also apparent using the conventional and absolute method, although it is apparent for both temperatures and not limited to the emulsion heated at 60 °C (**Figure 98-Figure 100**). The decrease could be caused by hydrolysis; however, there are no indications of this for the pH measurements (**Figure 95**). After t=3h, the molecular weight is increasing. The molecular weights obtained after t=24h are similar or lower (especially the M_z, absolute method) compared to the initial emulsion although they are generally slightly larger for the emulsion heated at 80 °C compared to at 60 °C.

The lower molecular weights obtained after heating contradicts the observations from the GPC analysis conducted at NTNU (**Figure 97**) as well as previous observations in section **4.9.1** where the molecular weight was found to increase, especially at t=22h.

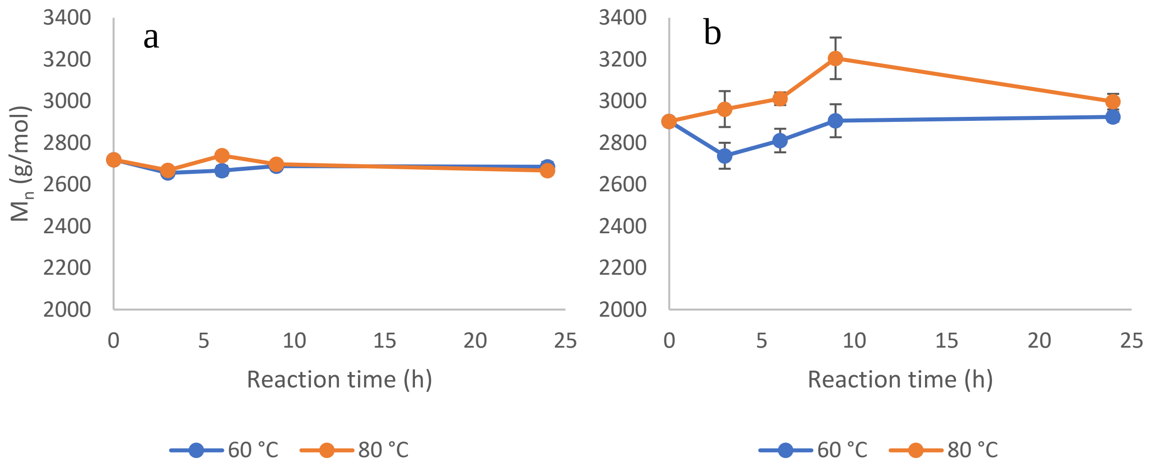


Figure 98: *Number average molecular weight (M_n) of emulsion heated to 60 and 80 °C for t=0h, 3h, 6h, 9h and 24h using the **a)** conventional method and **b)** absolute method.*

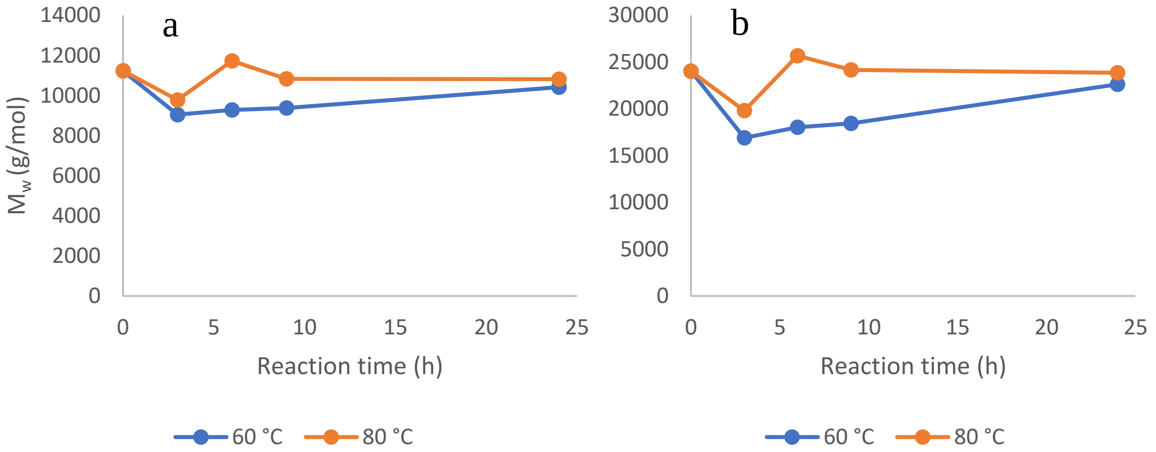


Figure 99: *Weight average molecular weight (M_w) of emulsion heated to 60 and 80 °C for t=0h, 3h, 6h, 9h and 24h using the **a)** conventional method and **b)** absolute method.*

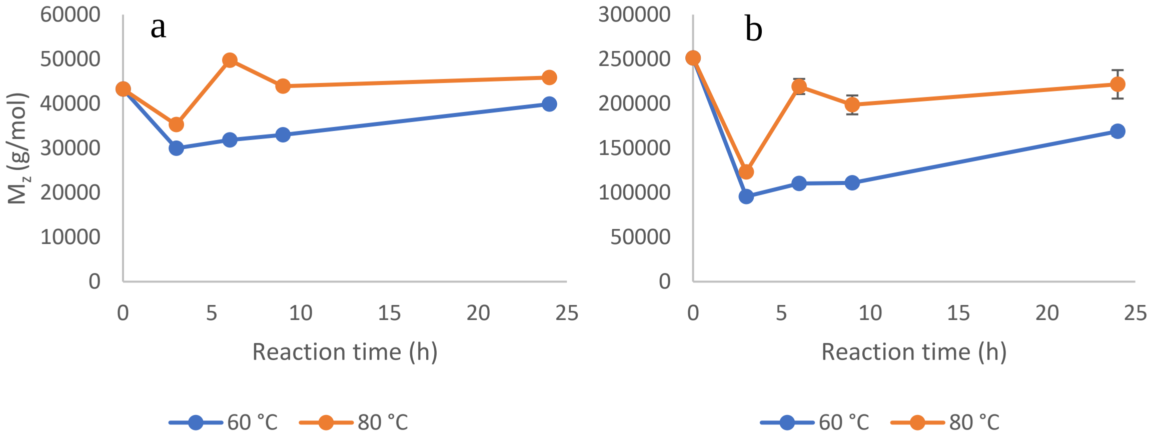


Figure 100: *Z-average molecular weight (M_z) of emulsion heated to 60 and 80 °C for t=0h, 3h, 6h, 9h and 24h using the **a)** conventional method and **b)** absolute method.*

For the emulsion heated at 60 °C, the emulsions heated for t≥9h form harder films than the unheated emulsion while the emulsion heated for t<9h form softer films (**Figure 101a**). This may be related to the changes in molecular weight, which appears to decrease at low reaction times and gradually increase. The increased hardness after heating for t≥9h was demonstrated previously (**Figure 77**). There is no clear correlation between the reaction time and pendulum hardness for the emulsions heated at 80 °C (**Figure 101b**).

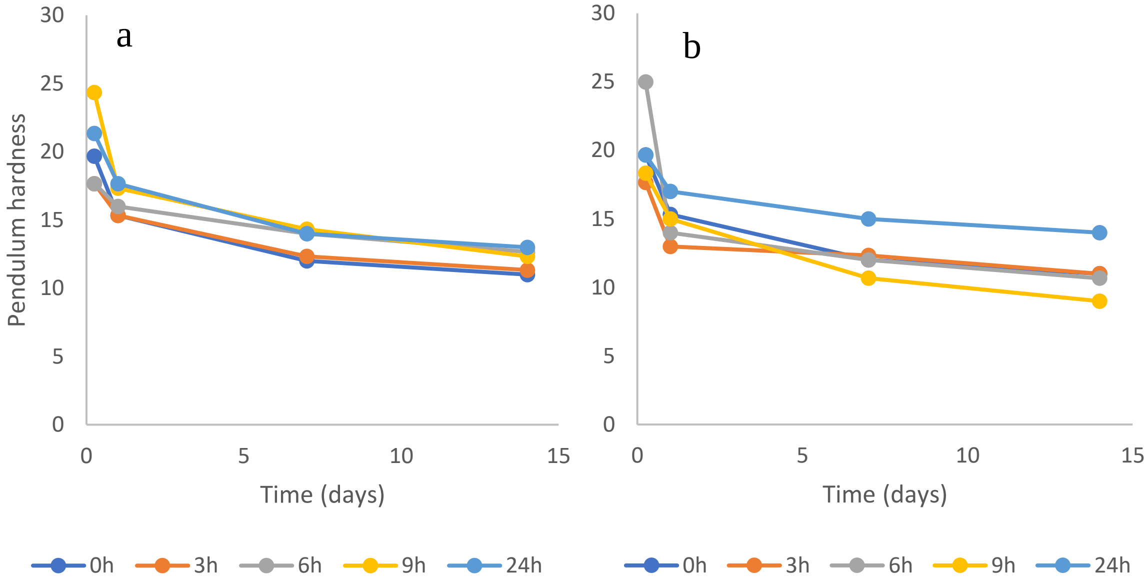


*Figure 101: Pendulum hardness for films formed by pure emulsion after heating at **a)** 60 °C and **b)** 80 °C at t=0h, 3h, 6h, 9h and 24h.*

In order to compare the effect of the temperature on the emulsion, the pendulum hardness was compared at constant reaction times (**Figure 102**). The emulsions which were subjected to heat generally show similar or improved hardness compared to the initial emulsion. Although no clear trend could be observed between the hardness and heating temperature, the results indicate that heating does not have a negative effect on the hardness.

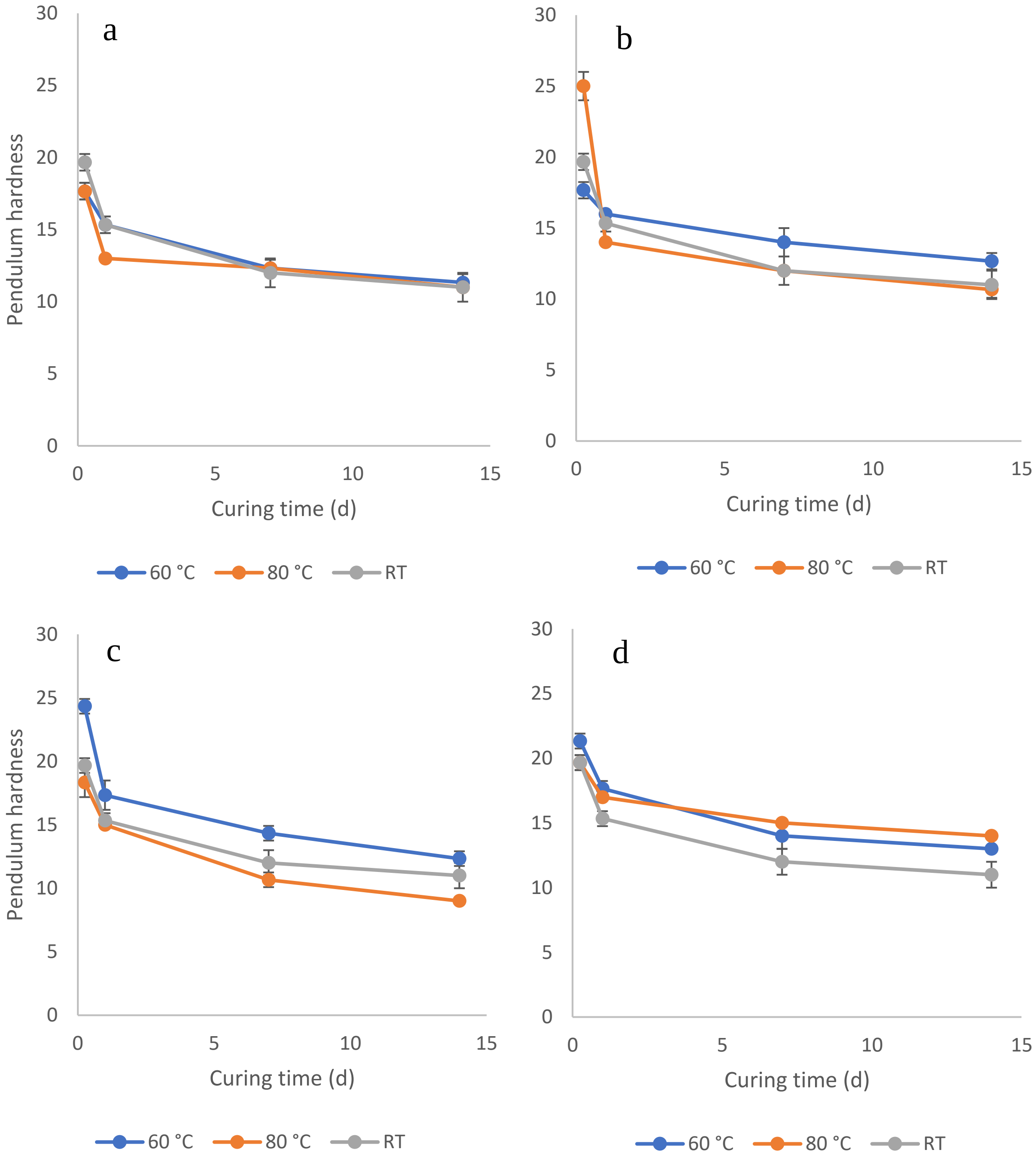


Figure 102: *Pendulum hardness of emulsion stored at room temperature (RT) and emulsion heated at 60 or 80 °C for* ***a)*** *t=3h,* ***b)*** *t=6h,* ***c)*** *t=9h and* ***d)*** *t=24h.*

4.12.1.2 Storage Stability

Small differences are generally observed in pH, drop size and PDI (**Figure 103** and **Figure 104**) after storage for t=1.5 months, indicating a good storage stability.

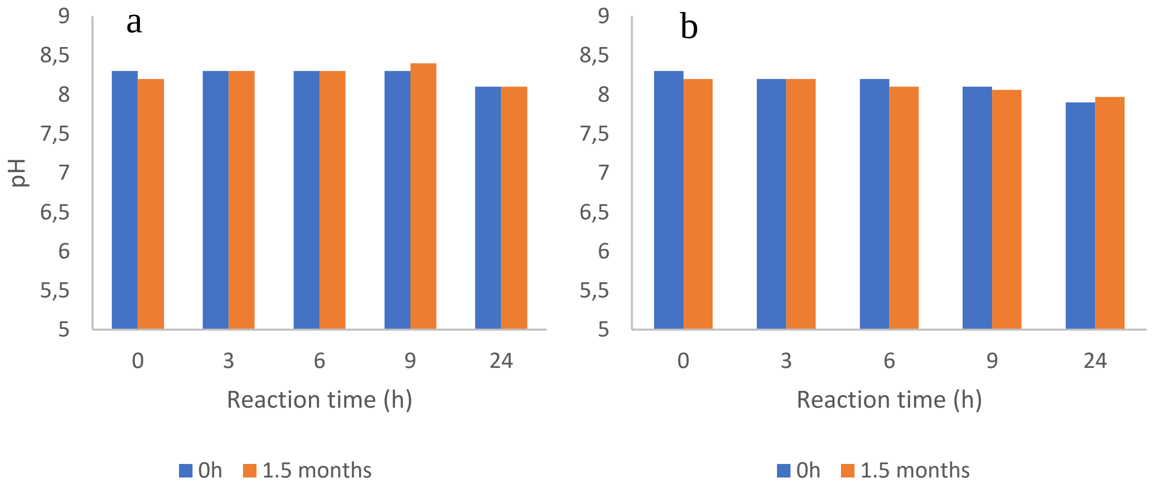


***Figure 103:** pH of emulsion heated at **a)** 60 °C and **b)** 80 °C at t=0h, 3h, 6h, 9h and 24h. pH was measured at t=0h and 1.5 months.*

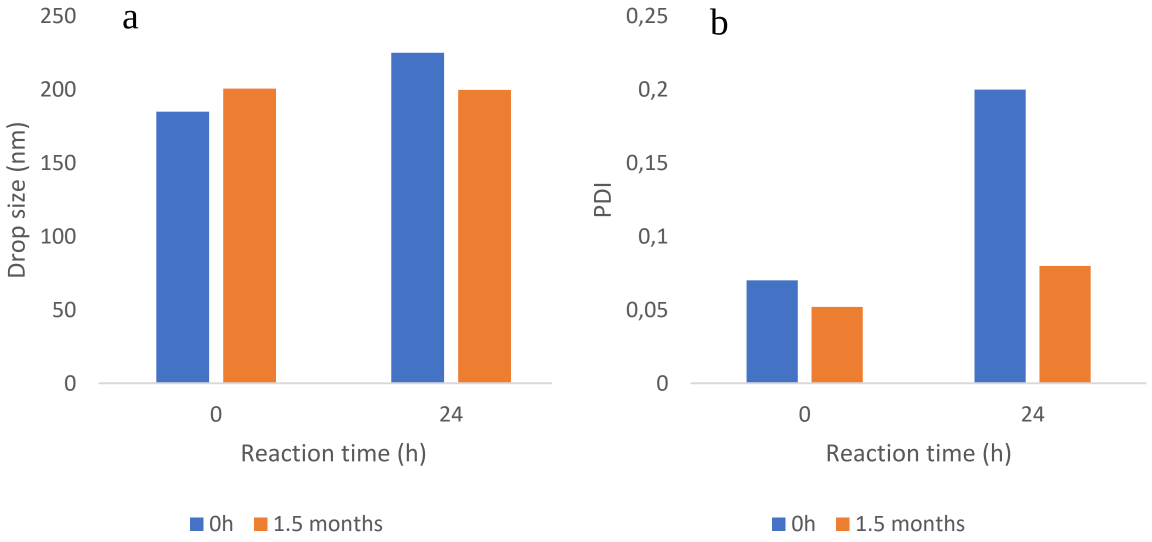


***Figure 104:** **a)** Drop size and **b)** PDI of emulsion at t=0h and after heating at t=24h at 80 °C. Measurements were at t=0h and 1.5 months.*

4.12.2 Pentaerythritol Tetraacrylate (PT)

4.12.2.1 Reaction Time and Temperature

As the reaction time is increased, the pH decreases (**Figure 105**) at both temperatures, although more significant at an elevated temperature. This could indicate that hydrolysis is occurring as a competing reaction also in this system, and that the rate is proportional to the temperature. The drop size (**Figure 106a**) and the drop size distribution (**Figure 106b**) remain constant for both temperatures except for the reaction mixture which was heated to 60 °C for t=24h. In this reaction mixture the total drop size is increased.

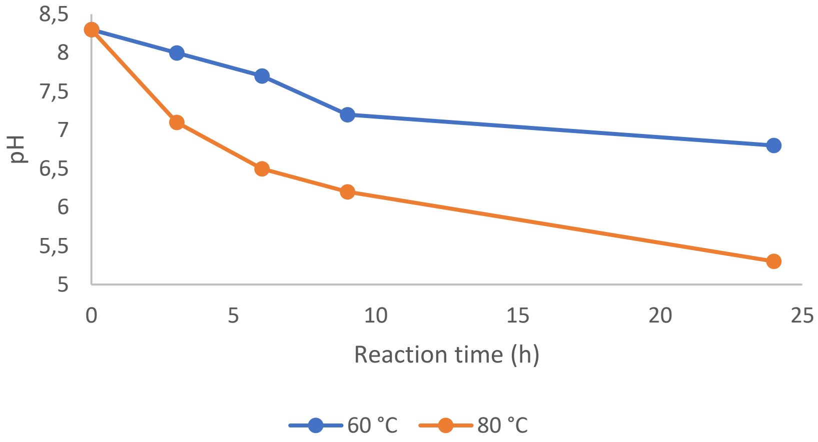


***Figure 105:** pH of emulsion and 20func% PT heated to 60 or 80 °C for t=0h, 3h, 6h, 9h and 24h.*

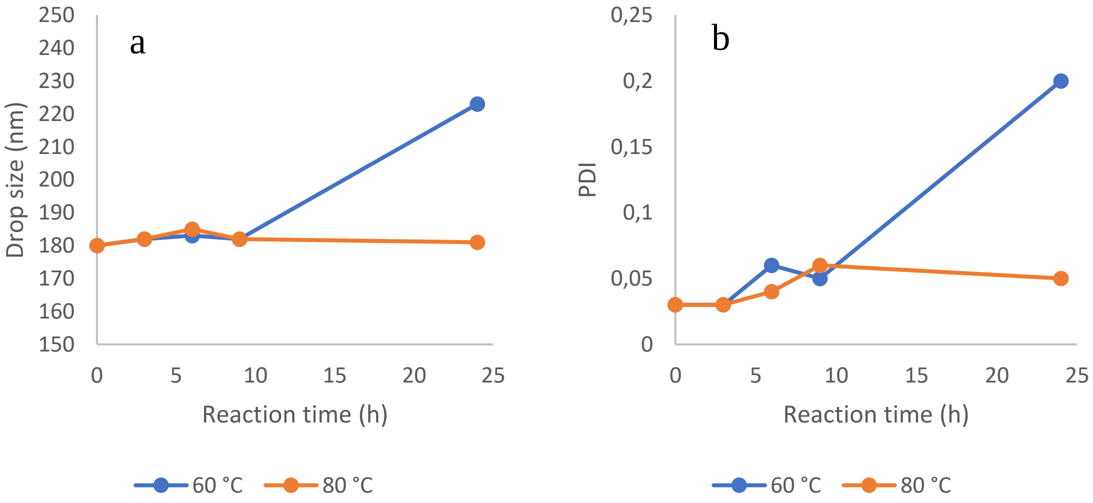


***Figure 106: a)** Drop size and **b)** PDI of emulsion and 20func% pentaerythritol tetraacrylate (PT) heated to 60 or 80 °C for t=0h, 3h, 6h, 9h and 24h.*

The reaction mixtures with PT heated at both temperatures show similar behavior in ^{1}H NMR (**Figure 107**). For t≤6h, ^{1}H NMR indicates that the reaction progress in a similar manner at both temperatures while at t>6h, the reaction progresses faster at increased temperature. The vinylic proton integral is inversely proportional to the reaction time except for the t=6h sample where an increase in the vinylic integral is observed for both temperatures. This could be due to an uneven distribution of the crosslinker in the mixtures.

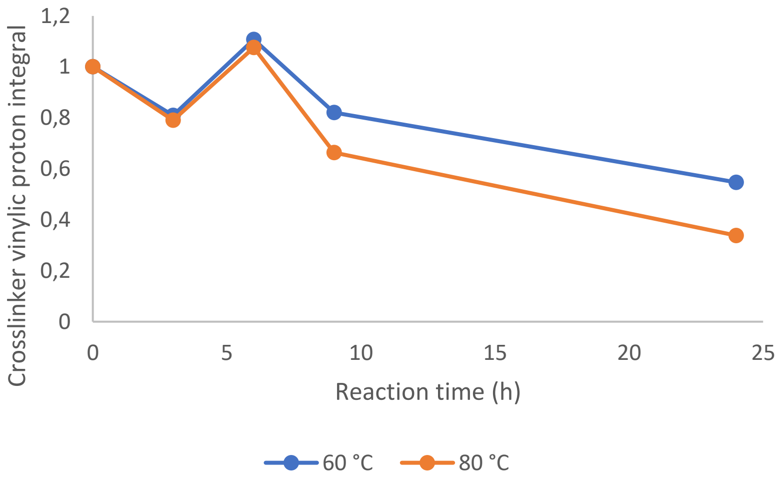


Figure 107: Decrease in vinylic integrals in reaction mixture consisting 20func% pentaerythritol tetraacrylate (PT) at 80 and 60 °C at t=0h, 3h, 6h, 9h and 24h. Peak at 8.61 ppm was used to normalize the spectra integrals.

For the reaction mixture heated at 60 °C, an initial decrease in molecular weight is observed at t=3h while the molecular weight of the 80 °C remain constant (**Figure 108**). This further indicates that hydrolysis occurs. At t≥3h, the molecular weights are increased, and the largest molecular weights are produced for the mixture heated at 80 °C.

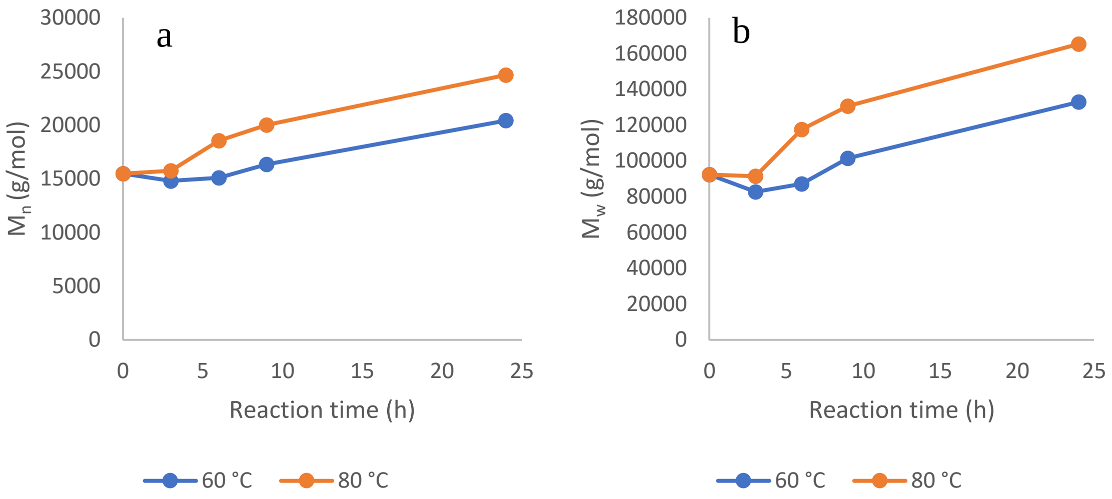


Figure 108: ***a)*** *Number average molecular weight (M_n) and* ***b)*** *weight average molecular weight (M_w) of emulsion and 20func% pentaerythritol tetraacrylate (PT) after heating at 60 or 80 °C for t=0h, 3h, 6h, 9h and 24h.*

The initial decrease at t=3h is also observed using the conventional and absolute method (**Figure 109-Figure 111**), analyzed by Jotun AS. These are particularly pronounced for the reaction mixture heated at 60 °C but can also be observed in the M_z for the reaction mixture heated at 80 °C. This further supports that hydrolysis occurs. Increases in the M_n are observed for the mixture heated at 80 °C, further indicating that the crosslinkers are reacting simultaneously as the hydrolysis. At t>3h, the molecular weights increase in a linear manner, resulting in the highest molecular weight obtained at t=24h. The largest increases in molecular weight are generally obtained for the mixture heated at 80 °C although the differences between the molecular weight obtained at the two temperatures are small, especially the M_z.

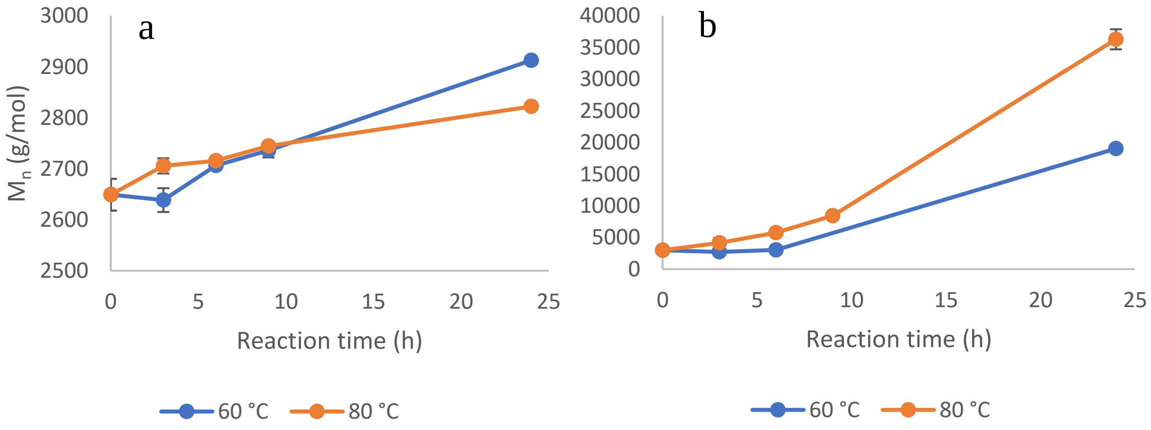


Figure 109: *Number average molecular weight (M_n) of emulsion with 20func% pentaerythritol tetraacrylate (PT) heated at 60 or 80 °C for t=0h, 3h, 6h, 9h and 24h using the* ***a)*** *conventional and* ***b)*** *absolute method.*

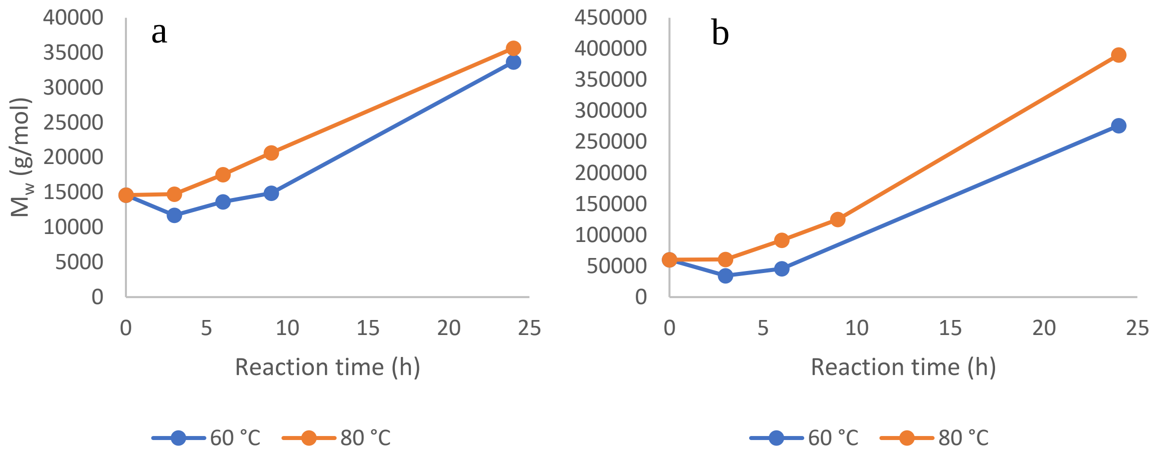


*Figure 110: Weight average molecular weight (M_w) of emulsion with 20func% pentaerythritol tetraacrylate (PT) heated at 60 or 80 °C for t=0h, 3h, 6h, 9h and 24h using the **a)** conventional and **b)** absolute method.*

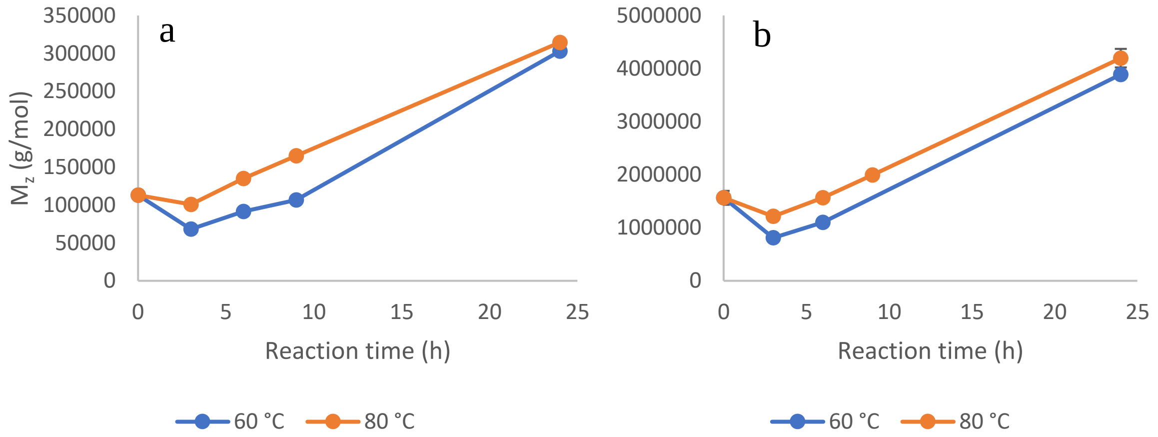


*Figure 111: Z-average molecular weight (M_z) of emulsion with 20func% pentaerythritol tetraacrylate (PT) heated at 60 or 80 °C for t=0h, 3h, 6h, 9h and 24h using the **a)** conventional and **b)** absolute method.*

For both temperatures, the hardest films are formed for the samples with crosslinker which were not subjected to heating (**Figure 112**), indicating that the residual crosslinker contributes to the curing process through its reactive unsaturated bonds. The second hardest films were initially formed by the pure emulsion, which had not been subjected to heating. The hardness is generally inversely proportional to the reaction times. At both temperatures, the softest films are generally formed for t=24h, followed by t=9h. This could be due to the loss of unsaturated bonds to contribute to the autoxidation reaction, despite the increased initial molecular weight.

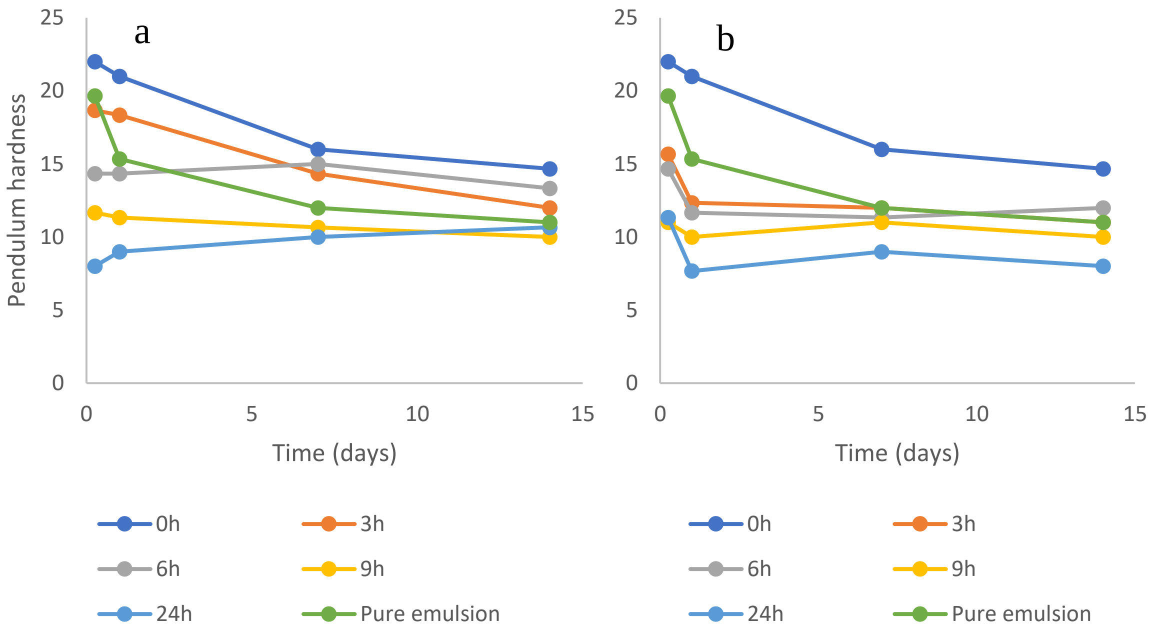


Figure 112: *Pendulum hardness of films formed by emulsion and 20func% pentaerythritol tetraacrylate (PT) which were heated at* ***a)*** *60 °C and* ***b)*** *80 °C for t=0h, 3h, 6h, 9h and 24h.*

The effect of the temperature was also investigated by comparing films obtained at constant reaction times (**Figure 113**). For all reaction times, the hardness of the films from the reactions mixtures which had been heated form softer films than the unheated reaction mixture, followed by the mixtures heated at 60 °C. This could be due to hydrolysis of the ester bond which is expected to occur more rapidly at higher temperatures or the loss of unsaturated bonds, also occurring more rapidly at elevated temperatures. Larger differences in hardness between the films from the mixtures heated at different temperatures are observed at low reaction times (t≤6h). As the reaction time increases further, smaller differences are observed between the films from the different temperatures.

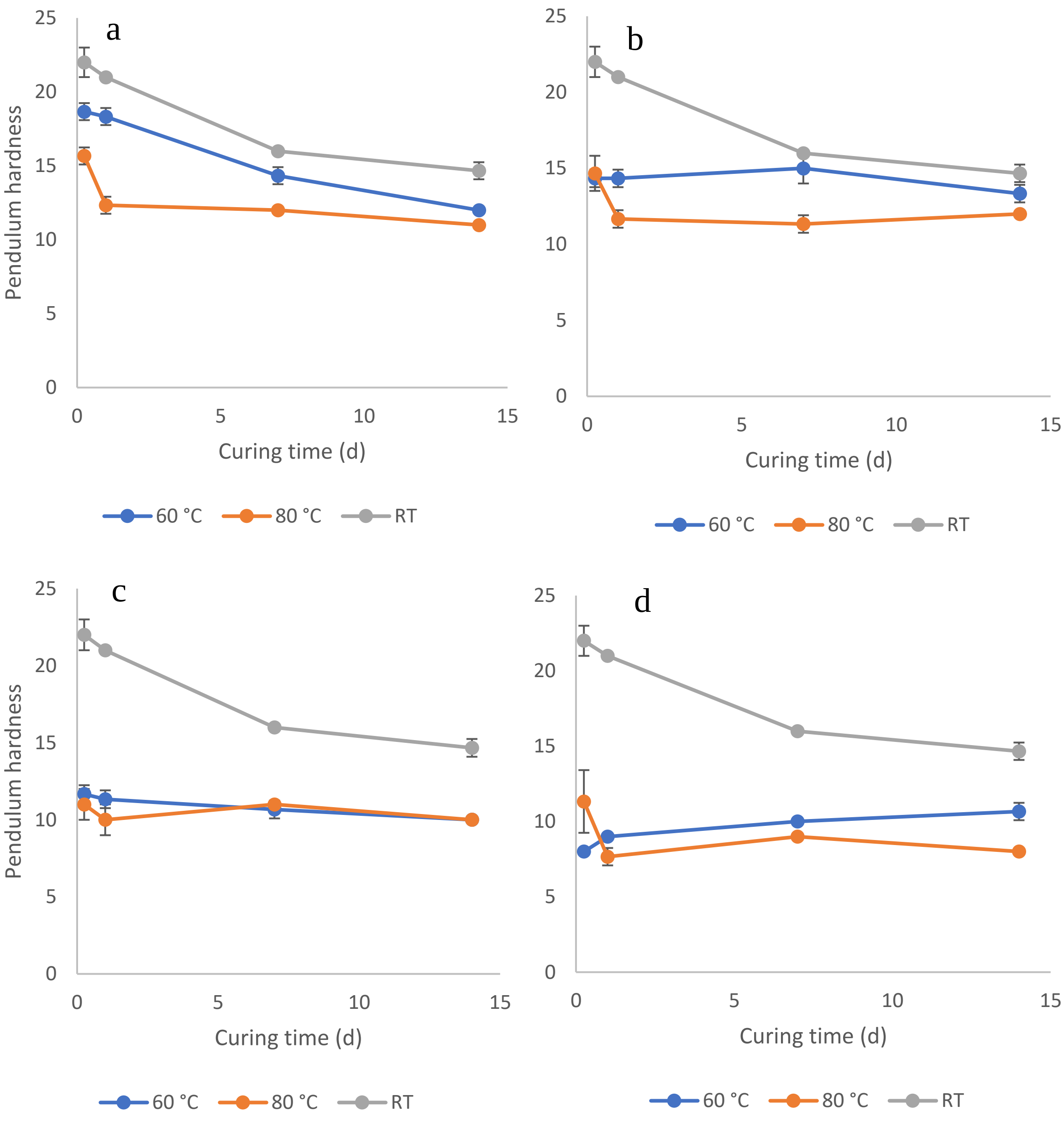


__Figure 113:__ Pendulum hardness of unheated emulsion with 20func% pentaerythritol tetraacrylate (PT) stored at room temperature (RT), and emulsion with 20func% PT heated at 60 or 80 °C for __a)__ t=3h, __b)__ t=6h, __c)__ t=9h, and __d)__ t=24h.

4.12.2.2 Storage Stability

The pH measurements indicate a low stability for several of the reaction mixtures containing 20func% PT. After storing the samples in RT for t=1.5 months, the pH was significantly lowered for many of the samples, especially those with short reaction times (**Figure 114**). This indicates that residual crosslinker in the reaction mixtures can be the cause of the decrease in pH, possible attributed to hydrolysis. The decrease in pH might have a negative effect on properties of the final product, including the molecular weight. However, the drop size and PDI are not significantly affected by the storage period (**Figure 115**).

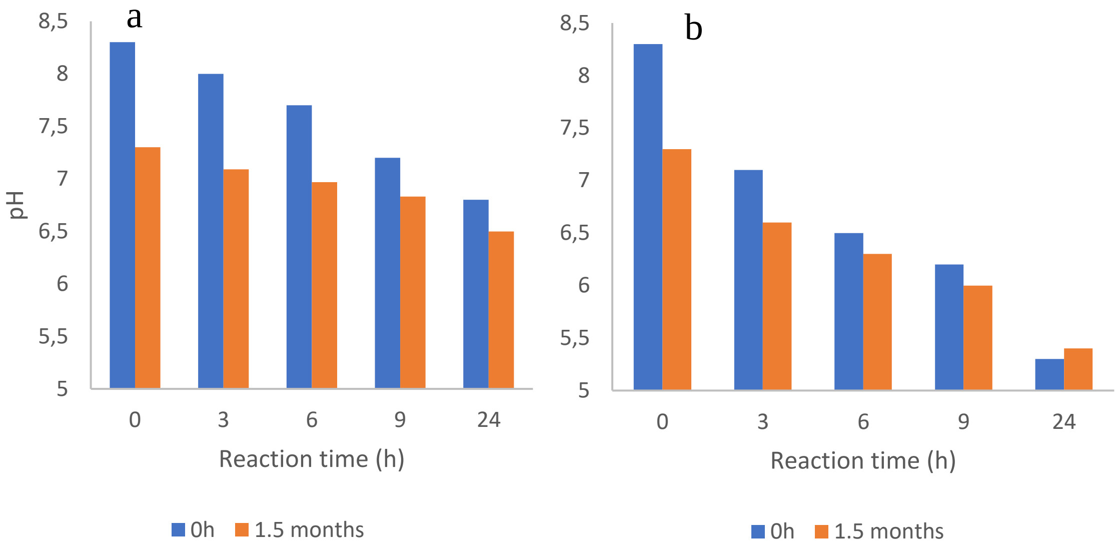


Figure 114: *pH of of emulsion with 20func% pentaerythritol tetraacrylate (PT) heated at* ***a)*** *60 °C and* ***b)*** *80 °C at t=0h, 3h, 6h, 9h and 24h. pH was measured at t=0h and 1.5 months.*

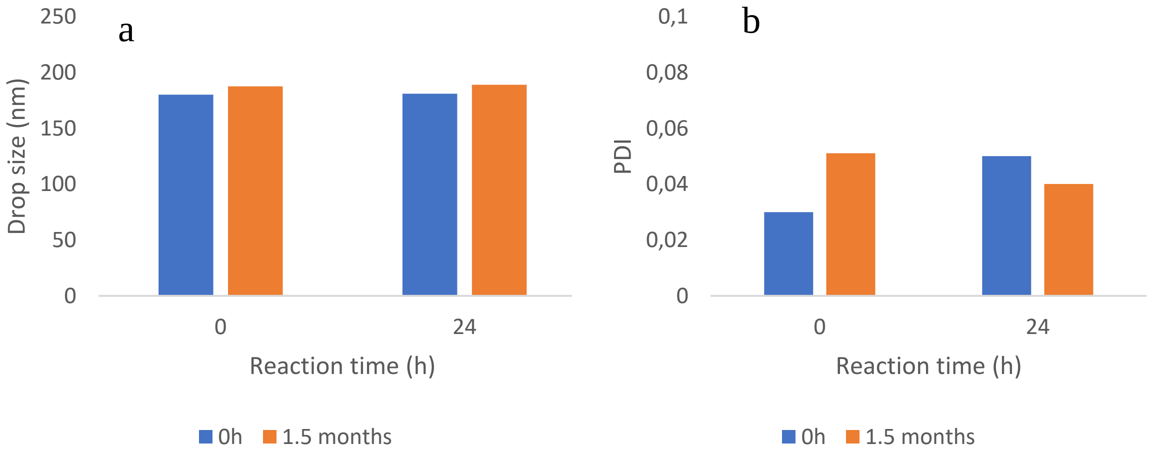


Figure 115: a) *Drop size and* ***b)*** *PDI of emulsion with 20func% pentaerythritol tetraacrylate (PT) at t=0h and after heating at t=24h at 80 °C. Measurements were done at t=0h and 1.5 months.*

4.12.2.3 Comparison of Reaction Systems

The CPE system with PT was compared to previously investigated systems in which the crosslinker was added directly to the alkyd or alkyd emulsion under the same conditions regarding temperature and concentration (**Table 11**, A24PT and E03PT, respectively). The alkyd reaction was designed as a model reaction and could not be emulsified due to restrictions of the process. It would therefore have no any practical application in regard to commercial or industrial use. Although many methods were used to investigate the reaction mixtures, pH, ^{1}H NMR and GPC are expected to reveal the most information about the differences.

Differences in the reaction systems may have affected the rates; while the CPE and emulsion systems were continuously stirred through mechanical and magnetic stirring, respectively, no stirring was applied in the alkyd system. The temperature was measured directly in the vial in the CPE system which may have provided more accurate temperatures.

The decrease in pH is observed regardless of whether the crosslinker was added pre- or post-emulsification (**Figure 116**). This indicates that hydrolysis occurs in both reaction systems. The reaction rate appears faster than the alkyd system and similar to the emulsion system based on the decrease in the vinylic crosslinker protons from ^{1}H NMR (**Figure 117**).

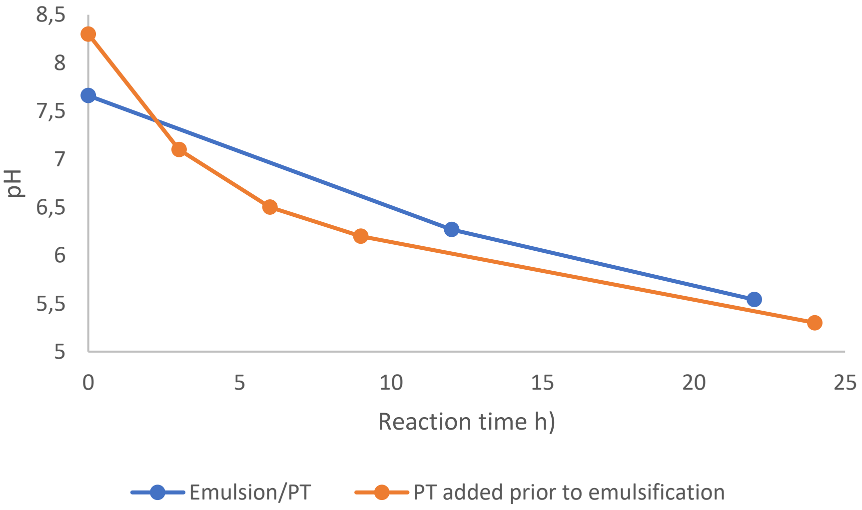


Figure 116: *pH in emulsion with 20func% pentaerythritol tetraacrylate (PT) after heating at 80 °C, where PT was added pre- or post-emulsification.*

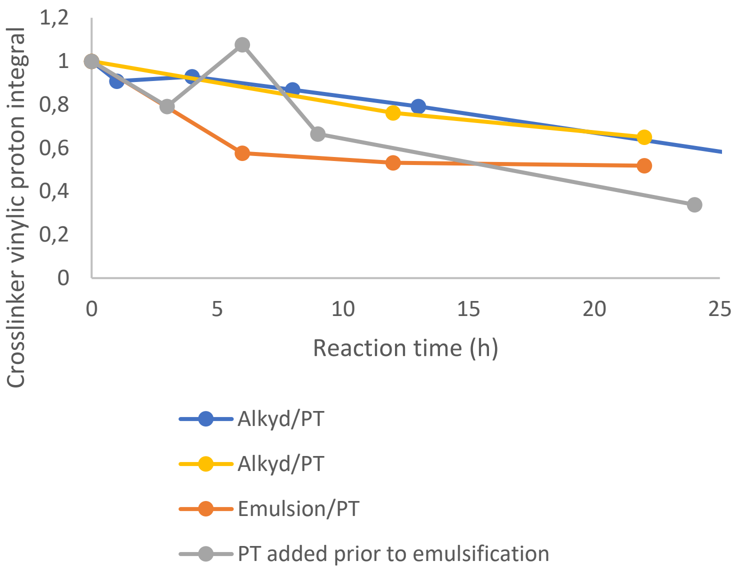


Figure 117: *Decrease in vinylic integrals in reaction mixtures containing 20func% pentaerythritol tetraacrylate (PT) after heating at 80 °C for various reaction times. PT was added directly to the alkyd, emulsion, or added to the alkyd prior to emulsification. Peak at 8.61 ppm was used to normalize the spectra integrals.*

Larger molecular weights are initially observed for the CPE system compared to the alkyd and emulsion system, indicating that the crosslinking reaction occurred to some extent during emulsification (**Figure 118**). Larger molecular weights are formed by the CPE system compared to adding the crosslinker post-emulsification. The molecular weight is increased even at low reaction times in the CPE reaction, as opposed to the previous emulsion reactions.

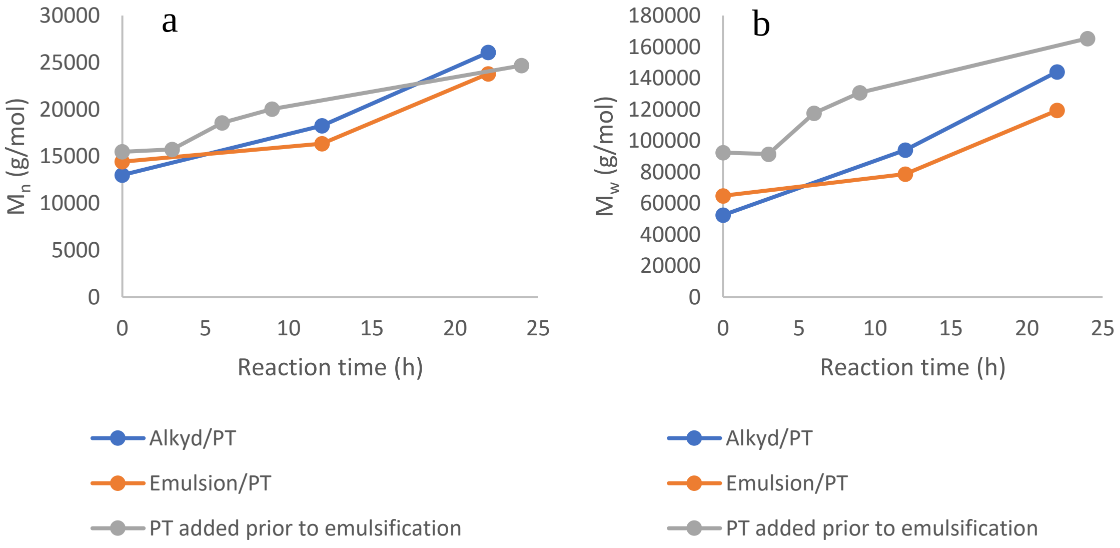


Figure 118: ***a)*** *Number average molecular weight (M_n) and* ***b)*** *weight average molecular weight (M_w) of reaction mixtures consisting of alkyd and pentaerythritol tetraacrylate (PT), emulsion and PT, and PT added to the alkyd prior to emulsification.*

The initial increase in molecular weight for the CPE system is not as evident in conventional and absolute method, analyzed by Jotun AS (**Figure 119-Figure 121**). The rate of the molecular weight increase appears more linear, as previously observed in the alkyd system, as opposed to the different rates observed in the emulsion system. This allows for shorter reaction times necessary to achieve high molecular weights by adding the crosslinker to the alkyd pre- rather than post-emulsification. The molecular weight of the CPE system is similar or comparable to the alkyd, and larger than for the emulsion system.

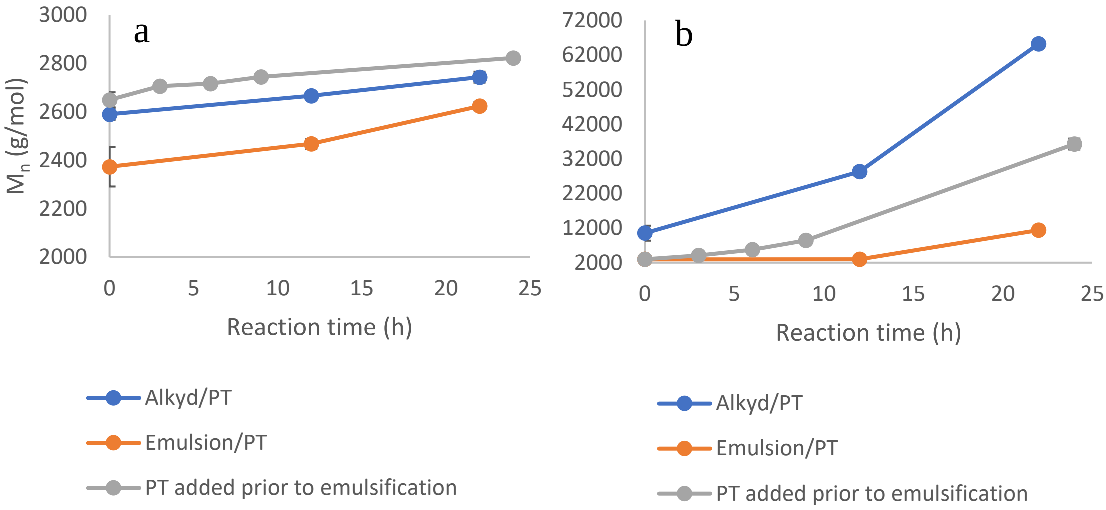


Figure 119: *Number average molecular weight (M_n) of reaction mixtures consisting of alkyd and pentaerythritol tetraacrylate (PT), emulsion and PT, and PT added to the alkyd prior to emulsification using the* ***a)*** *conventional method and* ***b)*** *absolute method.*

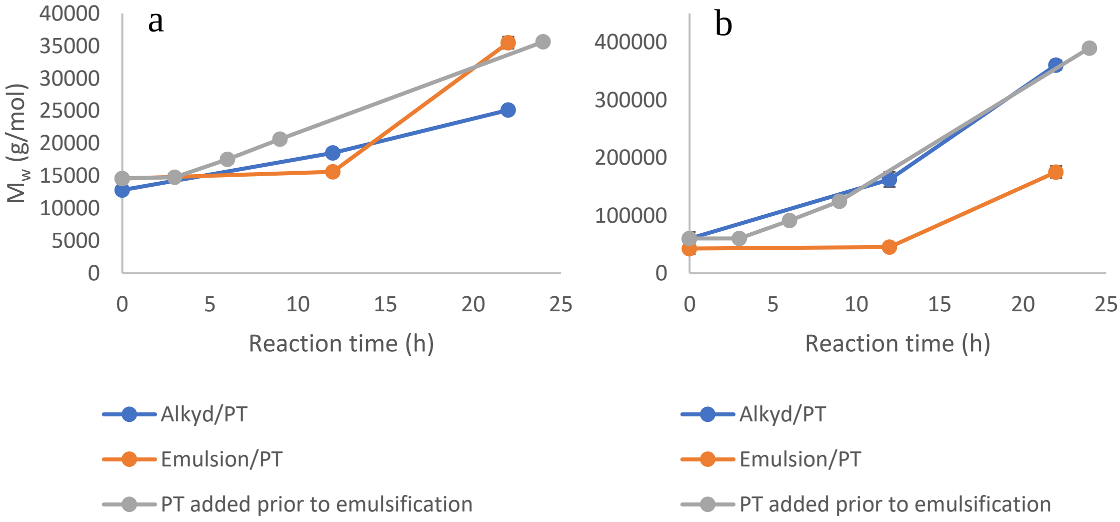


Figure 120: *Weight average molecular weight (M_w) of reaction mixtures consisting of alkyd and pentaerythritol tetraacrylate (PT), emulsion and PT, and PT added to the alkyd prior to emulsification using the* ***a)*** *conventional method and* ***b)*** *absolute method.*

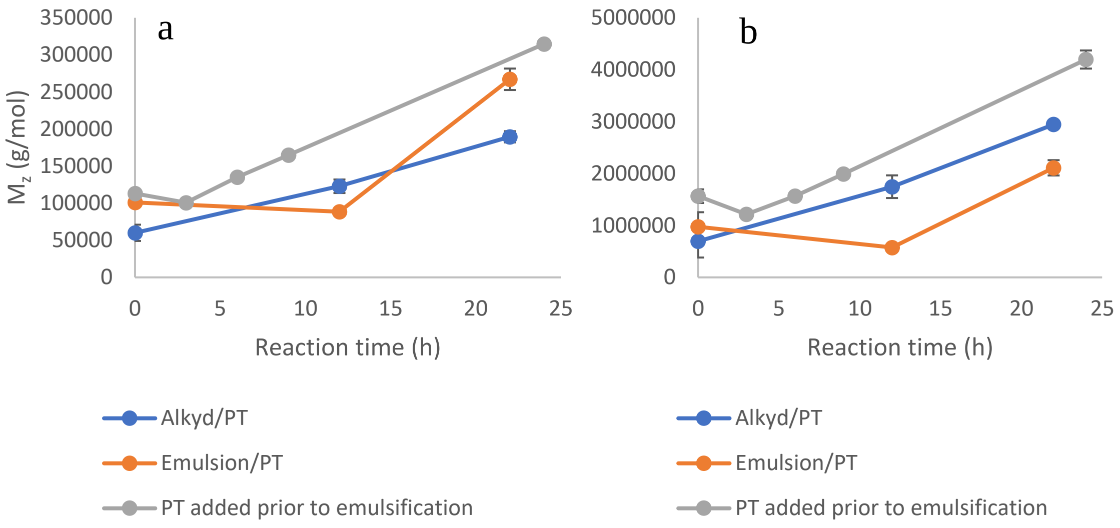


Figure 121: *Z-average molecular weight (M_z) of reaction mixtures consisting of alkyd and pentaerythritol tetraacrylate (PT), emulsion and PT, and PT added to the alkyd prior to emulsification using the* ***a)*** *conventional method and* ***b)*** *absolute method.*

Since the model system with the alkyd had no practical application, the comparisons are mainly concerned regarding whether the crosslinker should be added to the system pre- or post-emulsification. GPC indicates that higher molecular weights may be achieved by adding the crosslinker to the alkyd prior to emulsification rather than post-emulsification. It appears that the initial decrease in molecular weight which was observed for the emulsion system at t≤12h can be avoided by adding the crosslinker prior to emulsification. The CPE system allows for shorter reaction times (t<22h) to achieve increased molecular weights. This indicates that the possible side reaction occurring when the crosslinker is added to the emulsion may be avoided or less pronounced, despite the pH indicating that hydrolysis occurs at a similar rate in both reaction mixtures.

4.12.3 1,1'(Methylenedi-4,1-phenylene)bismaleimide (MPB)

4.12.3.1 Reaction Time and Temperature

MPB was tested in the CPE system. Although the crosslinker had not been tested in the alkyd nor the emulsion system previously, initial investigations had shown high reactivities for dimaleimides (Section **4.4**).

The pH is decreased when the reaction mixture was heated, with the largest decrease observed at 80 °C (**Figure 122**), indicating hydrolysis. Fluctuations are observed in the drop size (**Figure 123a**) and PDI (**Figure 123b**).

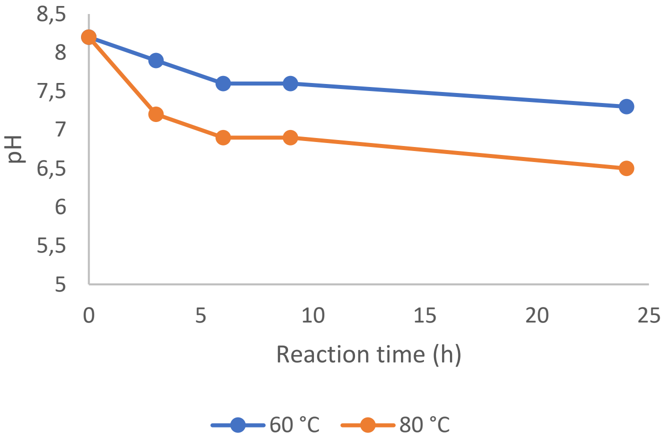


Figure 122: *pH of emulsion and 20func% 1,1'(methylenedi-4,1-phenylene)bismaleimide (MPB) heated to 60 or 80 °C for t=0h, 3h, 6h, 9h and 24h.*

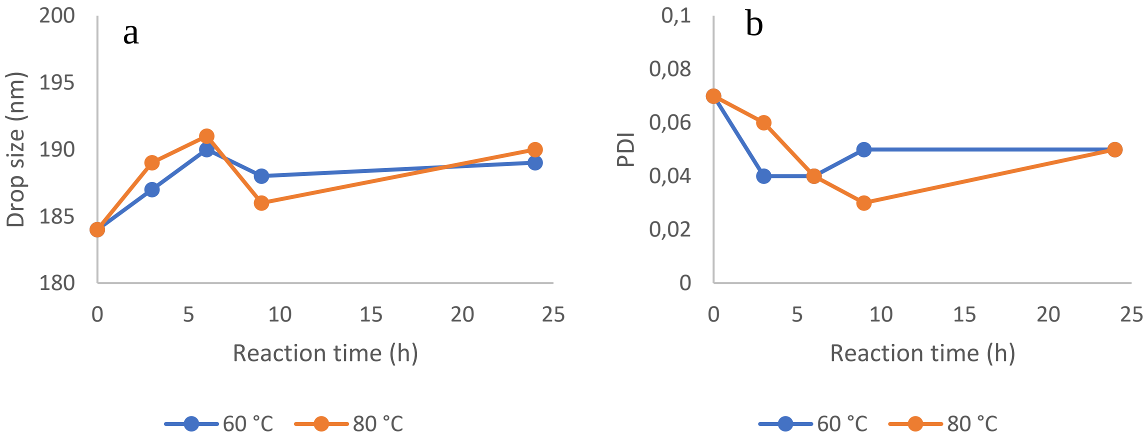


Figure 123: a) *Drop size and* ***b)*** *PDI of emulsion and 20func% 1,1'(methylenedi-4,1-phenylene)bismaleimide (MPB) heated to 60 or 80 °C for t=0h, 3h, 6h, 9h and 24h.*

For the reaction mixture heated at 80 °C, the largest increase in molecular weight is observed at t=3h, after which the rate decreases (**Figure 124**). No further increases are observed in molecular weight at t>9h, indicating that a reaction time between 3-9 hours is sufficient. The molecular weight increases more gradually at 60 °C and at t=24h, similar molecular weights are obtained at both temperatures.

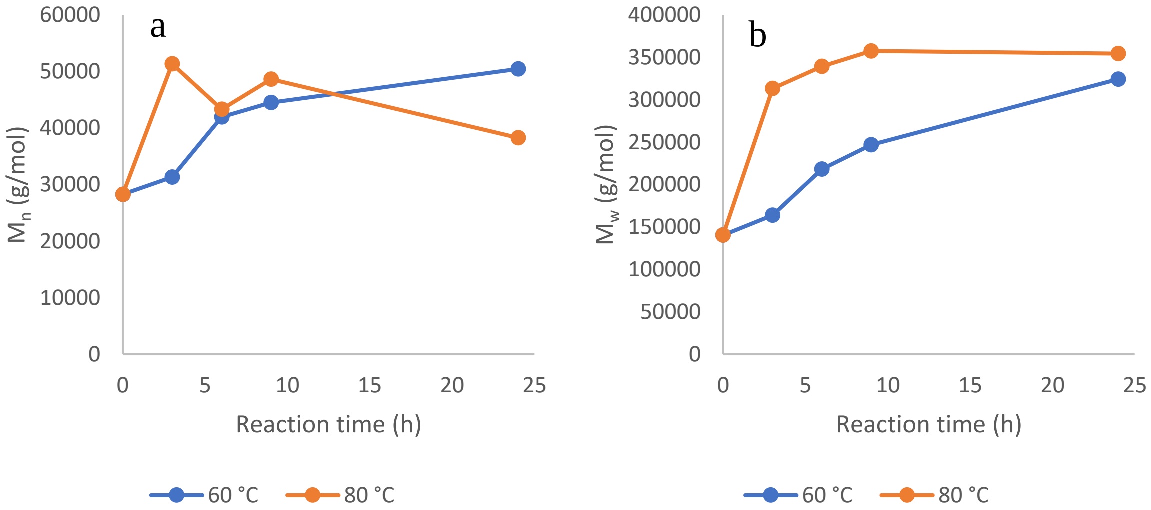


*Figure 124: **a)** Number average molecular weight (M_n) and **b)** weight average molecular weight (M_w) of emulsion with 20func% 1,1'(methylenedi-4,1-phenylene)bismaleimide (MPB) heated to 60 or 80 °C at t=0h, 3h, 6h, 9h and 24h.*

The molecular weights obtained using the conventional and absolute method show different trends than the previously measured molecular weights. The large increase in molecular weight at t=3h is still observed for the reaction mixture heated to 80 °C (**Figure 125-Figure 127**). However, this is followed by a significant decrease in the molecular weight. Although there are fluctuations, the molecular weight is not significantly changed between t=6h and t=24h, further indicating that short reaction times are sufficient to obtain high molecular weight polymers. The reaction mixture heated at 60 °C generally show a consecutive increase in the molecular weights for t≤9h (**Figure 125-Figure 127**) after which the molecular weight is not significantly increased. This suggests that t≤9h is sufficient, although this was not evident in the GPC analysis conducted at NTNU (**Figure 124**).

While the GPC analysis from NTNU (**Figure 124**) indicated that the molecular weights for samples at t<24h were largest for the reaction mixture heated at 80 °C, this was not always the case in the conventional and absolute method (**Figure 126** and **Figure 127a**). Although there are some contradictions in the molecular weights obtained for the different methods, there are clear indications that the molecular weights are significantly increased by the addition of MPB. It is also evident that shorter reaction times (t≤9h) are required to obtain high molecular weights at 80 °C.

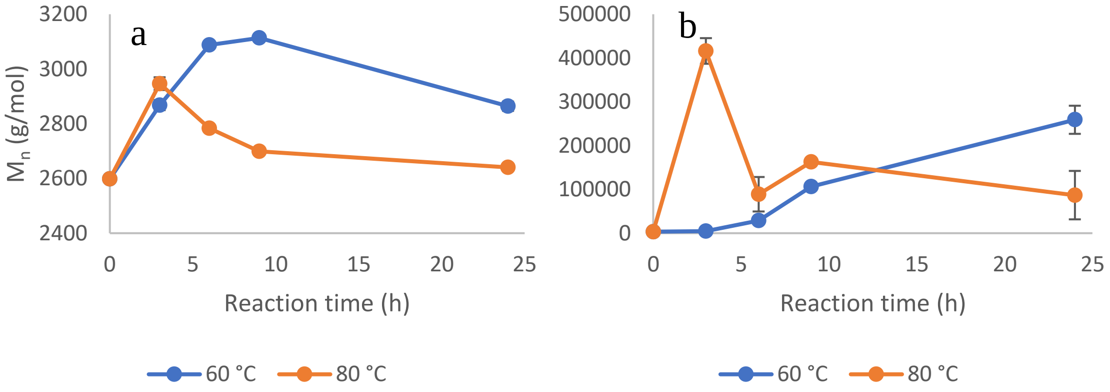


Figure 125: *Number average molecular weight (M_n) of emulsion with 20func% 1,1'(methylenedi-4,1-phenylene)bismaleimide (MPB) heated to 60 or 80 °C at t=0h, 3h, 6h, 9h and 24h using the* ***a)*** *conventional method and* ***b)*** *absolute method.*

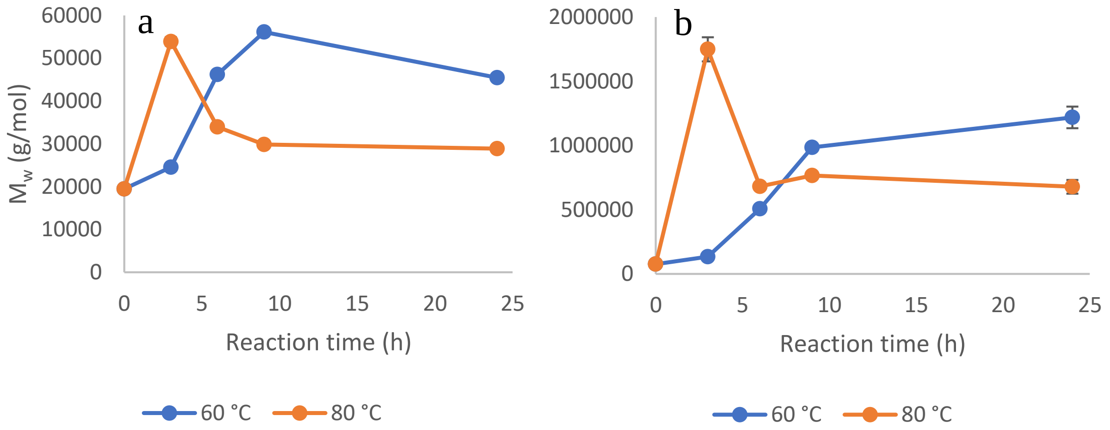


Figure 126: *Weight average molecular weight (M_w) of emulsion with 20func% 1,1'(methylenedi-4,1-phenylene)bismaleimide (MPB) heated to 60 or 80 °C at t=0h, 3h, 6h, 9h and 24h using the* ***a)*** *conventional method and* ***b)*** *absolute method.*

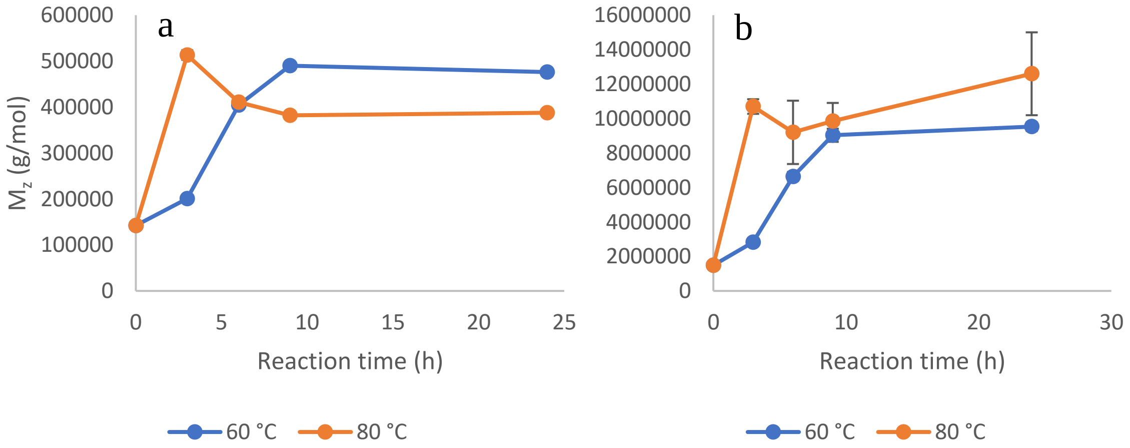


Figure 127: *Z-average molecular weight (M_z) of emulsion with 20func% 1,1'(methylenedi-4,1-phenylene)bismaleimide (MPB) heated to 60 or 80 °C at t=0h, 3h, 6h, 9h and 24h using the* ***a)*** *conventional method and* ***b)*** *absolute method.*

For both temperatures, the hardest films are formed by the pure emulsion and the reaction mixture with crosslinker, both prior to heating (**Figure 128**). The hardness is inversely proportional to the reaction time.

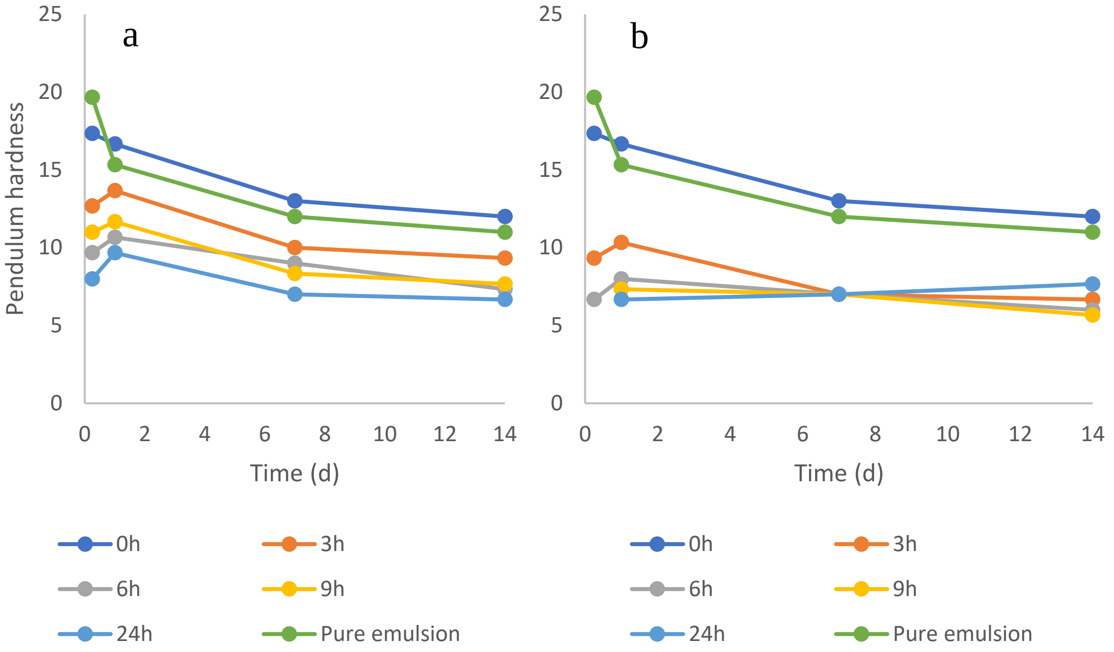


*Figure 128: Pendulum hardness of unheated pure emulsion and emulsion with 20func% 1,1'(methylenedi-4,1-phenylene)bismaleimide (MPB) heated to **a)** 60 °C or **b)** 80 °C at t=0h, 3h, 6h, 9h and 24h.*

The decrease in hardness when the reaction mixtures are subjected to heat is further demonstrated by comparing the films at constant reaction times (**Figure 129**). The reaction mixtures heated at 60 °C generally form harder films compared to 80 °C, as was observed for the PT crosslinker (see **Figure 113**).

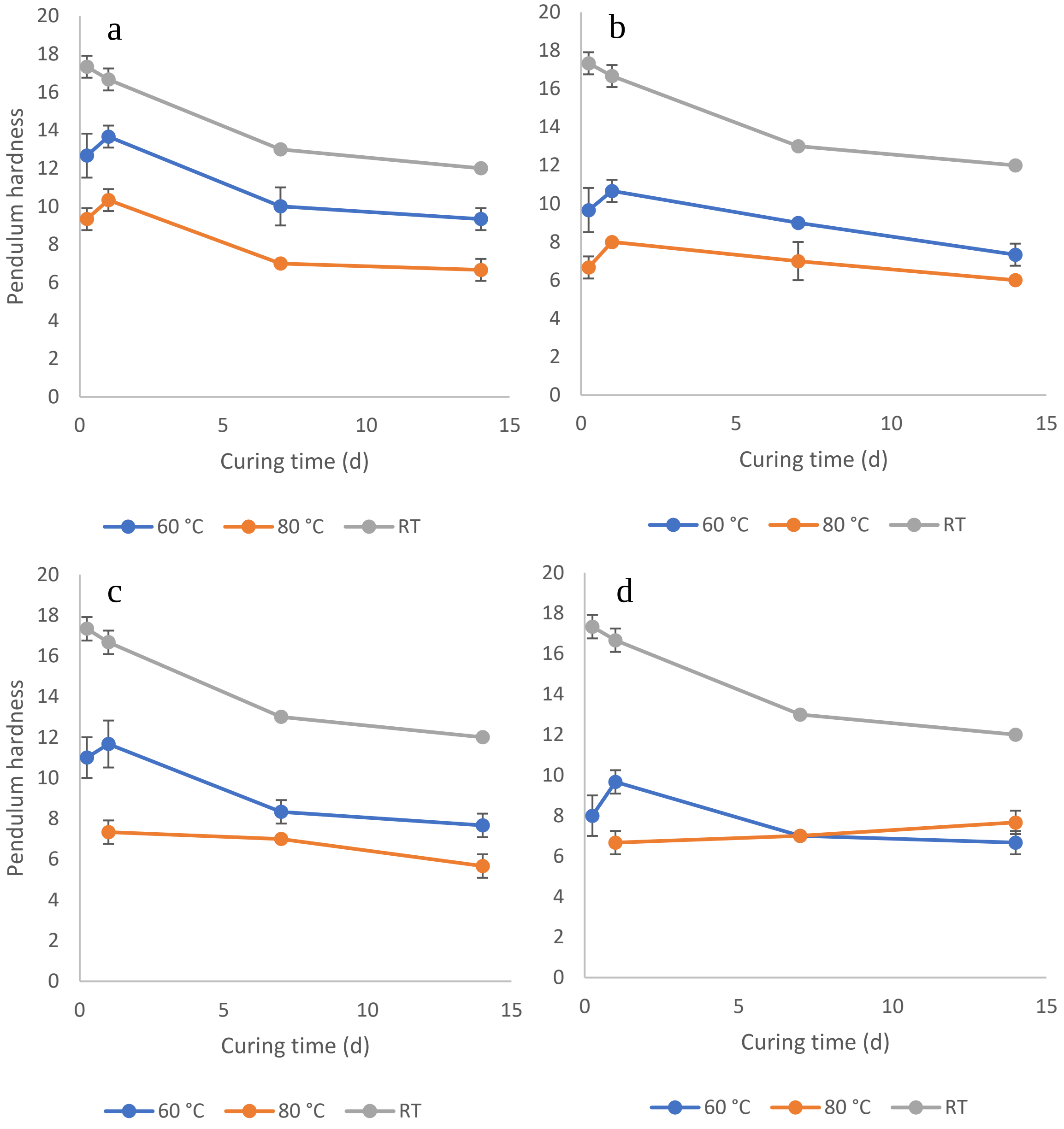


Figure 129: *Pendulum hardness of unheated emulsion with 20func% % 1,1'(methylenedi-4,1-phenylene)bismaleimide (MPB) stored at room temperature (RT), and emulsion with 20func% MPB heated at 60 or 80 °C for* ***a)*** *t=3h,* ***b)*** *t=6h,* ***c)*** *t=9h, and* ***d)*** *t=24h.*

4.12.3.2 Storage Stability

The pH of the reaction mixtures do not change significantly during storage at RT for t=1.5 months (**Figure 130**), indicating good storage stability. The drop size is slightly increased and the PDI slightly increased, indicating that a more thermodynamically stable mixture is formed by the formation of larger drops (**Figure 131**).

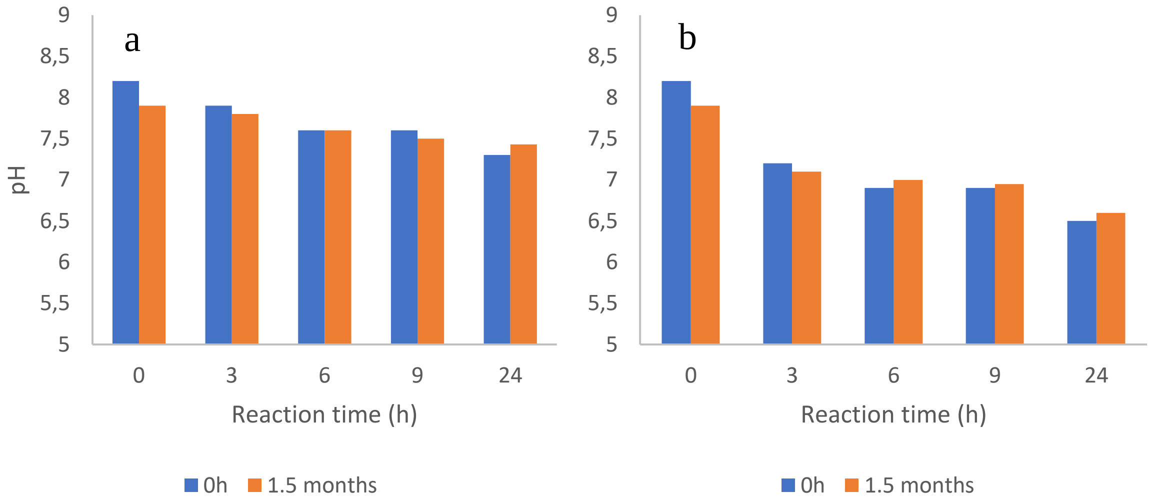


Figure 130: *pH of of emulsion with 20func% 1,1'(methylenedi-4,1-phenylene)bismaleimide (MPB) heated at* ***a)*** *60 °C and* ***b)*** *80 °C at t=0h, 3h, 6h, 9h and 24h. pH was measured at t=0h and 1.5 months.*

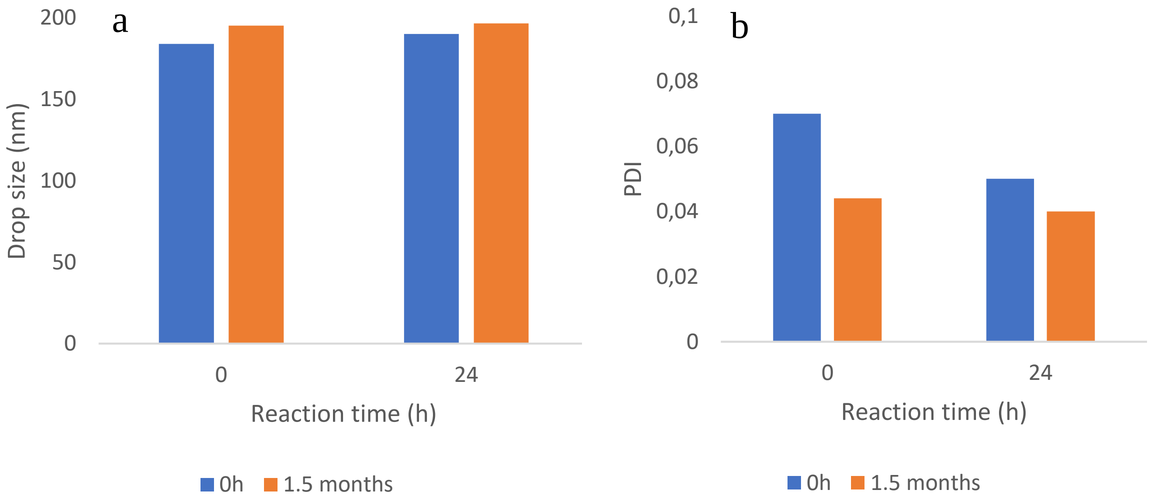


Figure 131: a) *Drop size and* ***b)*** *PDI of emulsion with 20func% 1,1'(methylenedi-4,1-phenylene)bismaleimide (MPB) at t=0h and after heating at t=24h at 80 °C. Measurements were done initially and after 1,5 months.*

4.12.4 Comparison of Crosslinkers

The reaction mixtures with crosslinkers PT or MPB added prior to emulsification were compared to the pure emulsion to give a clearer indication of which changes were attributed to the crosslinking reaction. The crosslinkers were also compared in regard to reactivity at the two temperatures.

No significant change in pH is observed as the pure emulsion was subjected to heating while decreases were observed for the PT and MPB mixtures (**Figure 132**). The pH in the PT and MPB mixtures show a similar rate for the first t=6h when heated at 60 °C, and for the t=3h when heated at 80 °C. The pH in the PT mixture continues to decrease in a similar rate while the pH stabilizes in the MPB mixture.

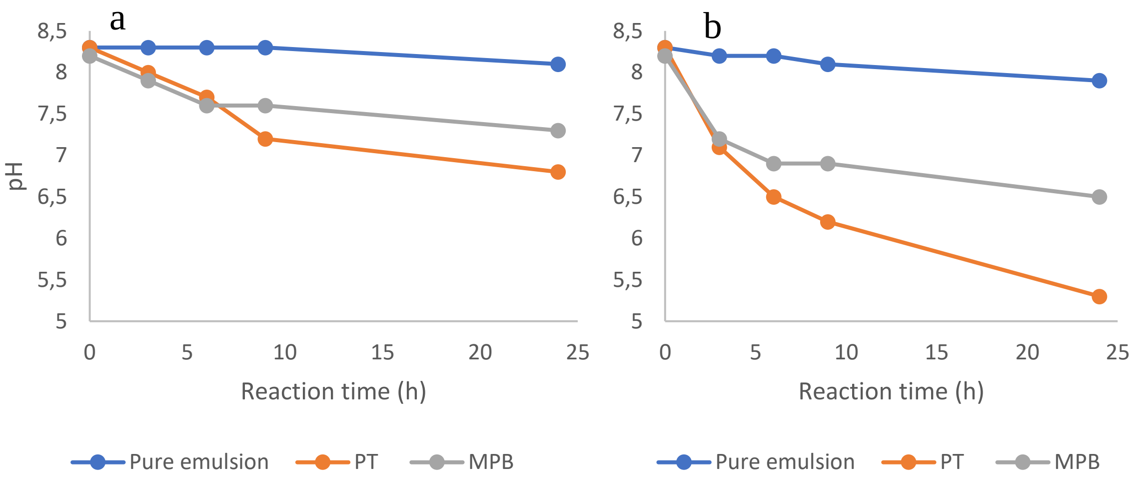


Figure 132: *pH of emulsion and emulsion with 20func% pentaerythritol tetraacrylate (PT) or 1,1'(methylenedi-4,1-phenylene)bismaleimide (MPB) after heating at* ***a)*** *60 °C and* ***b)*** *80 °C at t=0h, 3h, 6h, 9h and 24h. Crosslinkers were added prior to emulsification.*

Small changes are observed in the drop size (**Figure 133**) and PDI (**Figure 134**) as the reaction mixtures are heated. For the PT mixture heated at 80 °C and the pure emulsion at 60 °C for t=24h, the changes are larger.

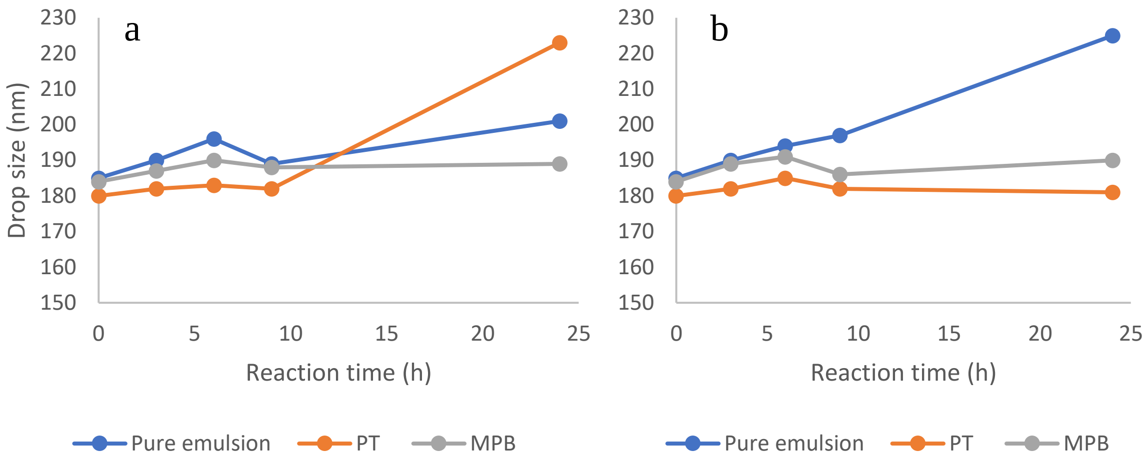


*Figure 133: Drop size of emulsion and emulsion with 20func% pentaerythritol tetraacrylate (PT) or 1,1'(methylenedi-4,1-phenylene)bismaleimide (MPB) after heating at **a)** 60 °C and **b)** 80 °C at t=0h, 3h, 6h, 9h and 24h. Crosslinkers were added prior to emulsification.*

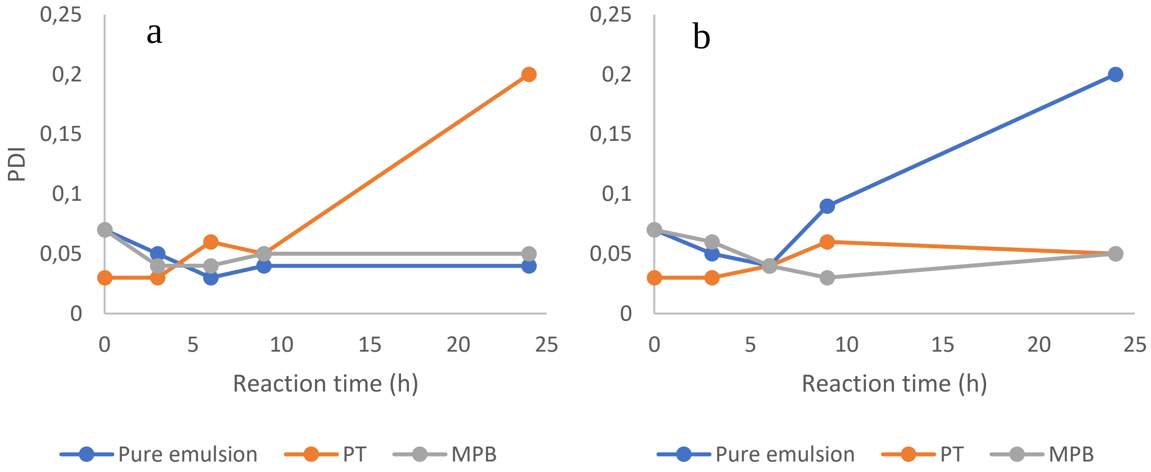


*Figure 134: PDI of emulsion and emulsion with 20func% pentaerythritol tetraacrylate (PT) or 1,1'(methylenedi-4,1-phenylene)bismaleimide (MPB) after heating at **a)** 60 °C and **b)** 80 °C at t=0h, 3h, 6h, 9h and 24h. Crosslinkers were added prior to emulsification.*

The molecular weight obtained with the MPB crosslinker is superior to the PT crosslinker and pure emulsion at all reaction times and both temperatures (**Figure 136** and **Figure 135**). The molecular weight of PT is slightly larger compared to the pure emulsion (**Figure 135b**). The initial molecular weight of the crosslinker mixtures are larger than for the pure emulsion, especially with MPB, indicating that the crosslinking reaction have occurred to some extent during emulsification. While the reaction mixture with MPB achieve high molecular weight at relatively short reaction times (t≤9h), longer reaction times are generally required for the PT reaction mixture (t=24h).

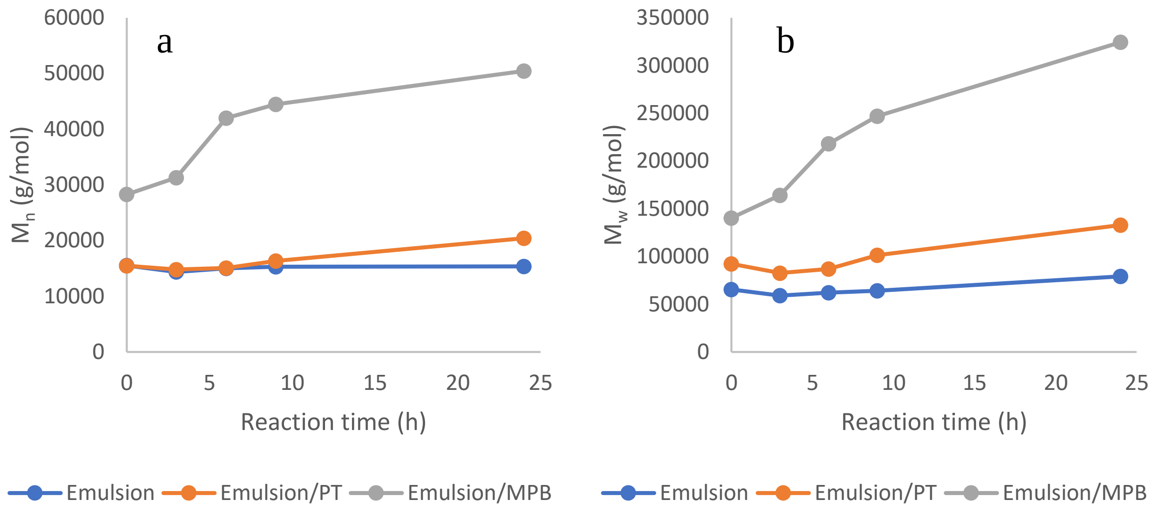


***Figure 135: a)** Number average molecular weight (M_n) and **b)** weight average molecular weight (M_w) of emulsion, and emulsion with 20func% pentaerythritol tetraacrylate (PT) or 1,1'(methylenedi-4,1-phenylene)bismaleimide (MPB) after heating at 60 °C for t=0h, 3h, 6h, 9h and 24h. Crosslinkers were added prior to emulsification.*

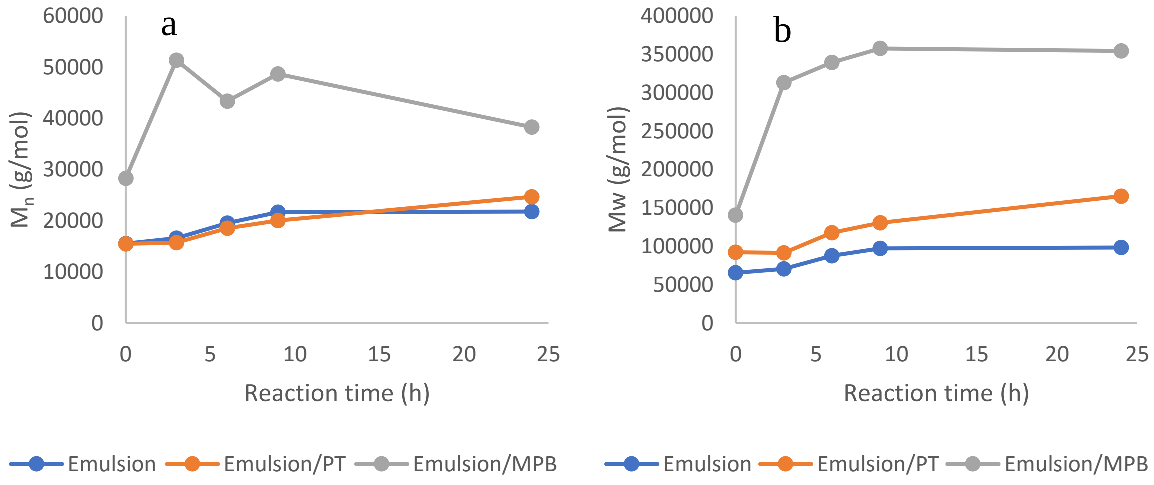


***Figure 136: a)** Number average molecular weight (M_n) and **b)** weight average molecular weight (M_w) of emulsion, and emulsion with 20func% pentaerythritol tetraacrylate (PT) or 1,1'(methylenedi-4,1-phenylene)bismaleimide (MPB) after heating at 80 °C for t=0h, 3h, 6h, 9h and 24h. Crosslinkers were added prior to emulsification.*

The same observations are illustrated in the conventional and absolute method, analyzed by Jotun AS (**Figure 137-Figure 142**).

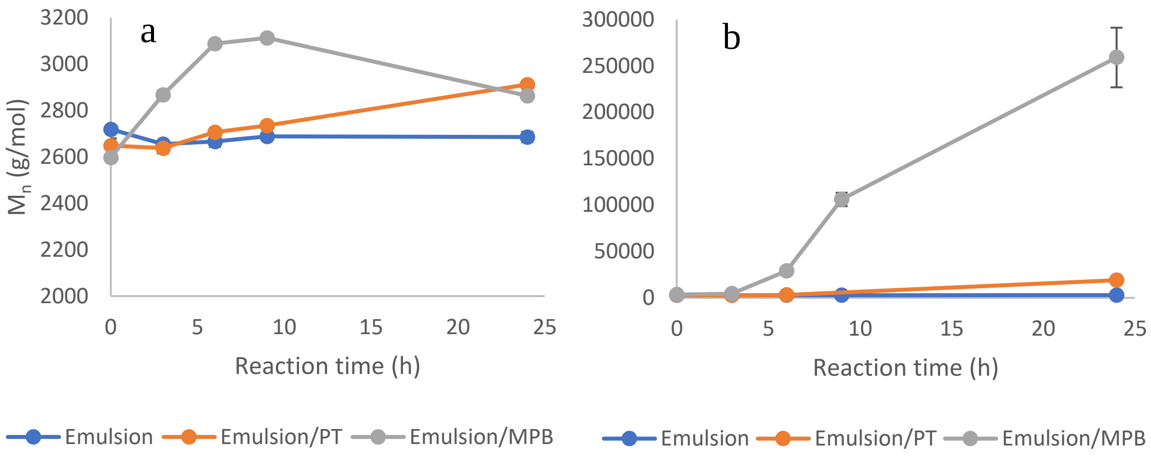


Figure 137: *Number average molecular weight (M_n) for emulsion and emulsion with 20func% pentaerythritol tetraacrylate (PT) or 1,1'(methylenedi-4,1-phenylene)bismaleimide (MPB) after heating at 60 °C at t=0h, 3h, 6h, 9h and 24h using the* ***a)*** *conventional method and* ***b)*** *absolute method. Crosslinkers were added prior to emulsification.*

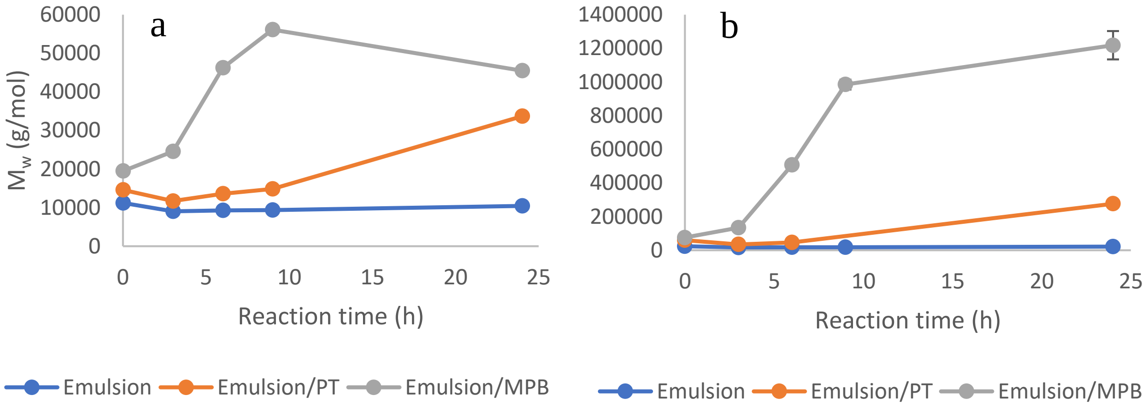


Figure 138: *Weight average molecular weight (M_w) for emulsion and emulsion with 20func% pentaerythritol tetraacrylate (PT) or 1,1'(methylenedi-4,1-phenylene)bismaleimide (MPB) after heating at 60 °C at t=0h, 3h, 6h, 9h and 24h using the* ***a)*** *conventional method and* ***b)*** *absolute method. Crosslinkers were added prior to emulsification.*

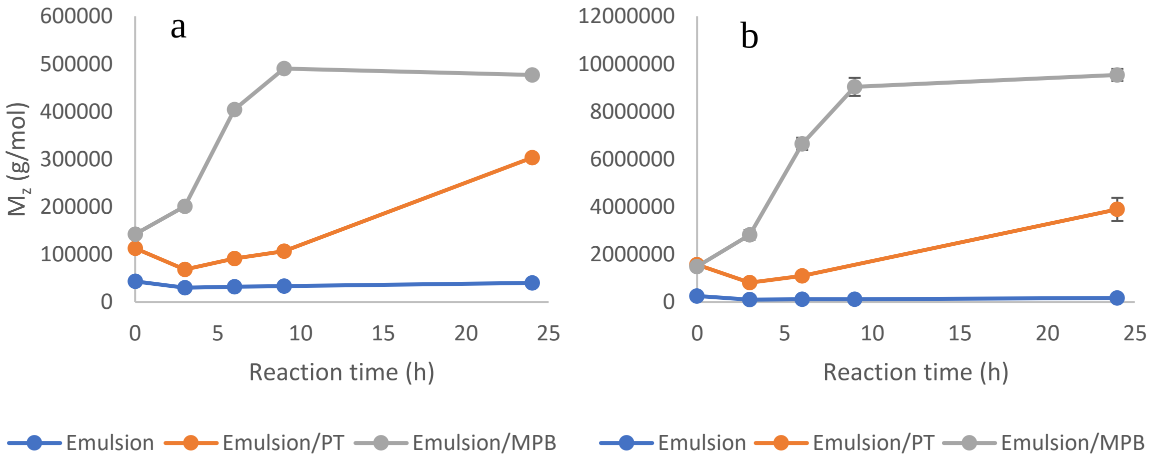


Figure 139: *Z-average molecular weight (M_z) for emulsion and emulsion with 20func% pentaerythritol tetraacrylate (PT) or 1,1'(Methylenedi-4,1-phenylene)bismaleimide (MPB) after heating at 60 °C at t=0h, 3h, 6h, 9h and 24h using the* ***a)*** *conventional method and* ***b)*** *absolute method. Crosslinkers were added prior to emulsification.*

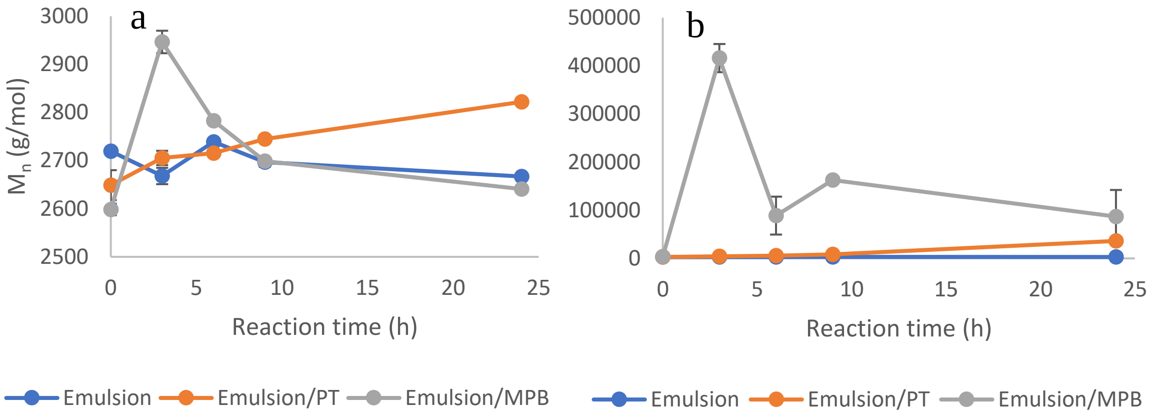


Figure 140: *Number average molecular weight (M_n) for emulsion and emulsion with 20func% pentaerythritol tetraacrylate (PT) or 1,1'(methylenedi-4,1-phenylene)bismaleimide (MPB) after heating at 80 °C at t=0h, 3h, 6h, 9h and 24h using the* ***a)*** *conventional method and* ***b)*** *absolute method. Crosslinkers were added prior to emulsification.*

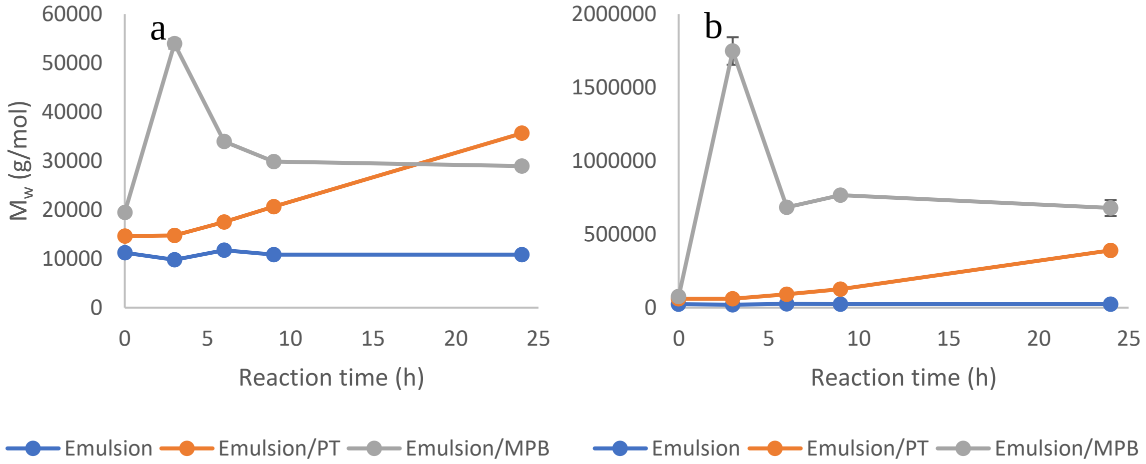


Figure 141: *Weight average molecular weight (M_w) for emulsion and emulsion with 20func% pentaerythritol tetraacrylate (PT) or 1,1'(methylenedi-4,1-phenylene)bismaleimide (MPB) after heating at 80 °C at t=0h, 3h, 6h, 9h and 24h using the* ***a)*** *conventional method and* ***b)*** *absolute method. Crosslinkers were added prior to emulsification.*

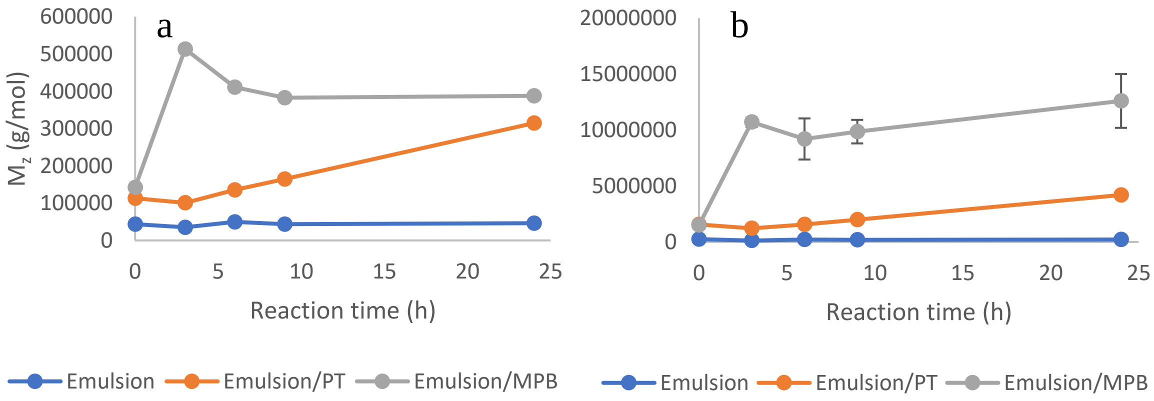


Figure 142: *Z-average molecular weight (M_z) for emulsion and emulsion with 20func% pentaerythritol tetraacrylate (PT) or 1,1'(methylenedi-4,1-phenylene)bismaleimide (MPB) after heating at 80 °C at t=0h, 3h, 6h, 9h and 24h using the* ***a)*** *conventional method and* ***b)*** *absolute method. Crosslinkers were added prior to emulsification.*

It is evident that high molecular weights can be obtained by adding crosslinkers to the alkyd prior to emulsification. As small differences are observed when the pure emulsion is heated, the increase in molecular weight can be attributed to the addition of the crosslinkers. High molecular weight polymers can be produced at 60 °C and 80 °C. MPB appear to generate overall higher molecular weight polymers combined at lower reaction times compared to PT.

The films formed by the pure emulsion and with crosslinkers was compared at constant reaction times. Prior to heating, the hardest film is achieved for the mixture with PT (**Figure 143**). Small differences are observed between the pure emulsion and MPB.

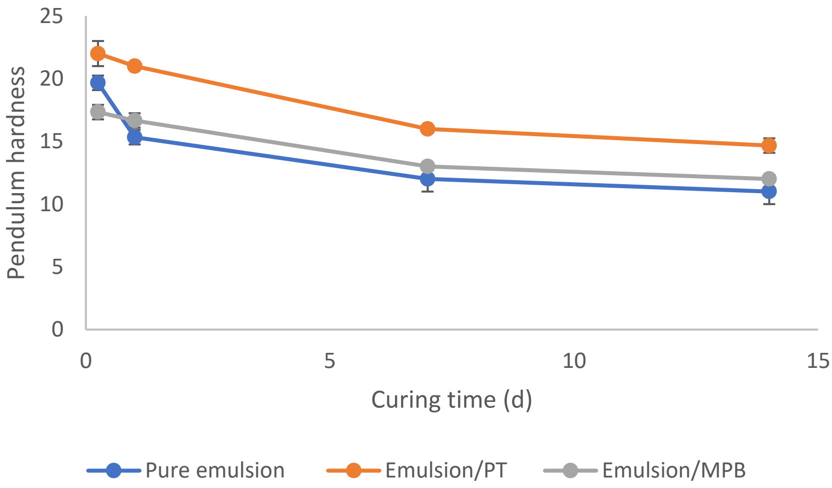


Figure 143: Pendulum hardness for pure emulsion and emulsion with 20func% pentaerythritol tetraacrylate (PT) or 1,1'(methylenedi-4,1-phenylene)bismaleimide (MPB) at t=0h. Crosslinkers were added prior to emulsification.

Heating the pure emulsion and reaction mixtures with PT or MPB resulted in the softest films formed by the MPB mixture at all reaction times (**Figure 144-Figure 147**). The reaction mixture with MPB heated to 80 °C for t≥9h formed films which were initially (after curing for t=6h) too soft to measure. PT forms the hardest films at short reaction times (t=3h) while the pure emulsion forms harder films at long reaction times (t≥9h).

The pendulum hardness does not seem to increase parallelly with the increased molecular weight as expected. This could indicate that the pendulum hardness depends more on the number of unsaturated bonds available for the autoxidation process than the initial molecular weight.

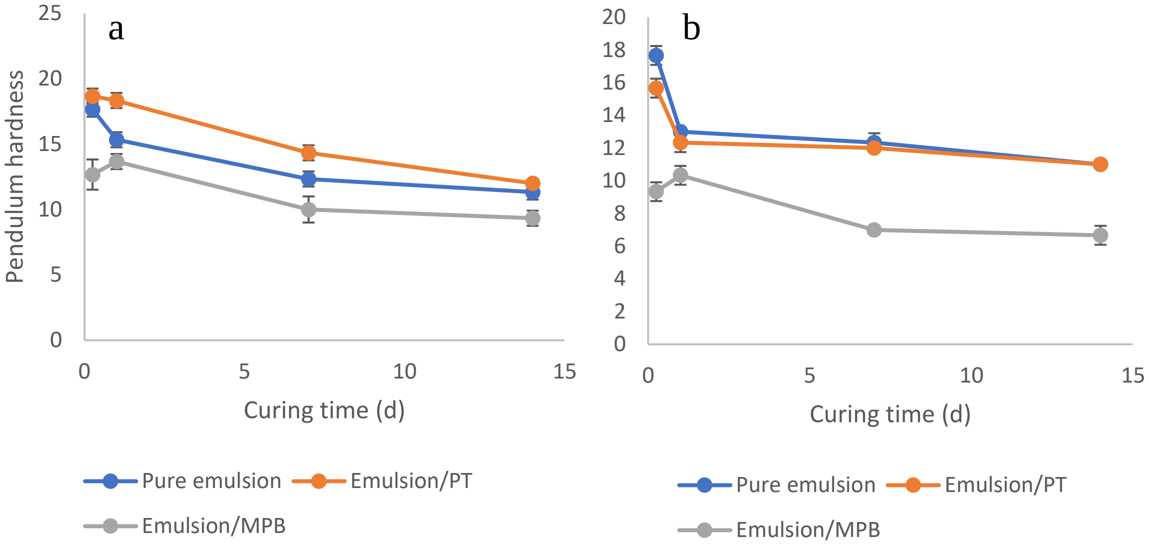


Figure 144: Pendulum hardness for pure emulsion and emulsion with 20func% pentaerythritol tetraacrylate (PT) or 1,1'(methylenedi-4,1-phenylene)bismaleimide (MPB) after heating at ***a)*** *60 °C and* ***b)*** *80 °C for t=3h. Crosslinkers were added prior to emulsification.*

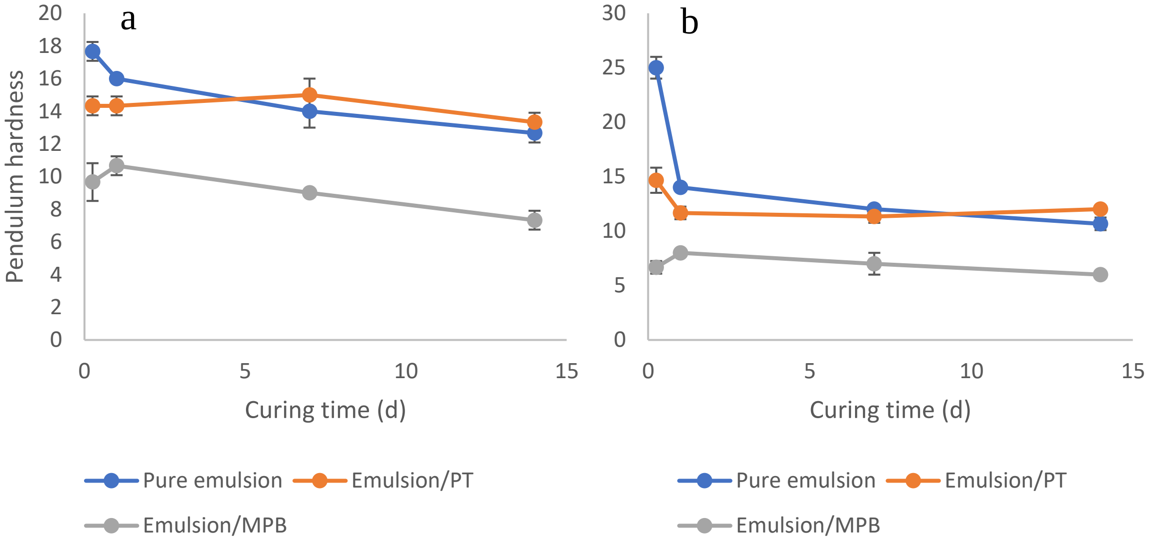


Figure 145: Pendulum hardness for pure emulsion and emulsion with 20func% pentaerythritol tetraacrylate (PT) or 1,1'(methylenedi-4,1-phenylene)bismaleimide (MPB) after heating at ***a)*** *60 °C and* ***b)*** *80 °C for t=6h. Crosslinkers were added prior to emulsification.*

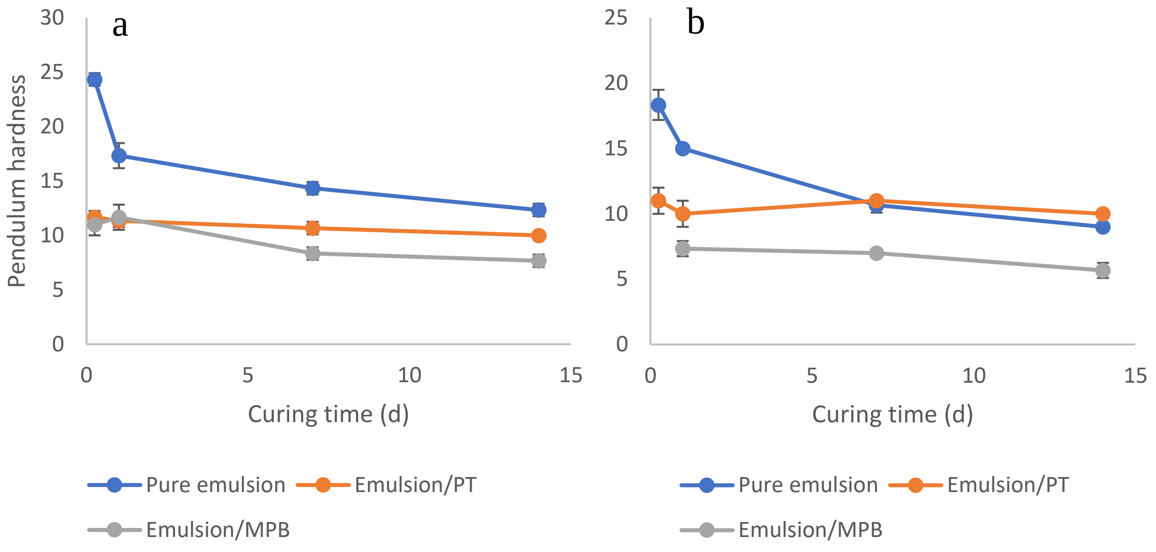


*Figure 146: Pendulum hardness for pure emulsion and emulsion with 20func% pentaerythritol tetraacrylate (PT) or 1,1'(methylenedi-4,1-phenylene)bismaleimide (MPB) after heating at **a)** 60 °C and **b)** 80 °C for t=9h. Crosslinkers were added prior to emulsification.*

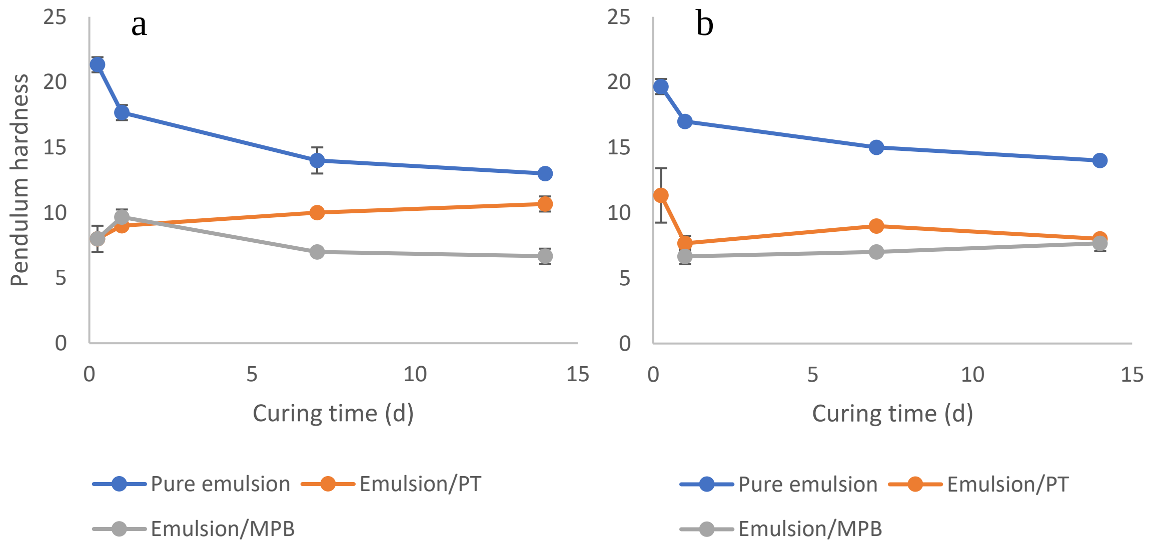


*Figure 147: Pendulum hardness for pure emulsion and emulsion with 20func% pentaerythritol tetraacrylate (PT) or 1,1'(methylenedi-4,1-phenylene)bismaleimide (MPB) after heating at **a)** 60 °C and **b)** 80 °C for t=24h. Crosslinkers were added prior to emulsification.*

4.13 Fatty Acid Reactions

The reaction mechanism causing the increased molecular weight in the alkyd and alkyd emulsions was further investigated by further simplifying the system to the fatty acid. This was expected to provide information about which reactions were occurring. For a direct comparison with the previous experiments, the reactions were carried out at 80 °C. The concentrations were calculated based on the reactive functionalities for the Diels-Alder reaction present in the fatty acid and the reactant, as in the previous alkyd reactions.

Initially, methyl acrylate (MA) (**Figure 217**) was used as a dienophile in the reactions for further simplification, as it only has one reactive functional group to react in a Diels-Alder reaction (**Table 18**). Pentaerythritol tetraacrylate (PT) was also employed as a dienophile. A possible side-reaction to the Diels-Alder reaction is an addition reaction between an unsaturated functionality and an alcohol (see Reaction 4, **Scheme 11**). To further investigate this, decanol (D) (**Figure 218**) was employed in reactions with the fatty acid.

Table 18: *Amounts of conjugated fatty acid (cFA) and concentration (c) of methyl acrylate (MA), decanol (D) and pentaerythritol tetraacrylate (PT) in fatty acid reactions. Reaction time is given.*

Exp.nr	Fatty acid mixture (g)	cFA (mmol)	Additive (mmol)	Additive (g)	c (func%)	Reaction time
FA01	5.010	8.528	MA (8.50)	0.731	49.92	70h
FA02*	5.000	8.511	MA (8.50)	0.731	49.97	1h
FA03**	3.004	5.113	MA (5.22)	0.449	50.51	5d
FA04**	2.996	5.100	D (5.14)	0.814	50.21	44h
FA05**	2.998	5.103	PT (12.80)	0.451	50.08	1h
FA06	1.502	2.557	PT (0.349)	0.123	35.32	1h
FA07	1.506	2.563	PT (0.142)	0.050	18.13	9h
FA08	0.960	1.770	N/A			40h
FA09	N/A		PT (1.67)	0.588	N/A	30h

*conducted in microwave reactor
**conducted in a hermetically sealed vial

4.13.1 Method

The reactions were monitored through ^{1}H NMR. While the aromatic signals were used as references in the reactions concerning the alkyd, the methylene peak from the fatty acid at 0.88 ppm was used as a reference in the following reactions. For simplicity, only the initial and final NMR spectra are shown.

4.13.2 Characterization of Fatty Acid

The fatty acid used for the alkyd synthesis and for the following set of experiments consisted of a mixture of fatty acids, including approximately 50wt% conjugated fatty acids. By using UPC2 coupled with MS, separation of the fatty acids was achieved (**Figure 148b**), and the molecular weight of these were found by comparing these with fatty acid standards of known molecular weight (**Figure 148a**). The analysis detected the main fatty acids to consist of 18 carbons and have molecular weights 279.232 and 281.2481 g/mol. The three signals with molecular weight 279.232 g/mol, associated with the molecular formula $C_{18}H_{32}O_2$ (see **Figure 222**), are isomers with two unsaturated carbon-carbon double bonds. The signal with molecular weight 281.2481 g/mol, associated with the molecular formula $C_{18}H_{34}O_2$ (see **Figure 223**), corresponds to a monounsaturated fatty acid.

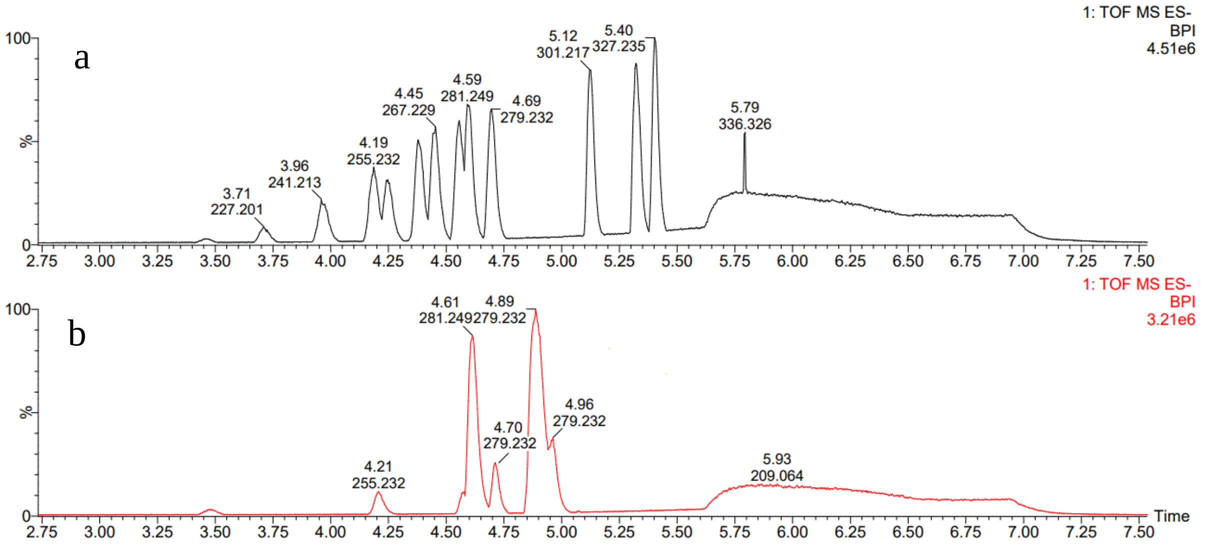
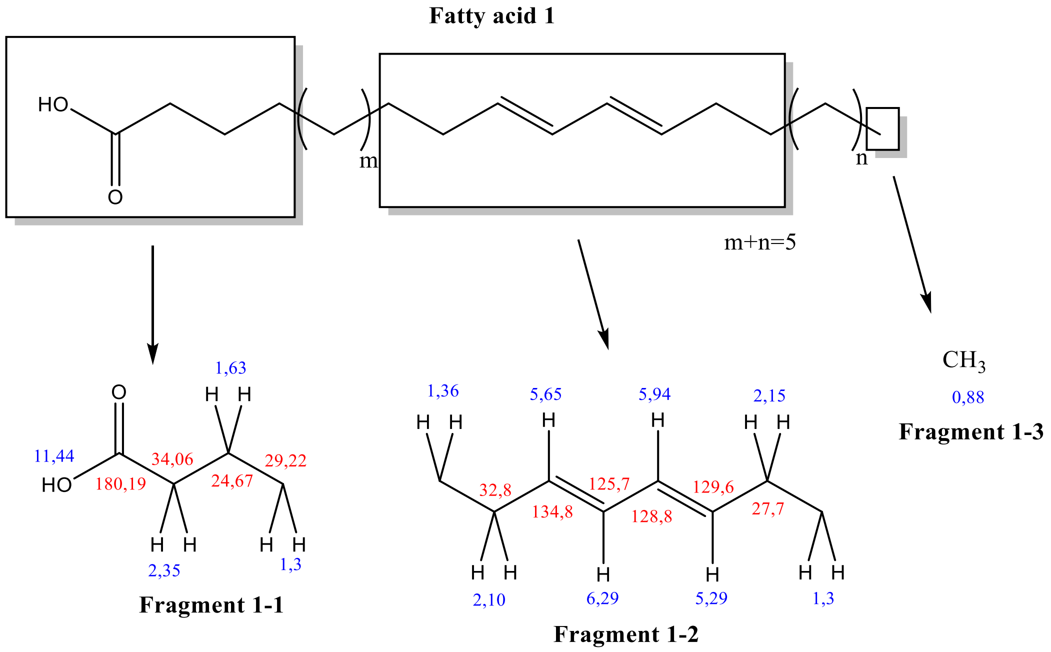
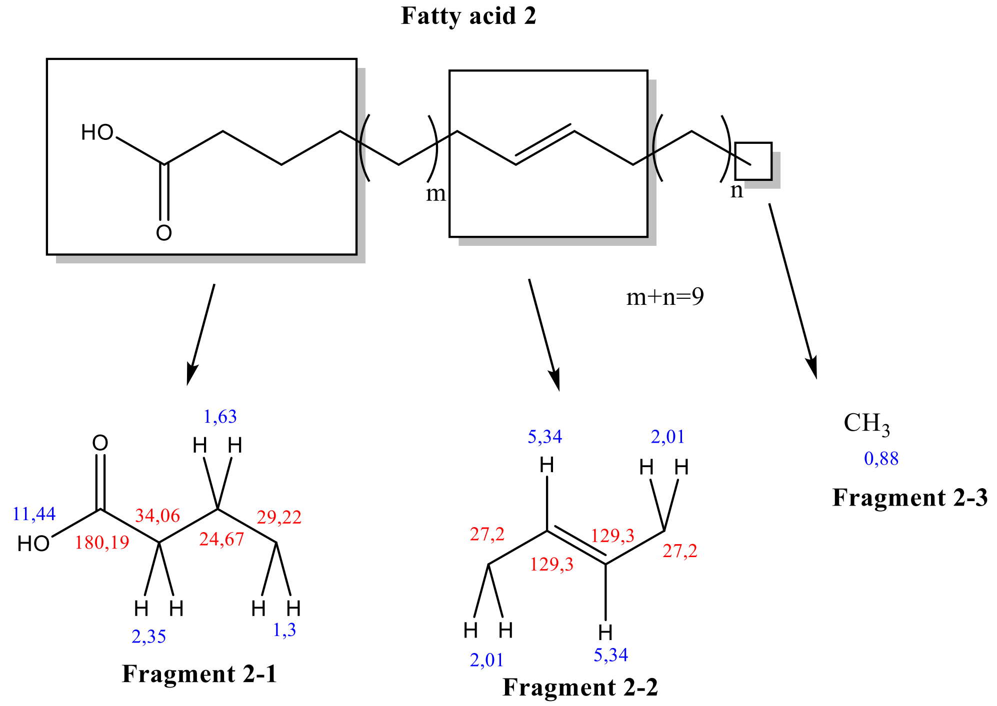


Figure 148: UPC2 coupled with MS for ***a)*** *fatty acid standards with known molecular weights and* ***b)*** *conjugated fatty acid mix.*

NMR was applied for further structure elucidation (Appendix **C.1**). Due to many overlapping signals in both ^{1}H NMR and ^{13}C NMR, the complete structure cannot be elucidated. Based on the correlations for the most dominant signals from the vinylic protons and the carboxylic acid, possible fragments of the fatty acids were identified (**Scheme 18** and **Scheme 19**). The vinylic protons were better separated than the vinylic carbons, allowing a more accurate elucidation of the protons. Due to a large number of CH_2 protons with overlapping signals, *m* and *n* were not established. For fatty acid 2 (**Scheme 19**), several double bonds might be present, although this cannot be established based on the NMR spectra. The configurations of the fatty acids were not determined due to the complexity of the ^1H NMR spectra.



Scheme 18: ^1H and ^{13}C NMR peak assignment of fragment 1-1, 1-2 and 1-3 of the conjugated fatty acid.

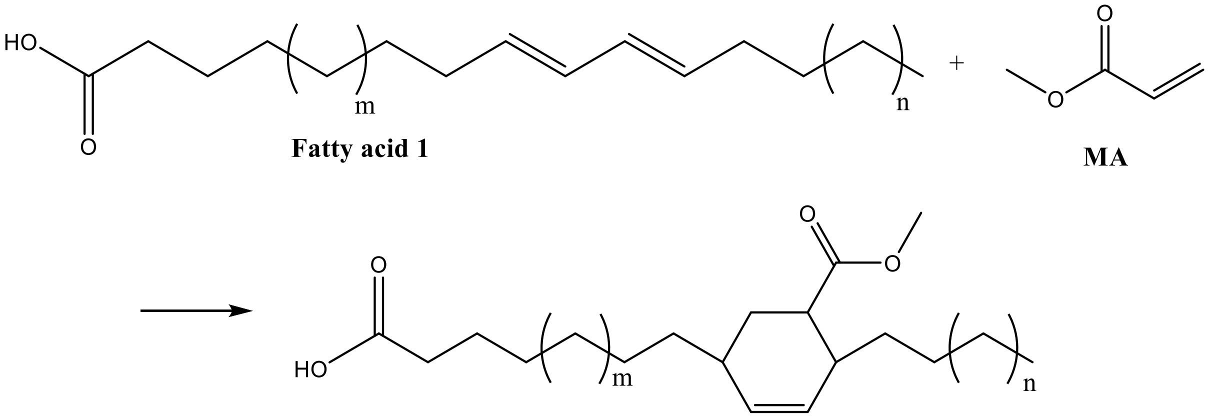


Scheme 19: ^1H and ^{13}C NMR peak assignment of fragment 2-1, 2-2 and 2-3 of an unsaturated fatty acid.

Linking this to the UPC2/MS results, it is likely that the fatty acid 1 and 2 corresponds to the signals at t=4.89 (molecular weight 279.232 g/mol) and t=4.61 (281.2481 g/mol), respectively, based on the intensities of the signals. This further indicates that fatty acid 2 is a monounsaturated fatty acid.

4.13.3 Methyl Acrylate (MA)

For the following set of experiments, methyl acrylate (MA) was employed as the dienophile with the conjugated fatty acid. The Diels-Alder reaction is illustrated in **Scheme 20**. Decreases in the vinylic and allylic peaks in the fatty acid 1 and MA are apparent in the ^{1}H NMR spectra (**Figure 149**) which is in accordance with the Diels-Alder reaction. An increase in the CH_2 peaks is also observed. A new peak is detected at 5.83 ppm in ^{1}H NMR at t=70h which may be attributed to the protons in the cyclohexene. However, the signal appears as a singlet and the integral is too small to account for the loss of vinylic protons through the Diels-Alder reaction. ^{13}C NMR further confirms a reaction involving the unsaturated bonds by the reduction in the vinylic and allylic carbons associated with fatty acid 1 (Fragment 1-2, **Figure 150**) although no new peaks from the cyclohexene are detected. Additionally, several new signals are observed in ^{1}H NMR at 3.5-4.5 ppm, with the most intense signal at 3.66 ppm, which are not associated with the Diels-Alder reaction occurring. The adduct was not detected in UPC2/MS. This indicates that the Diels-Alder reaction might occur to some extent but is not the dominant reaction.



Scheme 20: Diels-Alder reaction between fatty acid 1 and methyl acrylate (MA).

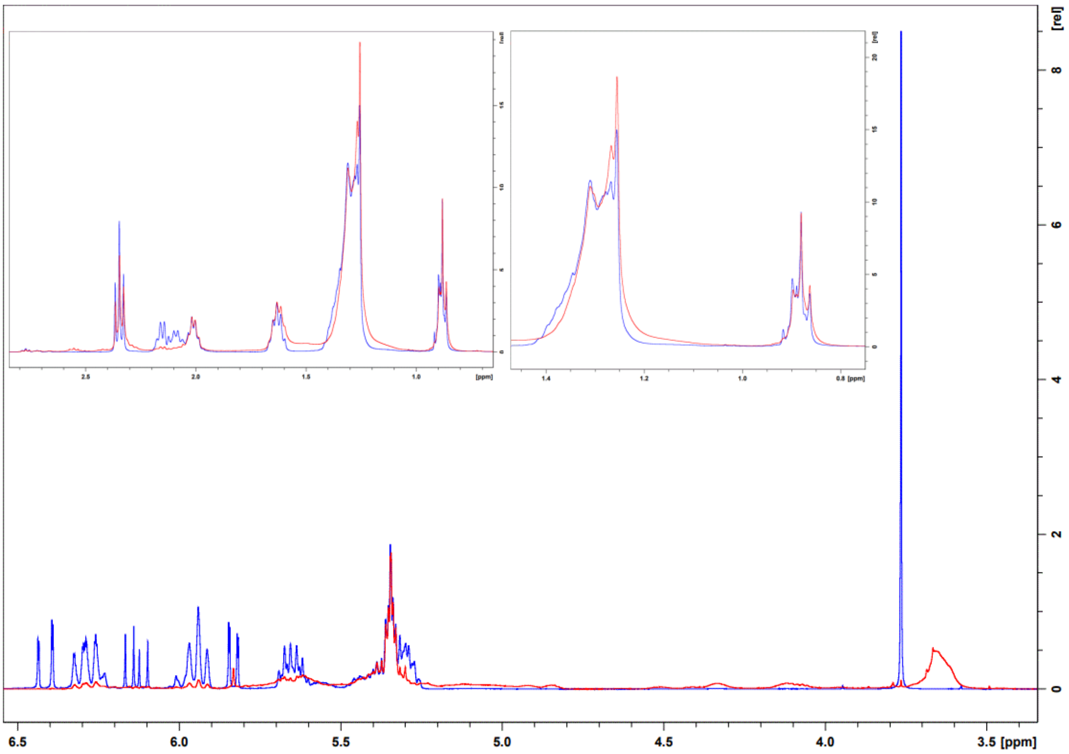


Figure 149: *^{1}H NMR spectra of the reaction mixture consisting of the fatty acid mixture and methyl acrylate (MA) at t=0h (red) and 70h (blue). Peak at 0.88 ppm was used to normalize the spectra integrals.*

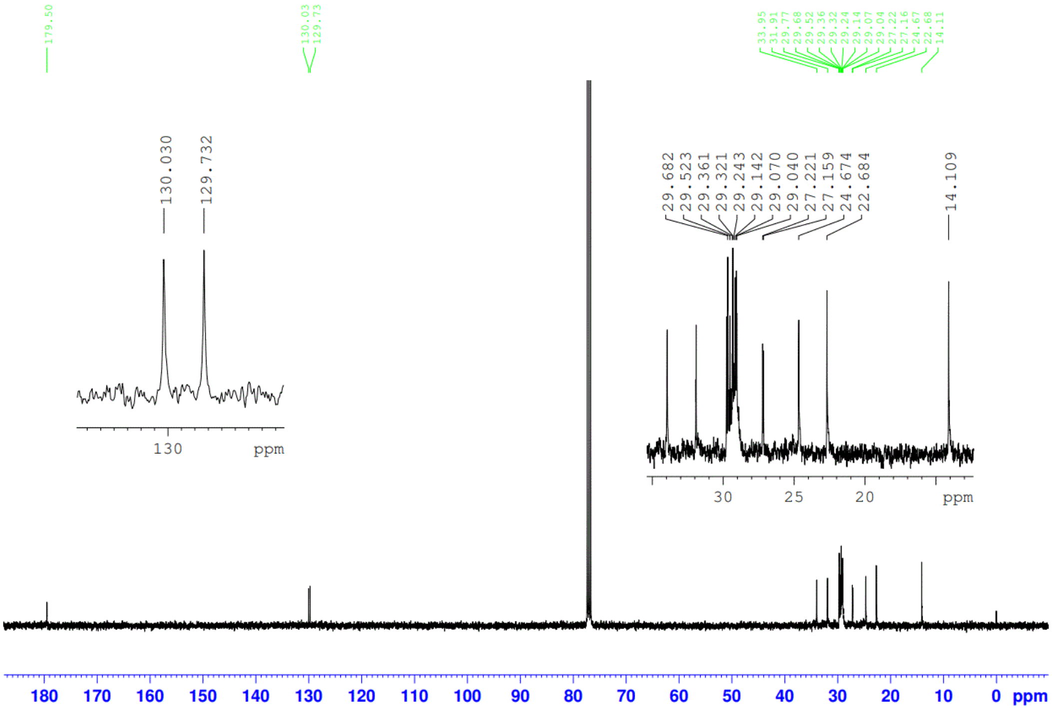


Figure 150: *^{13}C NMR spectra of the reaction mixture consisting of the fatty acid mixture and methyl acrylate (MA) at t=67h.*

UPC2/MS detected the formation of an adduct with molecular weight 577.479 g/mol (**Figure 151**), corresponding to molecular formula $C_{36}H_{66}O_5$ (Appendix **D**). This indicates that fatty acid 1 (Fragment 1-2, **Scheme 18**) reacts through an autoxidation reaction with oxygen from the atmosphere (**Scheme 21**). For simplicity, only one adducts is shown for the reactions mentioned although the autoxidation reaction occurs through a complex free radical mechanism which may form several isomers and oxygenated species (see **Scheme 6**). The reaction can also account for the decrease in vinylic and allylic protons and carbons (**Figure 149** and **Figure 150**), as well as the increase in CH_2 peaks. The autoxidation adducts can further explain the new peaks observed in ^{1}H NMR at 3.5-4.5 ppm as adjacent protons to the ether bond and other oxygenated species formed. An additional signal, although with much lower intensity, is also detected in UPC2/MS with molecular weight 295.230 g/mol, corresponding to the formation of an epoxide from fatty acid 1 (**Scheme 22**). The variety of products formed may result in low concentrations of each specie and might explain why no new signals are observed in ^{13}C NMR and no coupling is observed in COSY, HSQC and HMBC (Appendix **C.2**).

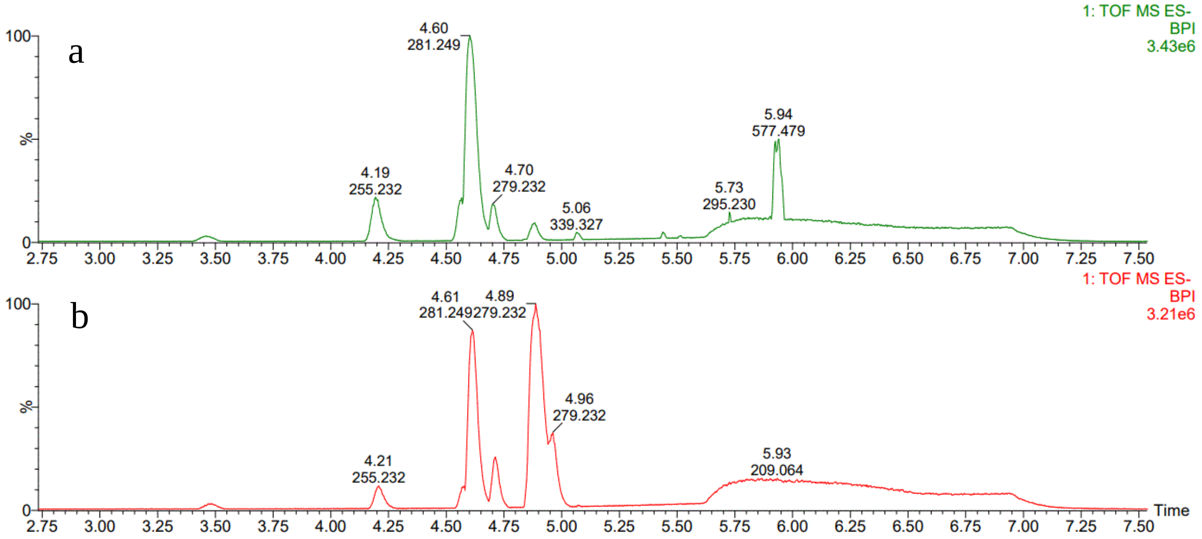
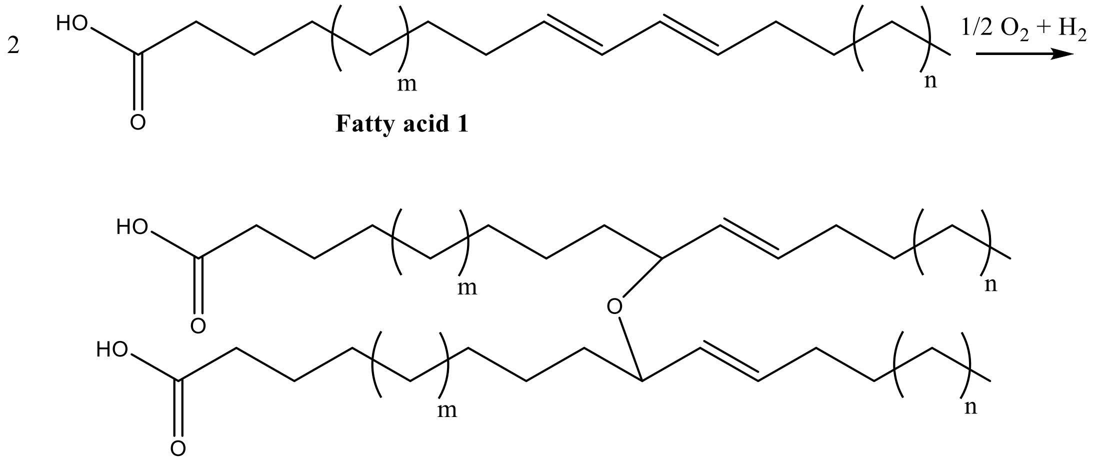
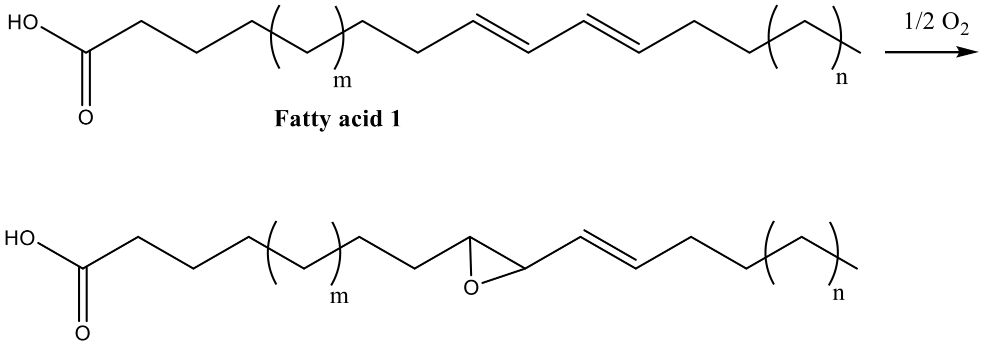


Figure 151: UPC2 coupled with MS for a) reaction mixture of fatty acids and methyl acrylate (MA) and b) conjugated fatty acid mix.



Scheme 21: *Autoxidation reaction between fatty acid 1 and oxygen from the atmosphere.*



Scheme 22: *Epoxide formed from fatty acid 1 during autoxidation.*

The UPC2/MS detected a decrease in the signals associated with the di-unsaturated fatty acids with molecular weights 279.232 g/mol (t=4.89 and 4.96). No significant decrease is observed for the signal for the isomer at t=4,70 nor for the monounsaturated fatty acid 2 (see **Scheme 19**). It may be hypothesized that these two signals at t=4.89 and 4.96 correspond to two isomers of the conjugated fatty acid (see fatty acid 1, **Scheme 18**), as these undergo the autoxidation reaction more readily compared to other unsaturated fatty acid. The signal at t=4.70 might not correspond to a conjugated fatty acid which would explain why no significant decrease is observed.

At t=70h, the methyl peaks do not overlap completely in the ^{1}H NMR spectra. The trend was also observed in the following experiment, including the reaction between the fatty acid and PT (Section **4.13.4**), and the pure fatty acid (Section 4.14.5). This might be due to the proximity to the vinylic peaks undergoing the autoxidation reaction which might impact the shielding of this peak.

All characteristic peaks from MA (see **Figure 217**) were completely reduced at t=70h (**Figure 149**). This may be caused by reactions involving the unsaturated bond in MA, breaking the conjugation which would also affect the shift of the methyl group. However, UPC2/MS did not detect any signals corresponding to an adduct involving the MA. The decrease in the MA peaks might be caused by evaporation of MA, which has a boiling point of 80.5 °C,[48] despite attempts to prevent the evaporation of MA. The reaction was therefore repeated in a hermetically sealed vial. The reaction was tested in a microwave reactor to increase the reaction rate, however, ^{1}H NMR indicated that the reaction did not occur. The reaction was therefore repeated under the same conditions as the previous reaction but in the sealed vial.

Many of the same trends were observed for this reaction, including the decrease in the vinylic and allylic peaks from fatty acid 1 (fragment 1-2, **Scheme 18**) and MA, and a slight increase in CH_2 peaks (**Figure 152**). Unlike the previous reaction, only the signal at 3.66 ppm is observed in the 3.5-4.5 ppm region. This is in accordance with the changes associated with the autoxidation reaction (**Scheme 21**). Additionally, a sharp peak at 3.69 ppm is detected while the methyl signal from MA is reduced. This could indicate that the MA is also reacting in this reaction through its reactive vinylic bonds (**Scheme 23**), as acrylates have previously been found to contribute to the autoxidative curing. Due to the loss of conjugation, it can shift the methyl peak upfield. As mentioned before, the exact location of the ether bond and remaining unsaturated bonds were not determined, and the formation of isomers and other oxidized adducts is highly possible. It may also be hypothesized that the autoxidation may occur between two MA molecules (**Scheme 24**).

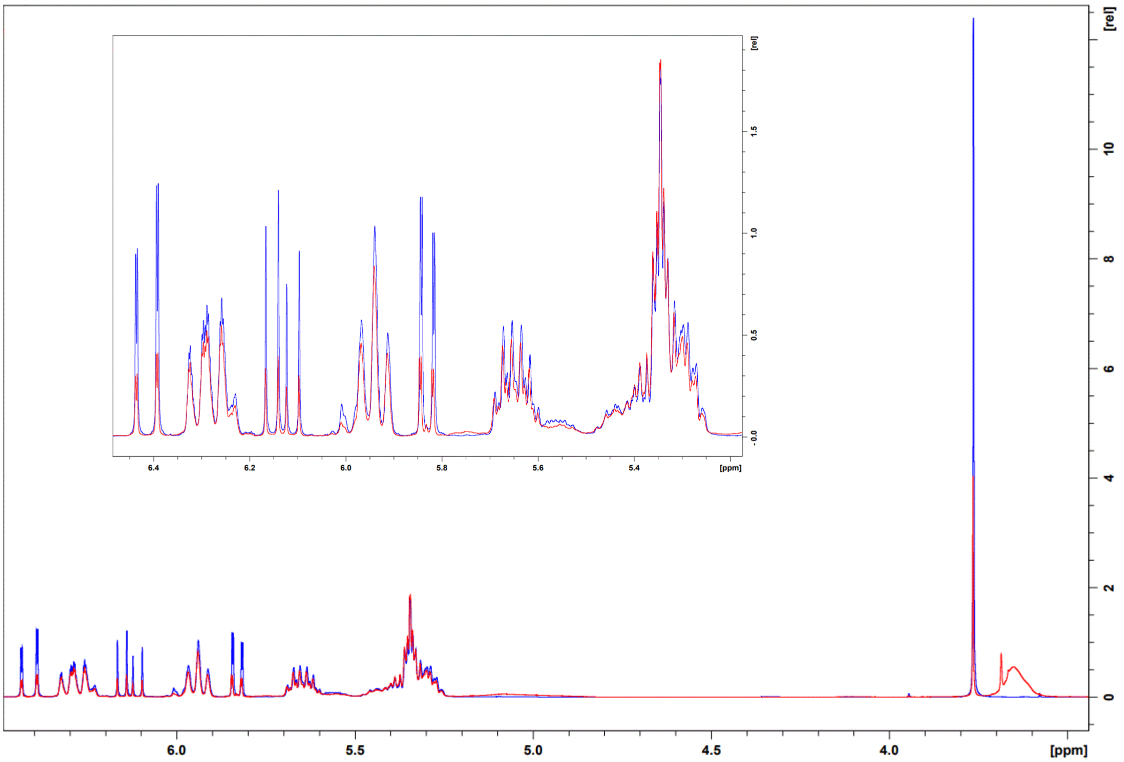
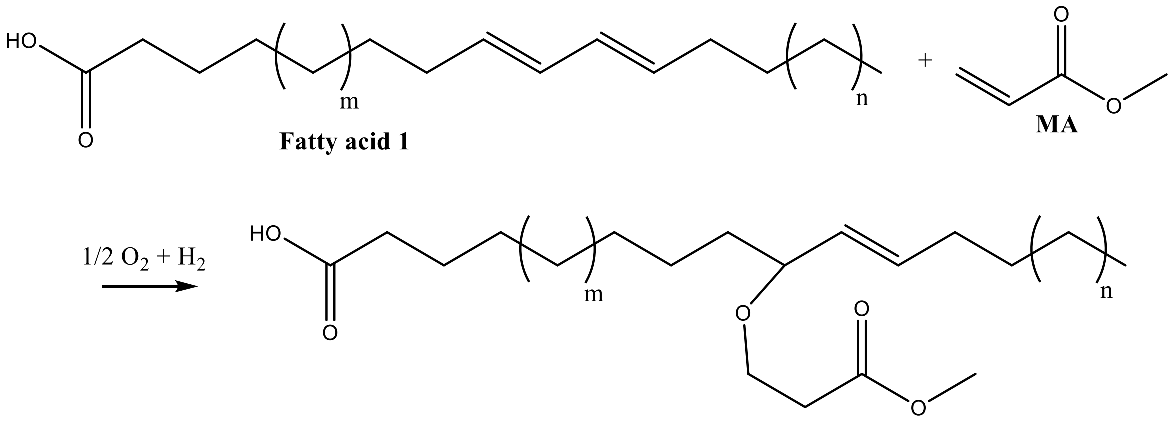
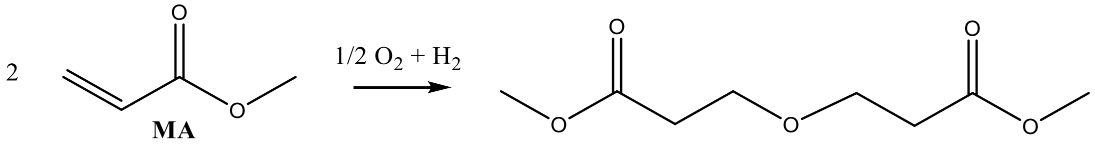


Figure 152: ^{1}H NMR spectra of the reaction mixture consisting of the fatty acid mixture and methyl acrylate (MA) at t=0h (blue) and 5d (red). Reaction was conducted in a hermetically sealed vial. Peak at 0.88 ppm was used to normalize the spectra integrals.



Scheme 23: Autoxidation reaction between fatty acid, methyl acrylate (MA) and oxygen from the atmosphere.

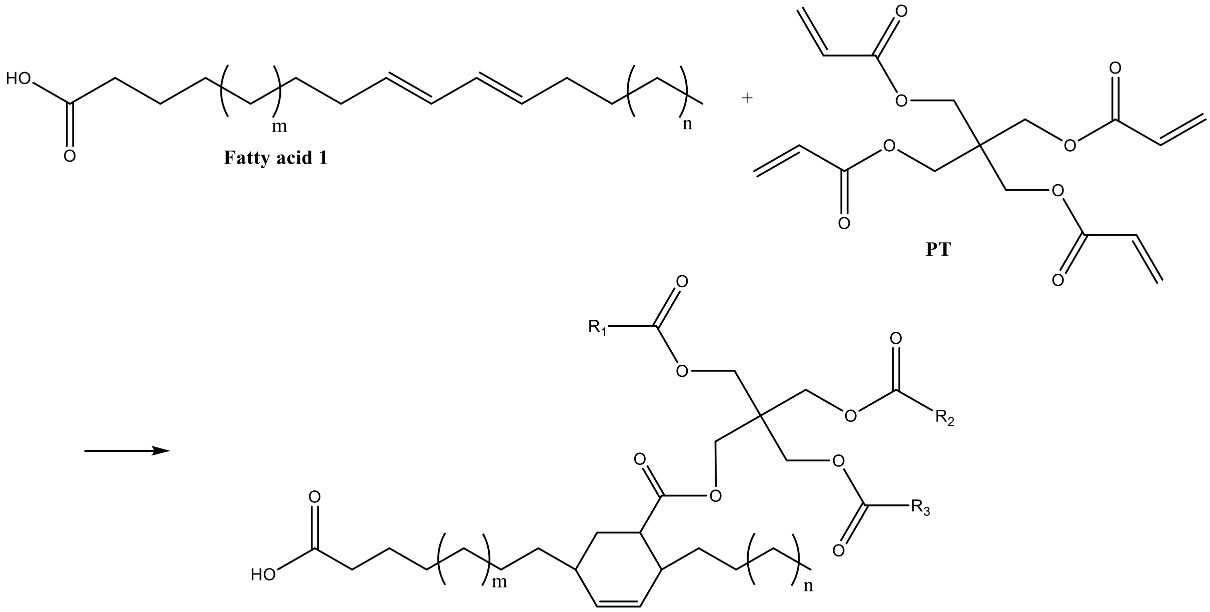


Scheme 24: Autoxidation reaction between methyl acrylate (MA) and oxygen from the atmosphere.

While the previous reaction mixture was heated for t=70h and resulted in an almost completely reduction of the vinylic signals from fatty acid 1 (see **Figure 149**), a much smaller decrease is observed in the vinylic signals in the mixture reacting in the hermetically sealed vial (**Figure 152**) for t=5d. This could be due to the limited access to oxygen in the sealed vial.

4.13.4 Pentaerythritol Tetraacrylate (PT)

PT was also employed as a dienophile for the Diels-Alder reaction with the conjugated fatty acid mixture, using 20func% PT (**Scheme 25**). A small signal was, as with the MA reactions, detected in ^{1}H NMR at 5.83 ppm which might be associated to the Diels-Alder reaction occurring (**Figure 153**). The decrease in vinylic and allylic protons associated with fatty acid 1 (fragment 1-2, **Scheme 18**) and PT was observed in NMR, combined with an increase in the integral for the CH_2 peaks. Although this is in accordance with the Diels-Alder reaction, the new peaks appearing at 3.5-5.0 ppm indicate that the main reaction is autoxidation. The decrease in the vinylic peaks associated with PT indicates that PT contributes to the autoxidation reaction. The loss of conjugation could also shift the CH_2 peaks in PT (see **Figure 177**) and would explain the full reduction in these peaks as well.



Scheme 25: Diels-Alder reaction between fatty acid 1 and pentaerythritol tetraacrylate (PT). R_1, R_2 and R_3 may represent unreacted vinyl bonds or further Diels-Alder reactions with fatty acid 1.

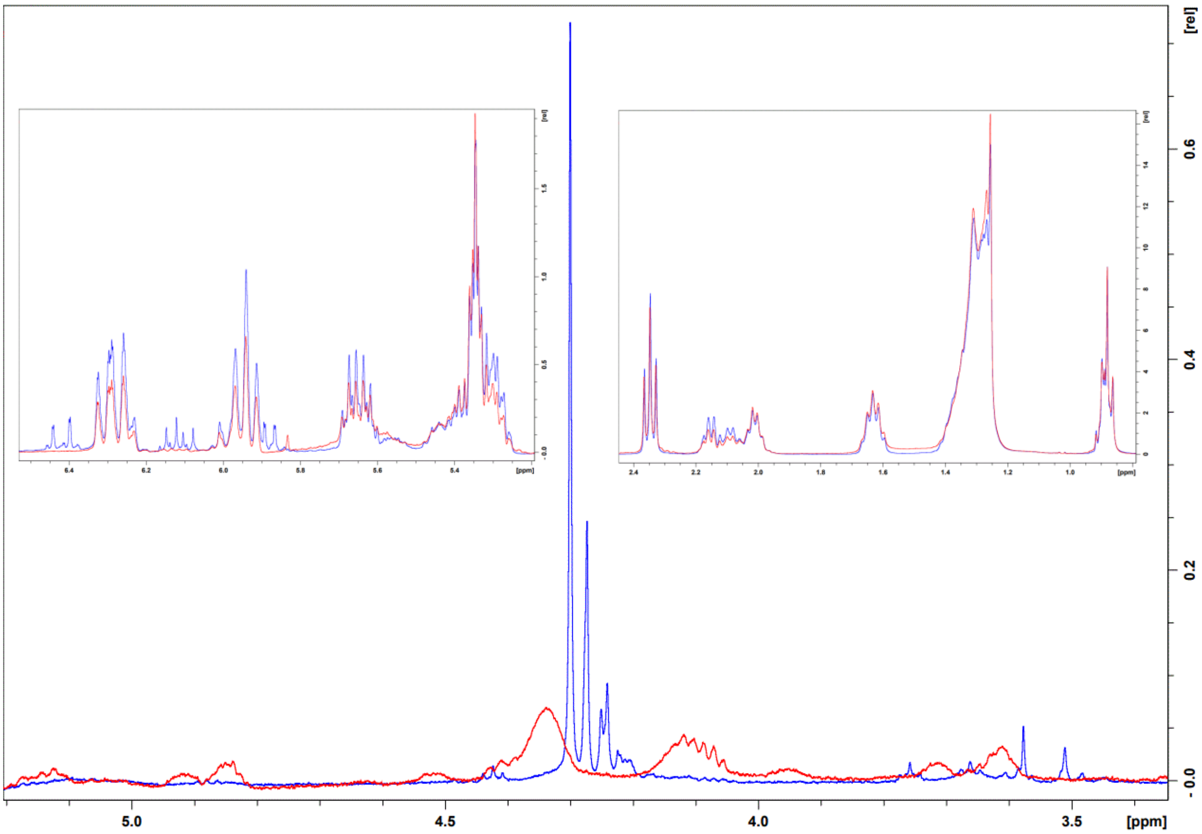
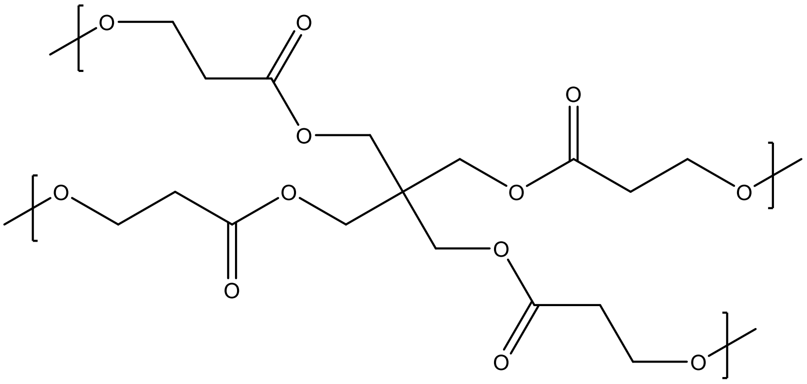


Figure 153: ^1H *NMR spectra of the reaction mixture consisting of the fatty acid mixture and pentaerythritol tetraacrylate (PT) at t=0h (red line) and 9h (red line). Peak at 0.88 ppm was used to normalize the spectra integrals.*

When high concentrations of PT were used (50func% and 33func%), visual changes were observed, and the mixture became insoluble within t=1h. Further lowering the concentration to 20func% PT prevented the mixture from becoming insoluble during the reaction time of t=9h. This further indicates that the PT is involved in the autoxidation reaction. Due to the four functional groups present in PT, the mixture can form various polymeric networks with other PT molecules or with the fatty acid, creating a complex mixture of products (**Scheme 26**). Fatty acid 1, on the other hand, acts as a chain stopper, given that only the conjugated fatty acid will react. The formation of such networks can also explain the insolubility with high concentrations of PT.



Scheme 26: *Autoxidative curing of pentaerythritol tetraacrylate (PT). The ether linkages could be linked to fatty acid 1 or another PT molecule.*

No signal from MS was detected from the PT crosslinker (Appendix **D**) in the reaction mixture, indicating that the crosslinker had reacted completely, which is in accordance with ^{1}H NMR. A signal corresponding to molecular weight 577.4832 g/mol was detected, indicating the formation of the adduct formed by fatty acid 1 reacting with oxygen from the atmosphere (**Scheme 21**). Combined with the infinite number of adducts formed by the four-functional PT, it may be hypothesized that the intensity of each specie was too low to detect.

The reaction mixture and reagents were analyzed by GPC (**Figure 154**). The chromatogram indicates that there are impurities present in the PT crosslinker. No new signals are detected to verify the formation of a networks, although the signal for the reaction mixture is weaker compared to the reagents which could suggest a reaction. The adducts might not be detectable in due to the loss of conjugation. In order to confirm the adduct, a different detector should be employed, such as DLS.

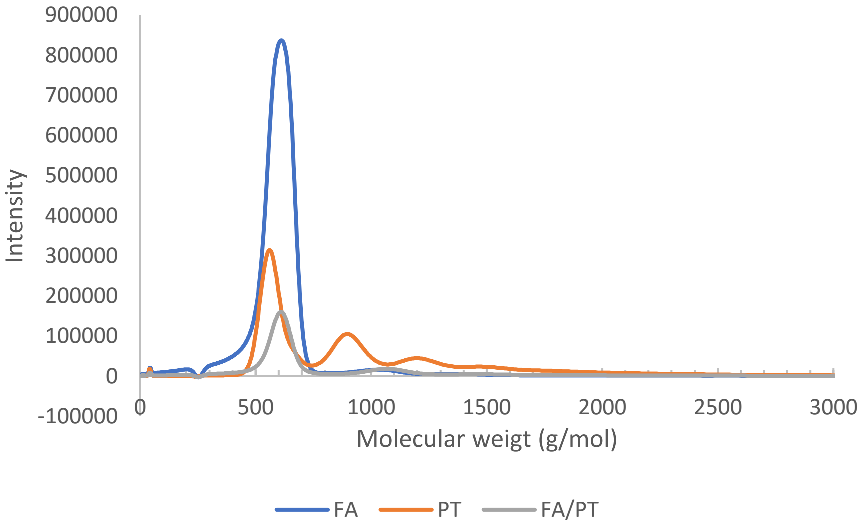


Figure 154: *GPC chromatogram of the fatty acid mixture (FA), pentaerythritol tetraacrylate (PT) and the reaction mixture of FA and 20func% PT at t=9h.*

In order to clarify any potential side reactions happening, pure PT was heated in the absence of a fatty acid for t=30h. Small changes were observed in the ^{1}H NMR spectra, however, these were associated with the impurities in PT (**Figure 155**). No new peaks were detected in the 3.5-5.0 ppm area, indicating that the autoxidative reaction does not occur for pure PT. This could indicate that the fatty acid is required for initiating the reaction.

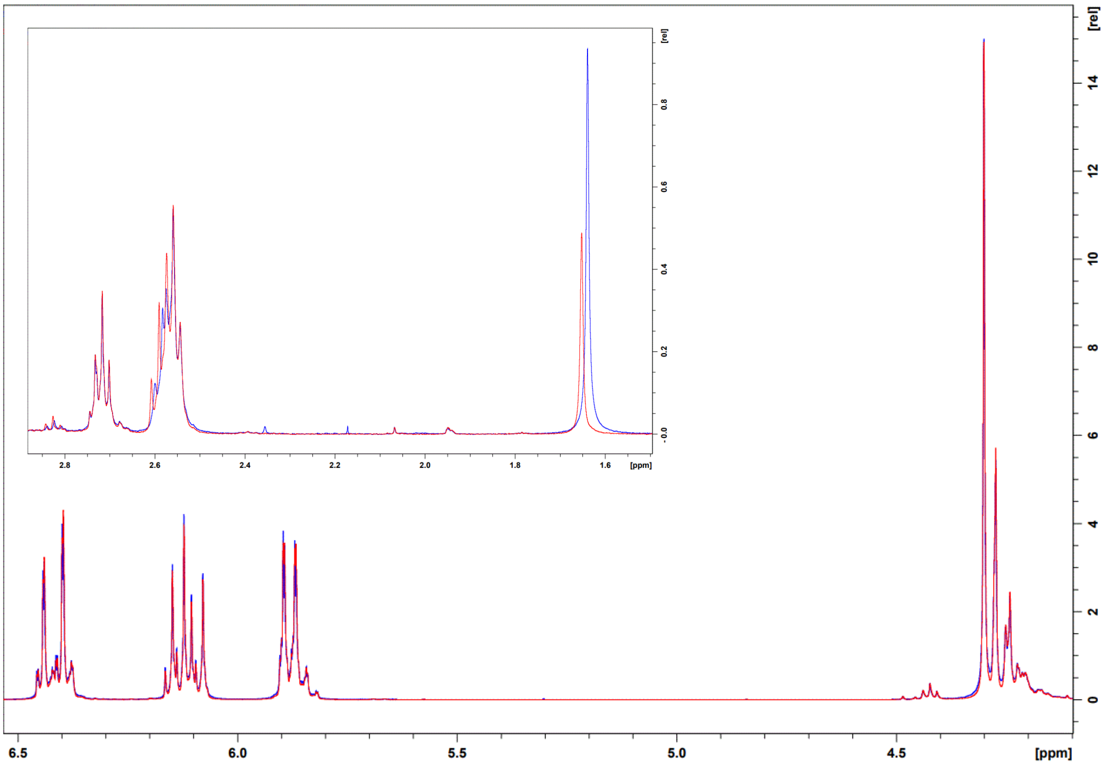


Figure 155: ^{1}H NMR spectra of pentaerythritol tetraacrylate (PT) after heating for t=0h (blue spectra) and 30h (red spectra). Peak at 0.88 ppm was used to normalize the spectra integrals.

4.14.5 Fatty Acid Mixture

From the reaction conducted with fatty acid and MA (Section **4.13.3**), the MA was expected to have evaporated and hence not have contributed to the reaction. To further verify this, the fatty acid mixture without any additives was heated for t=40h. As expected, the autoxidation occurred for the fatty acid (see **Scheme 21**) without additives, confirmed by the decrease in the vinylic and allylic protons, new peaks at 3.5-5.0 ppm and an increase in CH_2 peaks (**Figure 156**). The vinylic singlet peak at 5.83 ppm is also observed in the reaction mixture at t=30h. This negates that the signal is associated with the Diels-Alder reaction involving the fatty acid and the acrylate. Although the Diels-Alder reaction could occur among the fatty acids (see Reaction **2**, **Scheme 11**), it is more likely that it is yet another result of the complex autoxidation reaction, possibly involving rearrangements of the double bonds.

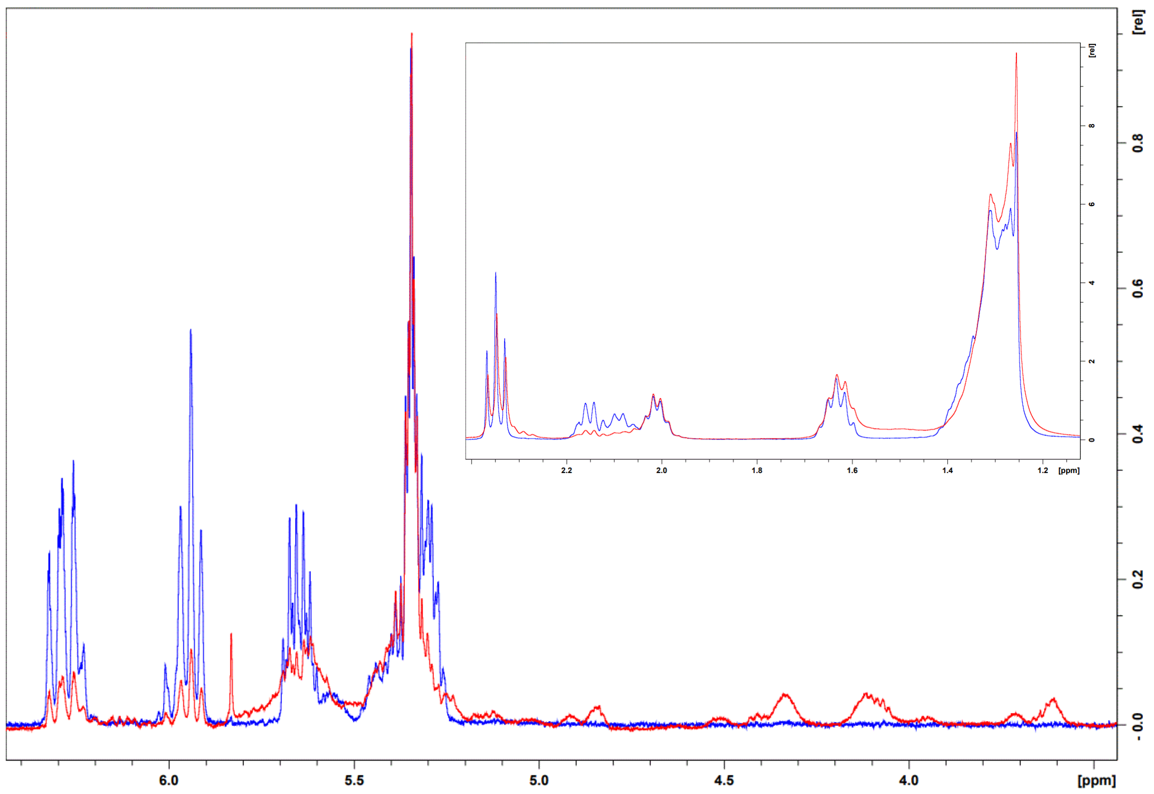
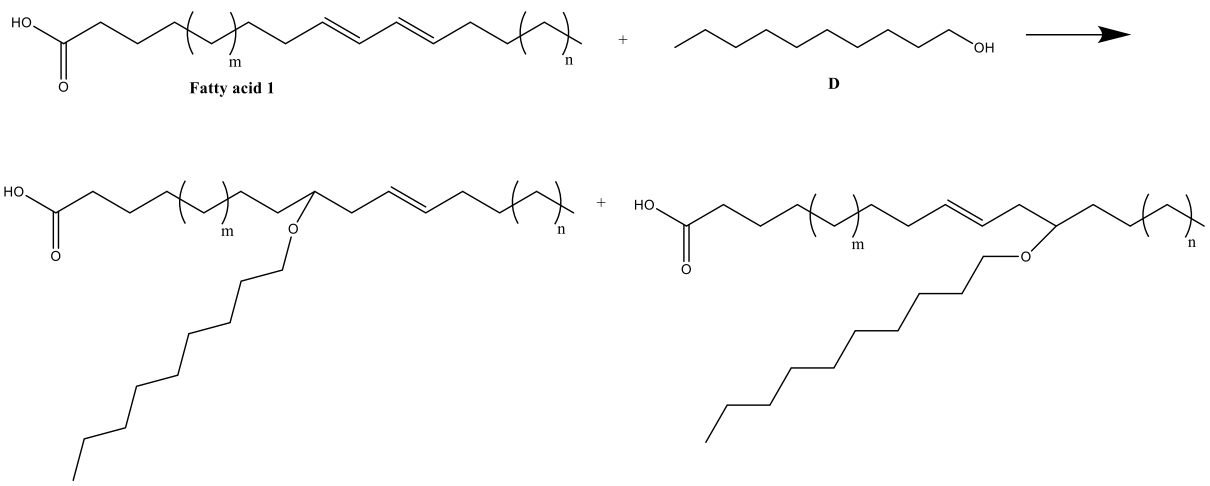


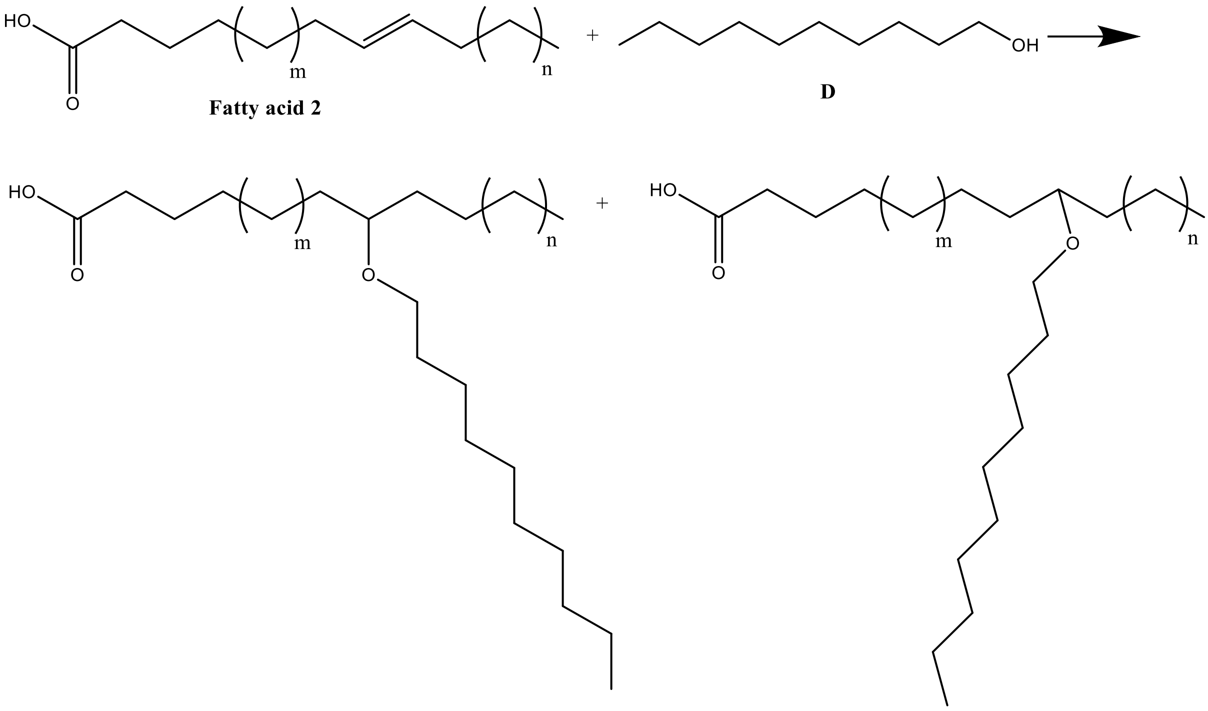
Figure 156: *^{1}H NMR spectra of the fatty acid mixture heated for t=0h (blue spectra) and 40h (red spectra). Peak at 0.88 ppm was used to normalize the spectra integrals.*

4.14.6 Decanol (D)

Another possible reaction to occur include the addition of an alcohol to the unsaturated carbon-carbon bond. To further investigate this, a monofunctional alcohol, decanol (D) (**Figure 218**), was added to the fatty acid mixture. This might occur for any of the unsaturated fatty acids in the mixture, including the main fatty acids, fatty acid 1 (**Scheme 27**) and fatty acid 2 (**Scheme 28**).



Scheme 27: *Addition of decanol (D) to fatty acid 1.*



Scheme 28: Addition of decanol (D) to fatty acid 2.

During heating for t=40h, no significant decreases were observed in the vinylic protons in ^{1}H NMR in neither fatty acid 1 nor fatty acid 2 (**Figure 157**) as would be expected if the addition reaction were to occur (**Scheme 27** and **Scheme 28**, respectively). Combined with the lack of new peaks in the 3.5-5.0 ppm area, this also indicated that the autoxidation reaction (see **Scheme 21**) did not occur in this reaction. This could partially be explained by the reaction being conducted in a hermetically sealed vial, limiting the access to oxygen.

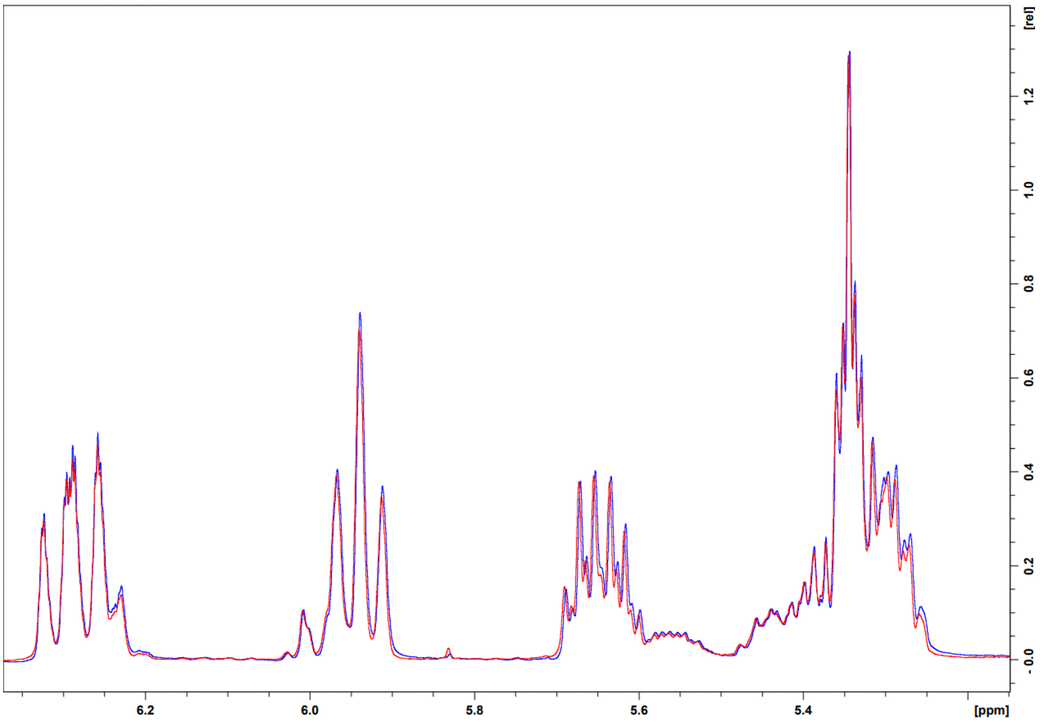


Figure 157: *^{1}H NMR spectra of the reaction mixture consisting of the fatty acid mixture and decanol (D) after t=0h (blue spectra) and 40h (red spectra). Peak at 0.88 ppm was used to normalize the spectra integrals.*

The ^{1}H NMR spectra shows a reduction in the signal at 2.35 ppm (**Figure 158**), corresponding to the protons adjacent to the carboxylic acid functionality in the fatty acids (see fragment 1-1, **Scheme 18** and fragment 2-1, **Scheme 19**). Simultaneously, a reduction is observed in the signal at 4.06 and 1.57 ppm, corresponding to the protons adjacent to the alcohol functionality in D (Appendix **C.2**). Two new triplet signals are appearing at 2.29 and 4.06 ppm while an increase in the peaks at 1.62 ppm is observed. The observations are in accordance with Fischer esterification (**Scheme 29**), which may be catalyzed by the carboxylic acids. The esterification reaction may occur with all of the fatty acids from the fatty acid mixture.

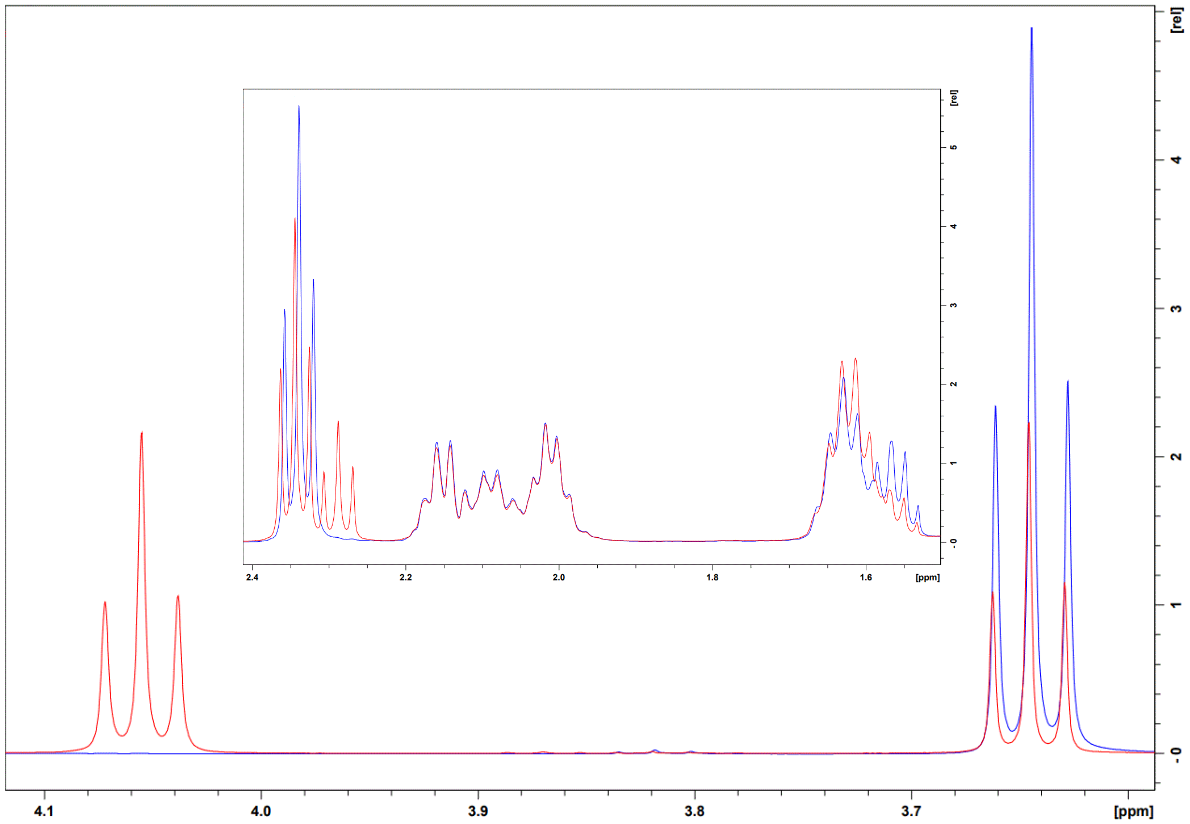
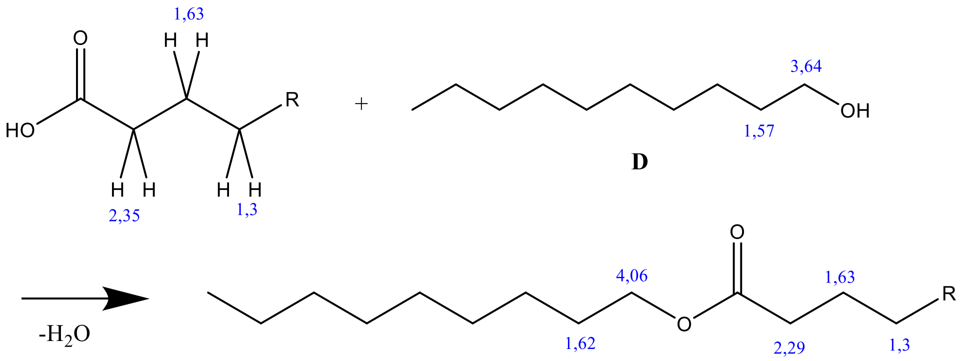
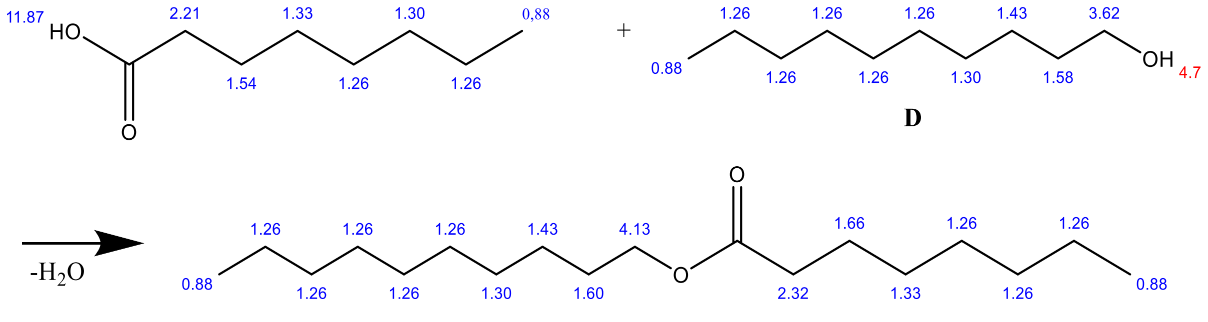


Figure 158: *^{1}H NMR spectra of the reaction mixture consisting of the mixture of fatty acids and decanol (D) after t=0h (blue spectra) and 40h (red line). Peak at 0.88 ppm was used to normalize the spectra integrals.*



Scheme 29: *Transesterification reaction between the fatty acid mixture and decanol (D) with relevant proton shifts from ^{1}H NMR. R corresponds to 14 carbons.*

The proton shifts for a similar esterification reaction between a generic carboxylic acid and D were predicted by ChemDraw (**Scheme 30**). The changes in the shifts associated with D is in good accordance with the predictions. However, the predicted shifts indicate that the protons adjacent to the carboxylic acids are shifted downfield as the reaction occurs. Yet, in the reaction, the protons are shifted upfield (**Figure 158**).



Scheme 30: *Predicted ^{1}H NMR shifts for a transesterification of decanol (D) and a generic carboxylic acid. Predictions were done with ChemDraw.*

A new signal was observed in FTIR at 1737 cm^{-1} for reaction mixture at t=40h which was not present in the reagents (**Figure 159**) which is associated with the C=O absorption band in saturated aliphatic esters (see **Table 3**). This further confirms that the esterification reaction occurs.

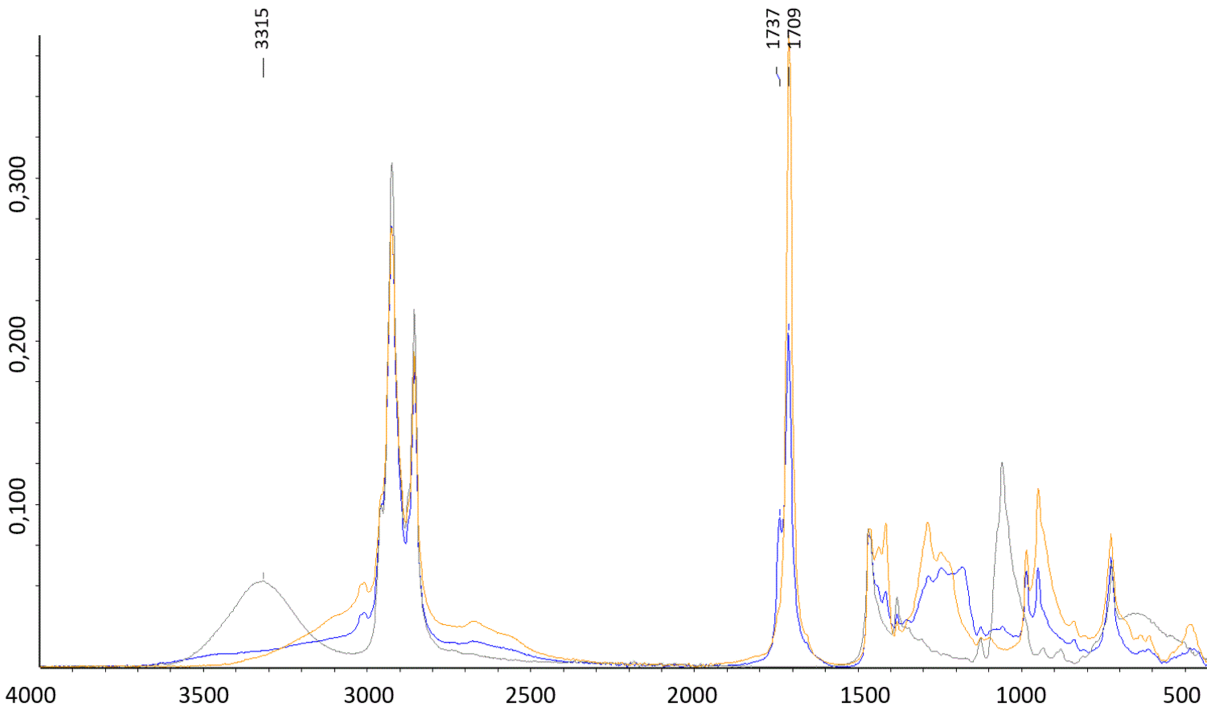


Figure 159: *FTIR spectra of the fatty acid mixture (yellow), decanol (D) (grey) and the reaction mixture of fatty acid and D at t=40h (blue).*

4.14.7 Correlation with Alkyd Reactions

The purpose of the fatty acid experiments was to reveal mechanisms of reactions which might be occurring in the alkyd, resulting in the increase in the molecular weight. Contrary to the expectations, the Diels-Alder reaction did not seem to occur. The main reaction seemed to be the autoxidation reaction occurring with oxygen from the atmosphere. It was deemed likely that this reaction would also include the acrylates, as these have previously been found to contribute in autoxidative curing of alkyds. The characteristics in ^{1}H NMR of this reaction occurring includes the decrease in vinylic and allylic peaks, new signals in the 3.5-5.0 ppm area and increase in the CH_2 peaks. The appearance of a singlet peak at 5.83 ppm was also commonly encountered although the correlation with the autoxidation reaction was not confirmed.

The autoxidation reaction may be extrapolated to the alkyd and alkyd emulsion reactions, as this reaction could explain the increase in molecular weight. However, these trends are not apparent in the alkyd reactions, illustrated by the reaction between alkyd MH-5mix and 50func% PT after heating at 80 °C for t=6h (**Figure 161** and **Figure 212**). The ^{1}H NMR spectra for this reaction is representative for the observations in all alkyd reactions. The only decrease that can be observed is associated to the crosslinker (**Figure 177**). There are no new peaks in the 3.5-5.0 ppm area, however, as can be seen in **Figure 160**, any new peaks might be disguised by the overlap with other peaks. Yet, no increase in the integrals are observed, rather the opposite. No significant increases are observed in the integral of the CH_2 peaks.

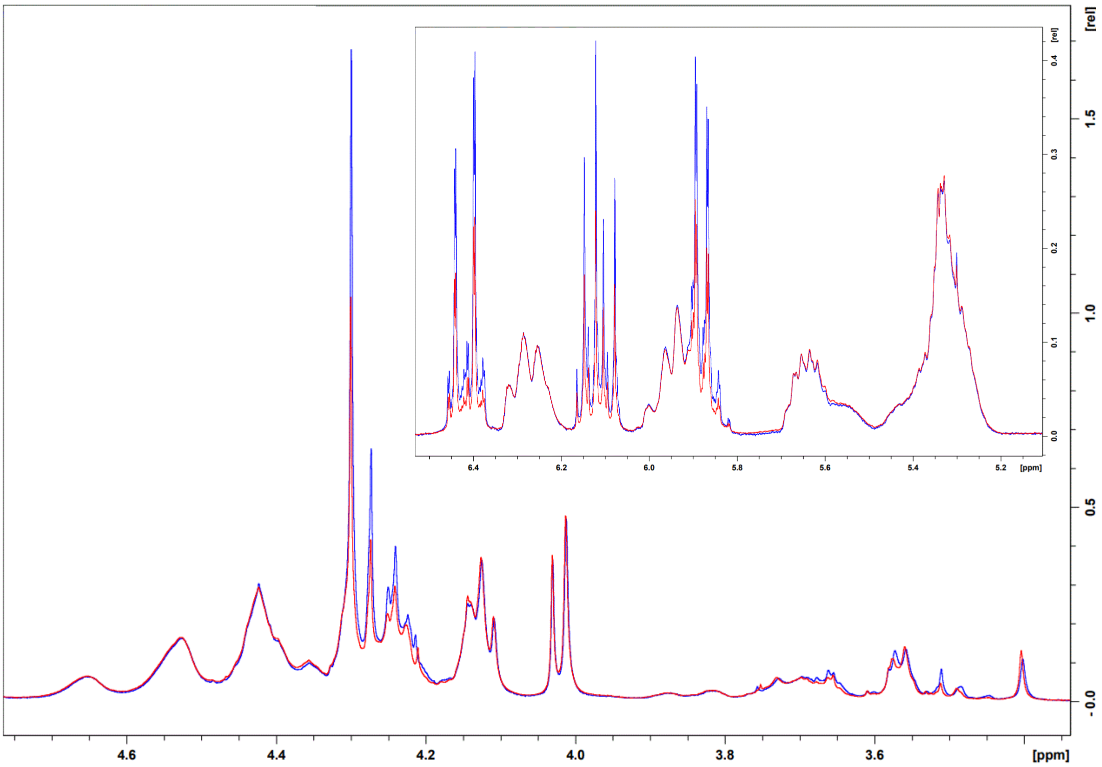


Figure 160: *^{1}H NMR spectra of alkyd MH-5mix and 50func% pentaerythritol tetraacrylate (PT) at t=0h (blue spectra) and 6h (red spectra). Peak at 8.61 ppm was used to normalize the spectra integrals.*

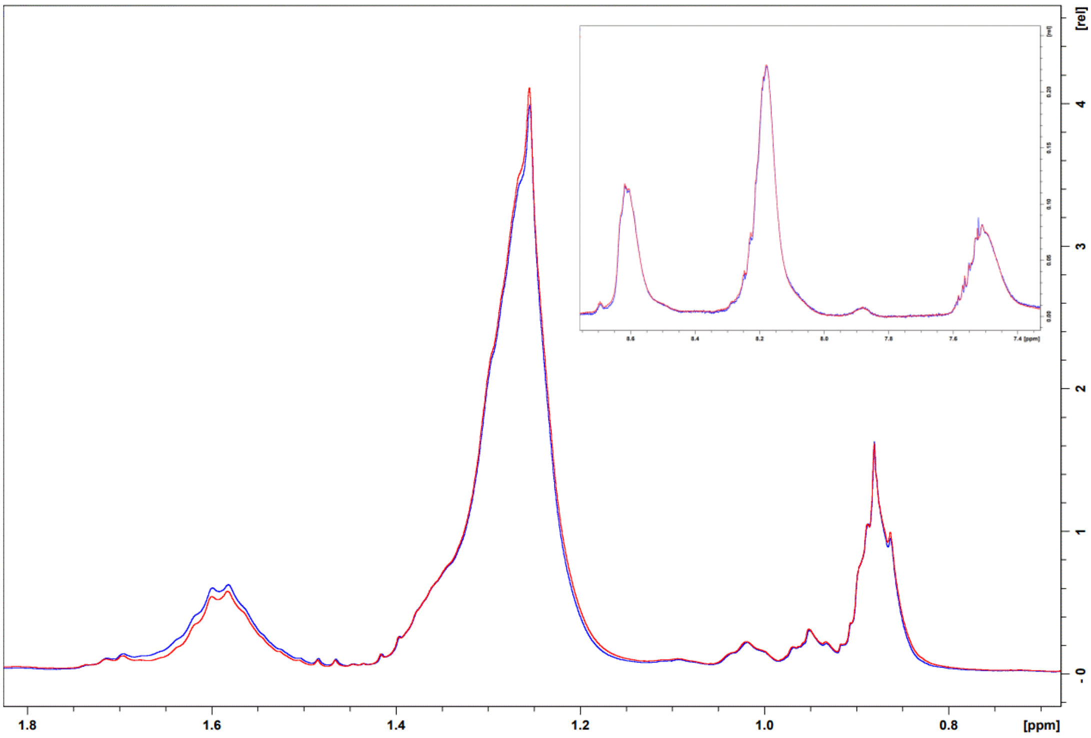


Figure 161: *^{1}H NMR spectra of alkyd MH-5mix and 50func% pentaerythritol tetraacrylate (PT) at t=0h (blue spectra) and 6h (red spectra). Peak at 8.61 ppm was used to normalize the spectra integrals.*

For the emulsion reactions with DG, the only difference observed for the alkyd is small decreases in the vinylic peaks associated with fatty acid 1 (Fragment 1-2, **Scheme 18**) (**Figure 162**). While this is not observed in the emulsion reactions with PT, new signals are observed in these reactions at 3.5-5.0 ppm might be associated with the autoxidation reaction.

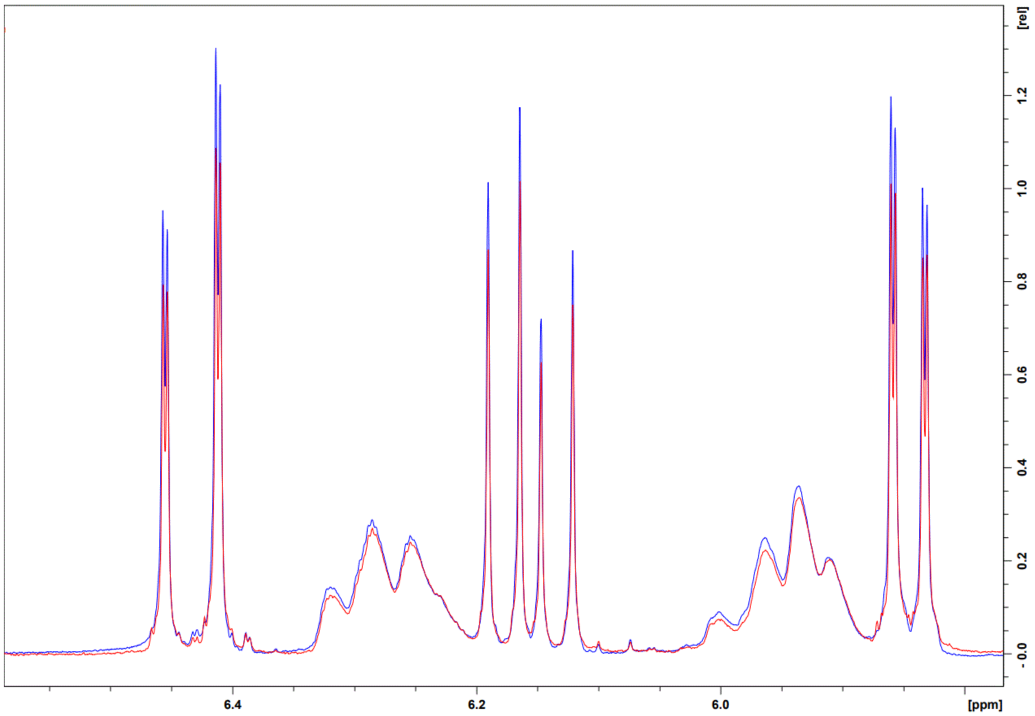


Figure 162: *^{1}H NMR spectra of emulsion with 50func% di(ethylene glycol)diacrylate (DG) at t=0h (blue spectra) and 22h (red spectra). Peak at 8.61 ppm was used to normalize the spectra integrals.*

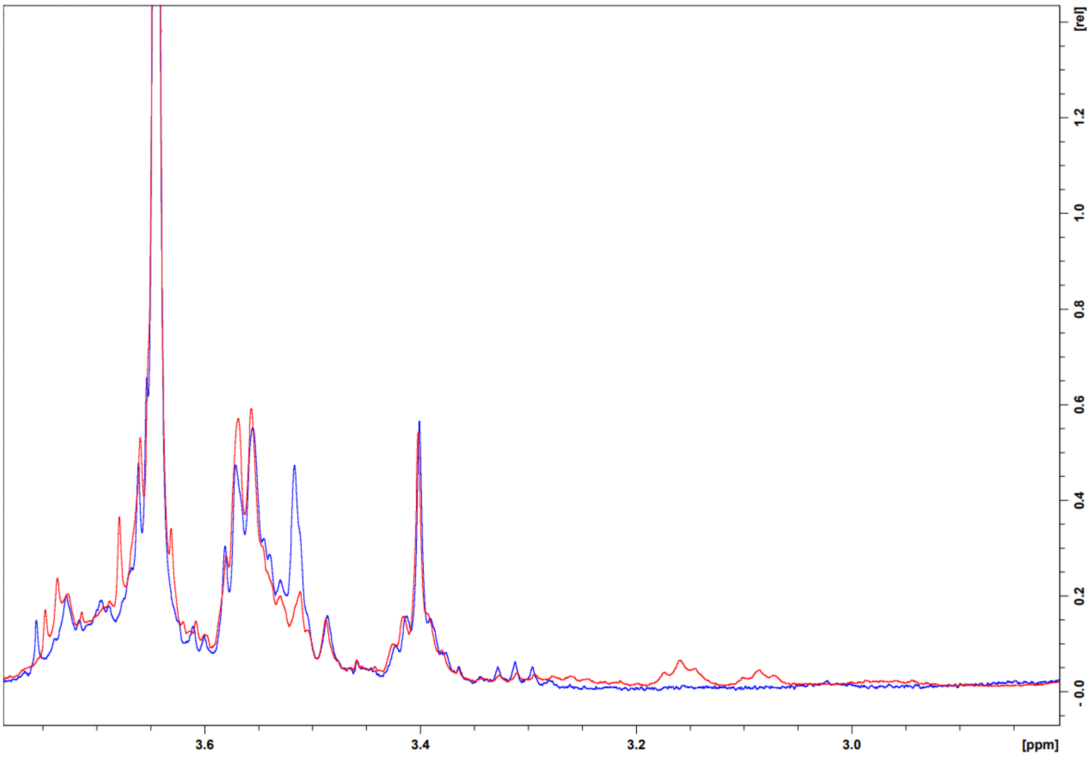


Figure 163: *^{1}H NMR spectra of emulsion with 50func% pentaerythritol tetraacrylate (PT) at t=0h (blue spectra) and 22h (red spectra). Peak at 8.61 ppm was used to normalize the spectra integrals.*

Fischer esterification was observed between the fatty acid and the alcohol rather than the addition reaction. This reaction might also occur in the alkyd system, in addition to a possible transesterification reaction as mentioned previously. Depending on the relative size of the involved species, it may lead to an increase or decrease in the molecular weight. If large polymers are cleaved, this may decrease the molecular weight, whereas an alcohol moiety attached to a high molecular weight polymer could lead to an increased molecular weight.

Although the fatty acid and alcohol did not react through an addition reaction, it cannot be ruled out a more reactive α,β-unsaturated crosslinkers may react through this reaction (see **Scheme 13**). If this reaction occurs, it would involve a decrease in the vinylic peaks associated with the crosslinker and not the vinylic peaks in the alkyd. It would also be visible through an increase in protons neighboring the newly formed ether bond. This reaction might produce similar trends as the autoxidation reaction. The reaction could not be verified through the decrease in the OH signals, illustrated by alkyd and 50func% PT (**Figure 164**).

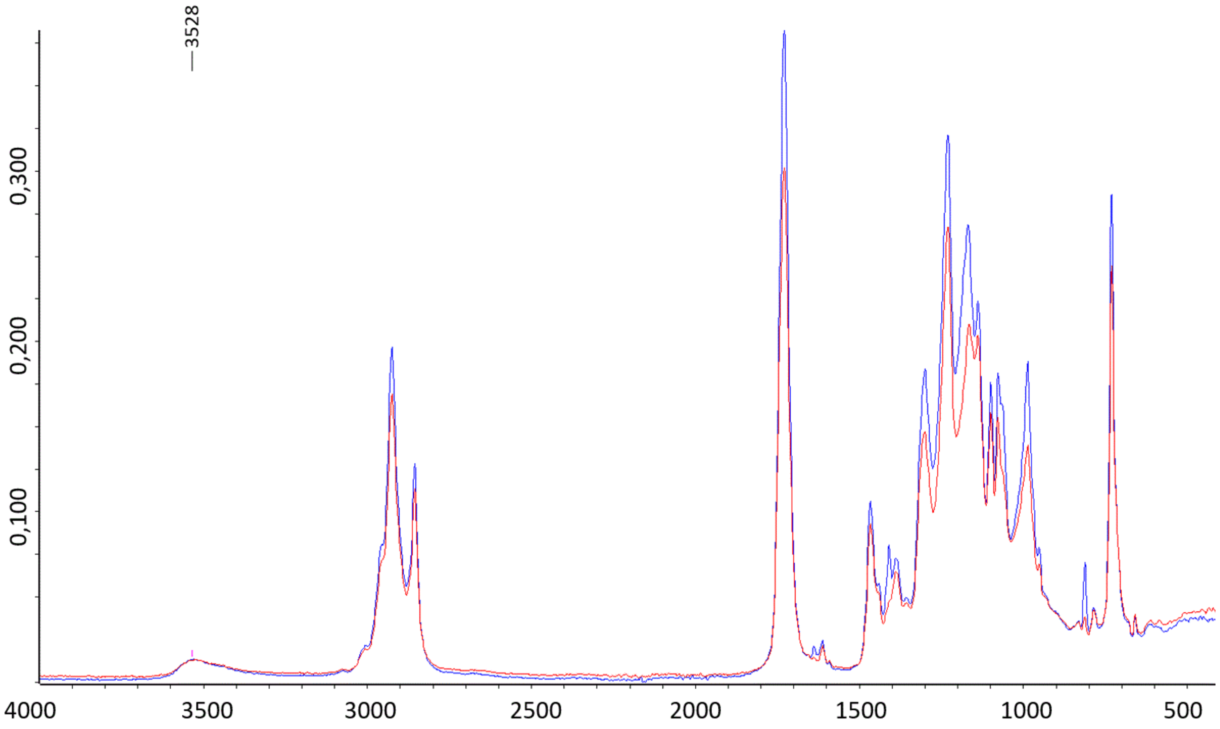


Figure 164: *FTIR spectra of alkyd with 50func% pentaerythritol tetraacrylate (PT) after heating at 80 °C for t=0h (blue spectra) and 7d (red spectra).*

The model reaction system with the fatty acid may not be fully representative for indicating what reaction are occurring in the alkyd and alkyd emulsions; however, it may provide some guidance. The Diels-Alder reaction has been proved to be catalyzed by conducting the reactions in water and in the presence of surfactants. Reactions that were not detected in the model system might therefore be responsible for the increased molecular weight. However, the complexity of the alkyd and alkyd emulsion spectra make it difficult to establish the mechanism completely.

5 Conclusion and Further Work

The molecular weight of the alkyd and alkyd emulsions were successfully increased through the incorporation of a crosslinker. The effect of different crosslinkers, concentration, temperature and reaction time on the resulting molecular weight were studied. Increasing the crosslinker concentration and temperature proved beneficial for the reaction. The reaction time was proportional to the molecular weight in the experiments conducted with the alkyd pre-emulsification while longer reaction times were generally required to obtain similar molecular weight by adding the crosslinker post-emulsification. This is believed to be due to hydrolysis occurring as a competing reaction in the emulsion.

Due to the low reactivity of the crosslinker at lower temperatures and short reaction times, it was found that the crosslinker could be added pre-emulsification and still surpass the viscosity limitations in the emulsification process. Adding the crosslinker pre-emulsification had a positive effect on the challenges encountered with the initial emulsion reactions and allowed for shorter reaction times to achieve high molecular weight alkyds.

The largest molecular weights were obtained by the addition of crosslinker 1,1'(methylenedi-4,1-phenylene)bismaleimide (MPB) to the alkyd prior to emulsification. The increase in molecular weight was achieved by heating the resulting emulsion mixture at both temperatures 60 and 80 °C and occurred within reaction times ($t \leq 9h$) shorter than with crosslinker pentaerythritol tetraacrylate (PT). Further work should be conducted with this crosslinker to further verify the trends. Shorter reaction times, lower temperatures and concentrations may also be investigated with the MPB mixture, as well as mechanistic studies to reveal the mechanism of the reaction. Further efforts should also be put into the drier system in order to overcome the softness of the films associated with the MPB reaction mixtures.

FTIR and NMR proved to be useful tools to monitor the reactions through decreases in signals associated with vinylic regions in the crosslinkers. Both methods were limited to reactions employing higher concentrations of crosslinker (≥11func%). None of the methods employed revealed any changes in the alkyd, nor were any new signals detected. This provides difficulties in establishing the mechanism causing the increased molecular weight. There were no indications that the desired Diels-Alder occurred. The Diels-Alder reaction might be promoted by the use of Lewis-acid catalysts, increasing the temperature or the pressure. In previous studies, the Diels-Alder reactions with the alkyd and acrylate dienophiles were carried out at 150-170 °C. For this study, the temperature was limited by the stability of the emulsion. The significantly lower temperatures used in this study (≤80 °C) might be the reason why the Diels-Alder reaction did not seem to occur.

Although the mechanism was not established, a correlation between the molecular weights and the crosslinker was established. This led to the conclusion that the crosslinker played a crucial role in increasing the molecular weight. A correlation was also established between the molecular weight and the vinylic protons from the acrylate crosslinker in the alkyd reactions, further demonstrating the reactive areas in the reactions. The crosslinking reaction in the emulsion system is more complex than the alkyd system and no clear correlation could be established between the molecular weight and the decrease in the vinylic protons from the crosslinker.

The fatty acid provided further information about possible reactions which could explain the increase in molecular weight. The autoxidation was determined between fatty acid chains. This may occur in the fatty acids incorporated in the alkyd chains although there were no clear indications of this. The fatty acid reactions also revealed Fischer transesterification as a possible reaction. Extrapolating this to the alkyd, this may increase molecular weight. There are also ester bonds present in the alkyd which might be susceptible to transesterification.

Another possible explanation for the increased molecular weight could be the Michael addition between an alcohol species from the alkyd and the vinylic crosslinker. Further efforts should be put into investigation of the mechanisms involved in these reactions to explain the increased molecular weights observed.

The hardness of the resulting films was expected to increase proportionally to the increased molecular weight. This was observed for the alkyd reaction mixtures, although not for the emulsion reaction, neither by the addition of crosslinker pre- or post-emulsification, especially for long reaction times and increased temperatures. The softness of the films may be a concern for practical application and should be further investigated. The problem might be resolved by changing the amounts of driers added to the paint formulations.

The drying procedure involves exposing the reaction mixtures to oxygen which may cause autoxidation to occur and “mask” the effect of the reaction introduced by the addition of crosslinker and heat. Although measures were taken to minimize the probability of this, it cannot be stated with certainty that this did not occur and affected the molecular weight. There were also indices showing that the autoxidation could occur to varying extents despite exposure to the same drying and storage conditions. Further work should be carried out to reveal the influence of the drying time on properties such as the molecular weight.

6 Experimental

6.1 Instruments

6.1.1 FTIR

FTIR spectra were recorded using a Bruker Alpha ECO-ATR FTIR-spectrometer and processed with OPUS software. Reported frequencies are in the range of 4000-400 cm^{-1}.

6.1.2 NMR

NMR spectra were collected using a Bruker Ascend 400 MHz equipped with a SmartProbe (5 mm) utilizing Avance III HD Nanobay electronics. The samples were analyzed in deuterated chloroform ($CDCl_3$) with an internal TMS standard. The NMR data is reported as chemical shift in ppm (integral of proton(s), multiplicity, coupling constant(s)).

6.1.3 Viscosity

No instrument was available to measure the viscosity changes. The time required for the reaction mixtures to turn from liquid to solid was limited to visual observation.

6.1.4 DSC

Differential scanning calorimetry (DSC) was analyzed using TA Instruments Q200 DSC. For the determination of Tg, lower temperature -80 °C and upper temperature 150 °C was employed. Heating rate 10 °C/min and cooling rate 5 °C/min were employed. Three parallels of each sample was measured.

6.1.5 Solid Content

The solid content was analyzed by Jotun AS. The solid content is determined by heating the samples at 150 °C until the changes in weights are less than 0,1% in 180 seconds.

6.1.6 Bath-Sonication

The bath-sonication was conducted using a VWR Ultrasonic Cleaner (USC-TH) at 23 °C.

6.1.7 Microwave Reactor

Microwave reactions were conducted in a hermetically sealed 5 ml vial using a Biotage Initiator at 80 °C and 5 bar. Stir rate 800 RPM was applied.

6.1.8 MS

Three different MS analysis were used during this thesis. Non target LC analysis were performed on an Acquity UPLC system (IClass Waters™) coupled to a Synapt G2-S (Waters™) electrospray Q-TOF instrument in positive or negative mode. An ACQUITY BEH

C18 (100 mm × 2.1 mm, 1.7 µm) column was used. Method was followed as described by Persson *et al.* without further modifications.[49]

Non target SFC (supercritical fluid) analysis were performed on an Acquity UPC2 system (Waters™) coupled to a Synapt G2-S (Waters™) electrospray Q-TOF instrument in positive or negative mode. An ACQUITY BEH C18 (100 mm × 2.1 mm, 1.7 µm) column was applied. Method described by Waters™ was applied without further modifications[50].

For analysis where no chromatographic separation was used, the accurate mass determination in positive and negative mode was performed on a "Synapt G2-S" Q-TOF (Water™). Samples were ionized by the use of ASAP probe (APCI) or ESI probe.

In all three methods the calculated exact mass and spectra processing was done by Software Masslynx V4.1 SCN871 (Water™).

6.1.9 GPC

Molecular weight measurements were conducted using HPLC-SEC. Two packed bed columns, KF-804 followed by KF-803, allowed for separation of polymers with lower exclusion limit of 1000 g/mol and upper exclusion limit of 400 000 g/mol polystyrene (PS) equivalent. PS standards with molecular weights ranging from 1200-326 000 g/mol were used for calibration. A Shimadzu SPD-20A UV-detector was employed, measuring at wavelength 220 nm. THF was used as bulk solvent with flow rate 1 ml/min. Sample concentration was 1 mg/ml with injection volume 20 µl. The chromatograms were manually baselined, and trapezoidal integration was used to calculate the area for each data increment.

Molecular weight measurements using GPC were also conducted by Jotun AS using Malvern OMNISEC. Two PL-gel 5 µm Mixed-C (exclusion limits 0-2 000 000 g/mol) or Mixed-D (exclusion limits 0-500 000 g/mol) in series columns were applied. THF was used as solvent with flow rate 1 ml/min. Sample concentration was 5 mg/ml with injection volume 100 µl. For the conventional method, a refractive index detector (RI) was employed. The calibration standards were PS Medium EasiVials Red, Yellow and Green. For the absolute method, a triple point detector was employed, including RI, light scattering (right angle light scattering (RALS) and low angle light scattering (LALS)) and intrinsic viscosity. Standards used for absolute calculations were 105 K from Malvern.

6.1.10 Emulsion Characterization

The droplet size and polydispersity index (PDI) were analyzed by Jotun AS and are performed using dynamic light scattering (Malvern Zetasizer Nano-S) at 25 °C. The PDI ranges from 0-1, where 0 indicates that all drops are of identical size and 1 that all drops are of different sizes. The pH meter was calibrated with buffer with pH 7 and 10 for emulsions with pH>7, and calibrated with buffer 3 and 7 for emulsions with pH<7. The pH was measured at ambient temperature.

6.1.11 Film Formation Studies

Driers were added to the alkyd emulsions. For the alkyds, they were also dissolved in a suitable solvent. The alkyd emulsions were applied to a cleaned glass cover using a 100 µm applicator. The films were dried overnight in room temperature (RT) and moved to a controlled temperature and humidity room (23 °C, 50% humidity). The hardness of the films were measured by Jotun AS using König pendulum test with a TQC Pendulum damping tester. The König pendulum test measured the pendulum's oscillation time from 6° to 3°.[51] The pendulum hardness gives a measure of the hardness properties of the film. depending on the hardness of the film, the oscillations of a pendulum supported by the film are dampened.[10] The pendulum hardness is commonly measured after t=1, 3, 7, 14 and 28d.

6.1.12 Drying

The alkyd emulsions were dried prior to NMR and GPC measurements using a desiccator and vacuum. The emulsions were dried until the samples turned from white to transparent. The samples originally contained approximately 48% water and the drying procedure successfully removed 38-45wt% of water from the emulsion samples. The removal of water was confirmed by ^{1}H NMR.

6.2 Reagents

The crosslinkers were purchased from Sigma Aldrich and were used without further purification. The alkyd and alkyd emulsions were synthesized in collaboration with Jotun AS.

6.2.1 Characterization of Acrylate Crosslinkers

Spectroscopic data for 1,6-hexanediol diacrylate (HD) (**Scheme 16**): ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 1.70 (4H, m), 1.43 (4H, m), 4.16 (4H, tr), 5.82 (4H, dd, $^2J_{HH}$ = 1.51, $^3J_{HH}$ = 10.45), 6.12 (4H, dd, $^3J_{HH}$ = 10.45, 17.38), 6.40 (4H, dd, $^2J_{HH}$ = 1.51, $^3J_{HH}$ = 17.43). The compound contains impurities. The spectra is given in **Figure 175**.

Spectroscopic data for di(ethylene glycol)diacrylate (DG) (**Scheme 16**): ^{1}H NMR (400 MHz, CDCl$_3$) δ_H: 3.76 (4H, tr), 4.32 (4H, tr), 5.85 (4H, dd, $^2J_{HH}$ = 1.40, $^3J_{HH}$ = 10.50), 6.16 (4H, dd, $^3J_{HH}$ = 10.40, 17.34), 6.43 (4H, dd, $^2J_{HH}$ = 1.40, $^3J_{HH}$ = 17.29). The compound contains impurities. The spectra is given in **Figure 176**.

Spectroscopic data for pentaerythritol tetraacrylate (PT) (**Scheme 16**): ^{1}H NMR (400 MHz, CDCl$_3$) δ_H: 4.27 (8H, m), 5.88 (4H, dd, $^2J_{HH}$ = 1.38, $^3J_{HH}$ = 10.54), 6.12 (4H, dd, $^3J_{HH}$ = 10.37, 17.45), 6.42 (4H, dd, $^2J_{HH}$ = 1.21, $^3J_{HH}$ = 17.45). The compound contains impurities, some of which overlap with the signals from PT. The spectra is given in **Figure 177**.

Spectroscopic data for methyl acrylate (MA): ^{1}H NMR (400 MHz, CDCl$_3$) δ: 3.76 (3H, s), 5.83 (1H, dd, $^2J_{HH}$ = 1.46, $^3J_{HH}$ = 10.38), 6.12 (1H, dd, $^3J_{HH}$ = 10.38, 17.36), 6.41 (1H, dd, $^2J_{HH}$ = 1.55, $^3J_{HH}$ = 17.50). The spectra is given in **Figure 217**.

Spectroscopic data for decanol (D): ^{1}H NMR (400 MHz, CDCl$_3$) δ: 0.88 (3H, tr), 1.27 (14H, m), 1.57 (2H, m), 3.64 (2H, tr). The spectra is given in **Figure 218**.

6.3 Alkyd Synthesis

The alkyds were synthesized from diacids, polyols and a mixture of fatty acids, including conjugated fatty acids. The alkyd was synthesized through a standard alkyd synthesis route with azeotropic distillation.[11, 17, 38] Further specifications regarding the synthesis and monomers are not provided due to confidentiality.

6.4 Emulsification

The alkyds are heated to 60 °C overnight to ensure uniform temperature. The alkyd is partially neutralized with a base and emulsified through catastrophic phase inversion using non-ionic and ionic surfactants. The emulsification process is commonly conducted at 50-60 °C for approximately 20 minutes. Further specifications regarding the emulsification is not provided due to confidentiality.

6.5 Modifications of the Alkyds

6.5.1 Preliminary Reactions

6.5.1.1 Emulsion Reactions

Emulsion MHE-1 and crosslinker were stirred in an ice bath, then heated to 80 °C with magnetic stirring. The same procedure was followed for all of the reactions presented in

Table 19, **Table 21** and **Table 23**. For these reactions, the crosslinker concentration was calculated based on the weight.

GPC and pendulum hardness analysis were conducted by Jotun AS.

6.5.1.2 Alkyd Reactions

Appropriate amounts of alkyd MH-5mix and 10wt% HD or mM were mixed and heated at 80 °C at varying reaction times presented in **Table 25**. In reactions J01 and J02, the mixtures were stirred mechanically while no stirring was applied in reactions J03 and J04. In reaction J02, mM mixed with di(propylene glycol) methyl ether (DPM) (59.89 g) prior to addition to the alkyd.

The GPC analysis were conducted by Jotun AS.

Two samples containing MH-5mix were prepared and heated at 80 °C. One of the samples were flashed with N_2 for t=1h before heating and flashed for each sample extraction.

6.5.2 Crosslinker and Temperature Study

The appropriate amount of alkyd MH-5mix and crosslinkers (HD, DG, PT and pM) were mixed and heated to 80 °C, 60 °C and RT at reaction times presented in **Table 6**.

6.5.3 Crosslinker Concentration Study

The appropriate amount of alkyd MH-5mix and crosslinkers (HD, DG, PT and pM) were mixed and heated to 80 °C at reaction times presented in **Table 7**.

6.5.4 Effect of Sonication/Stirring

Appropriate amounts of alkyd MH-5mix and PT were initially mixed thoroughly to yield a concentration of 50func% (**Table 9**) and heated at 80 °C. For the bath-sonicated reaction mixture, sonication was carried out every 30 minutes for the first 2.5 hours, then hourly for 13 hours.

6.5.5 Comparison of Alkyd and Emulsion Reactivity

6.5.5.1 50func% PT and DG in Emulsion

Appropriate amounts of emulsion MHE-1mix and crosslinkers PT or DG were heated to 80 °C with magnetic stirring (**Table 10**).

6.5.5.2 20func% PT and DG

6.5.5.2.1 Alkyd

Appropriate amounts of alkyd MH-5mix and PT or DG were heated at 80 °C as presented in **Table 11**. Pendulum hardness, solid content and GPC were analyzed by Jotun AS.

6.5.5.2.2 Emulsion

Emulsion MHE-1mix and 20func% PT or DG were heated with magnetic stirring at 80 °C as presented in **Table 11**. Pendulum hardness, solid content, drop size, pH and GPC analysis were conducted by Jotun AS.

6.5.6 Study of Starting Reagents

Alkyd MH-5mix and emulsion MHE-1mix were heated at 60 °C or 80 °C as presented in **Table 14**. The emulsion was stirred magnetically. Pendulum hardness, solid content, drop size, pH and GPC of the emulsion were measured by Jotun AS.

6.5.7 Repeatability

6.5.7.1 Alkyd Reactions

Appropriate amount of alkyd and 20func% PT or DG were heated at 80 °C for reaction times presented in **Table 7** and **Table 11** using different batch sizes. The mixtures were not subjected to stirring.

6.5.7.2 Emulsion Reactions

Appropriate amounts of emulsion and 20func% PT was heated at 80 °C, presented in **Table 15**. Pendulum hardness, solid content, drop size and pH was measured by Jotun AS. Similar batch sizes were prepared for both reaction mixtures. The mixtures were stirred with a magnetic stirrer.

6.5.8 Concentration Study in Emulsion System

Appropriate amounts of emulsion MHE-1mix and PT were heated at 80 °C for 22 hours, presented in **Table 16**. Pendulum hardness, solid content, drop size and pH was measured by Jotun AS for the reaction mixture with 10.69func%.

6.5.9 Addition of Crosslinker Prior to Emulsification

Alkyd MH-5e was synthesized by Jotun AS. Crosslinkers PT or MPB was added to the alkyd prior to emulsification as presented in **Table 17**. The alkyd was also emulsified without crosslinker (MHE-5e). The experiments were conducted by Jotun AS.

6.5.10 Fatty Acid Reactions

Fatty acid mixture, provided by Jotun AS, and appropriate amount of MA, PT or D were heated at 80 °C for reaction times as presented in **Table 18**.

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Appendix

A: FTIR and NMR spectra of pure compounds

A.1 Alkyd and emulsions

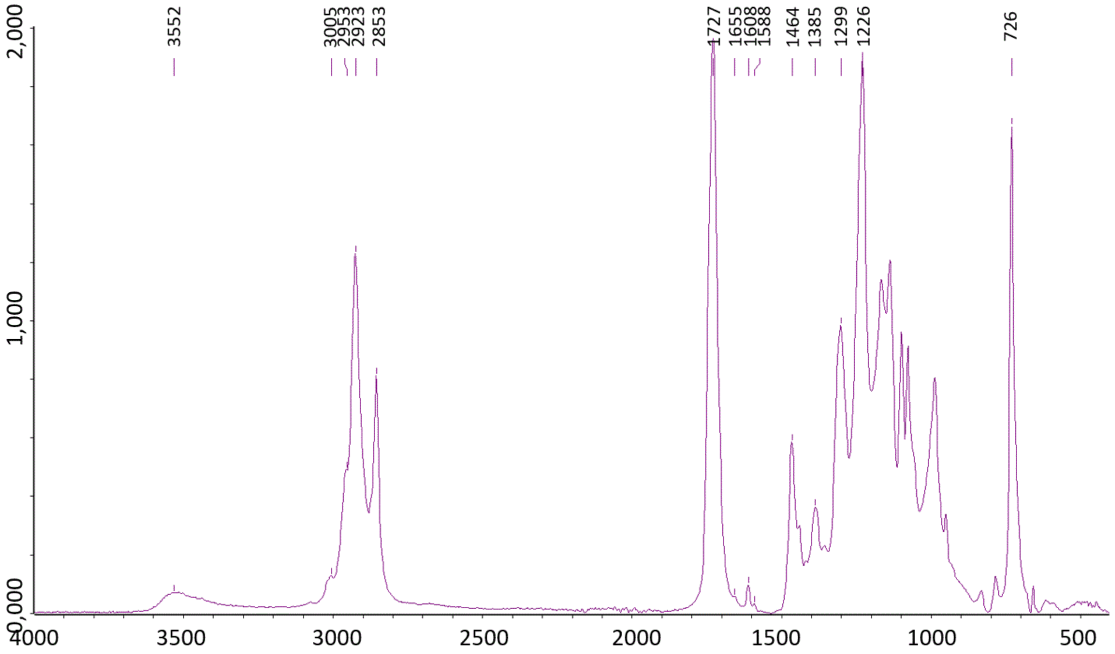


Figure 165: *FTIR spectra of alkyd MH-5mix.*

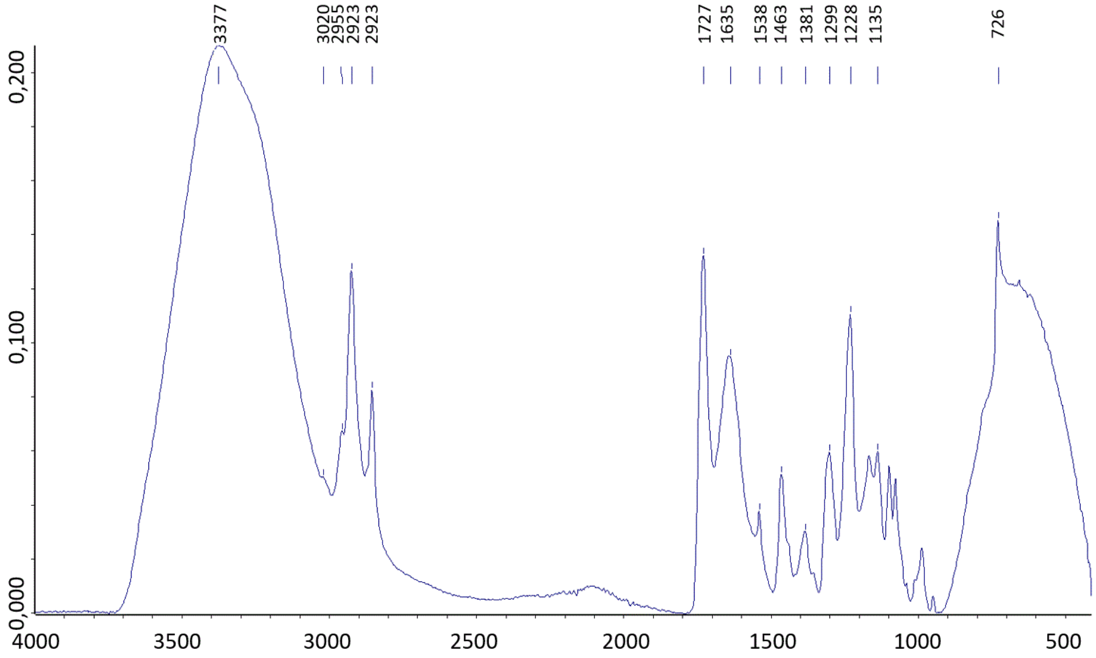


Figure 166: *FTIR spectra of emulsion MHE-1.*

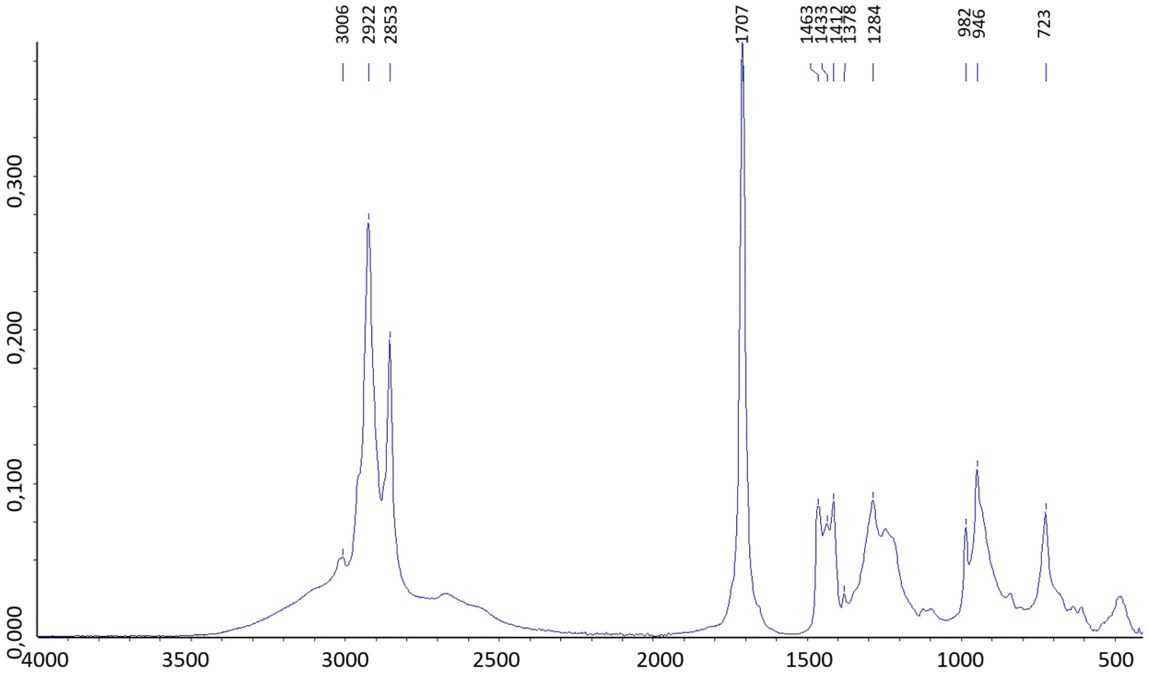


Figure 167: *FTIR spectra of conjugated fatty acid.*

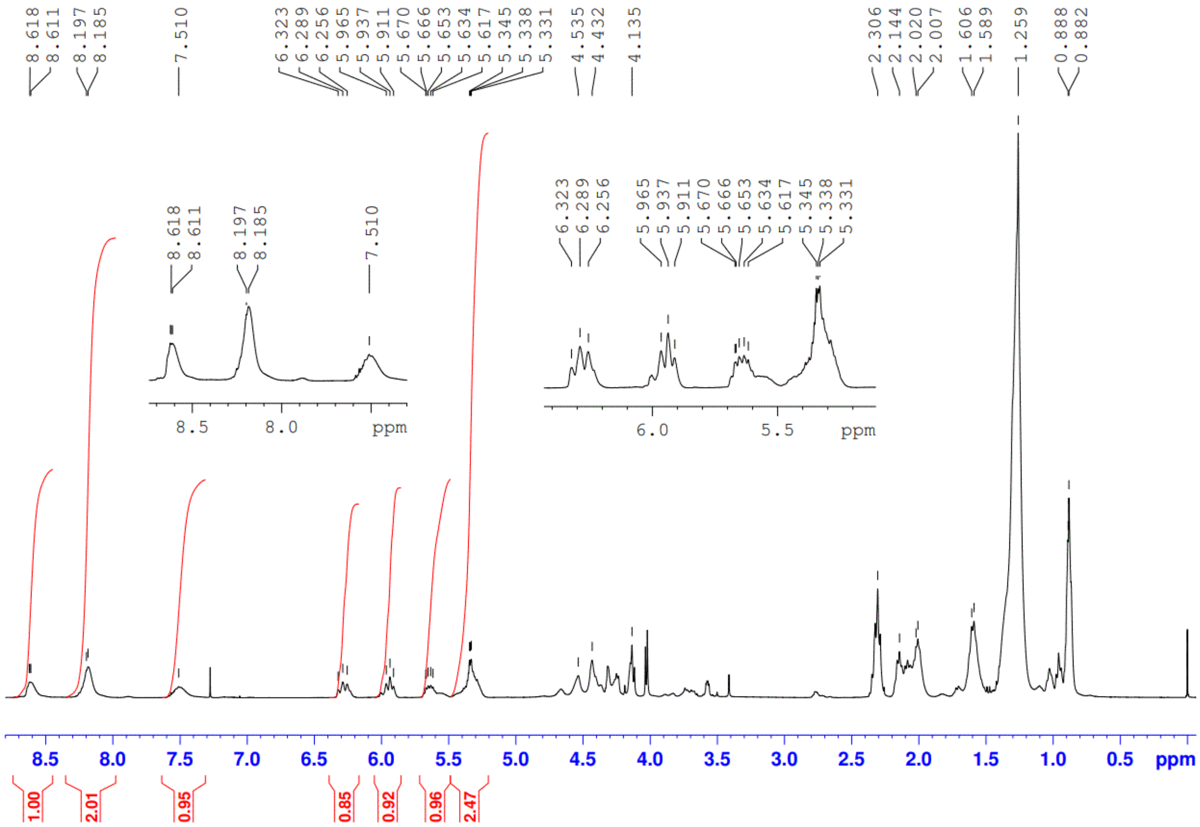


Figure 168: *^{1}H NMR spectra of alkyd MH-5mix.*

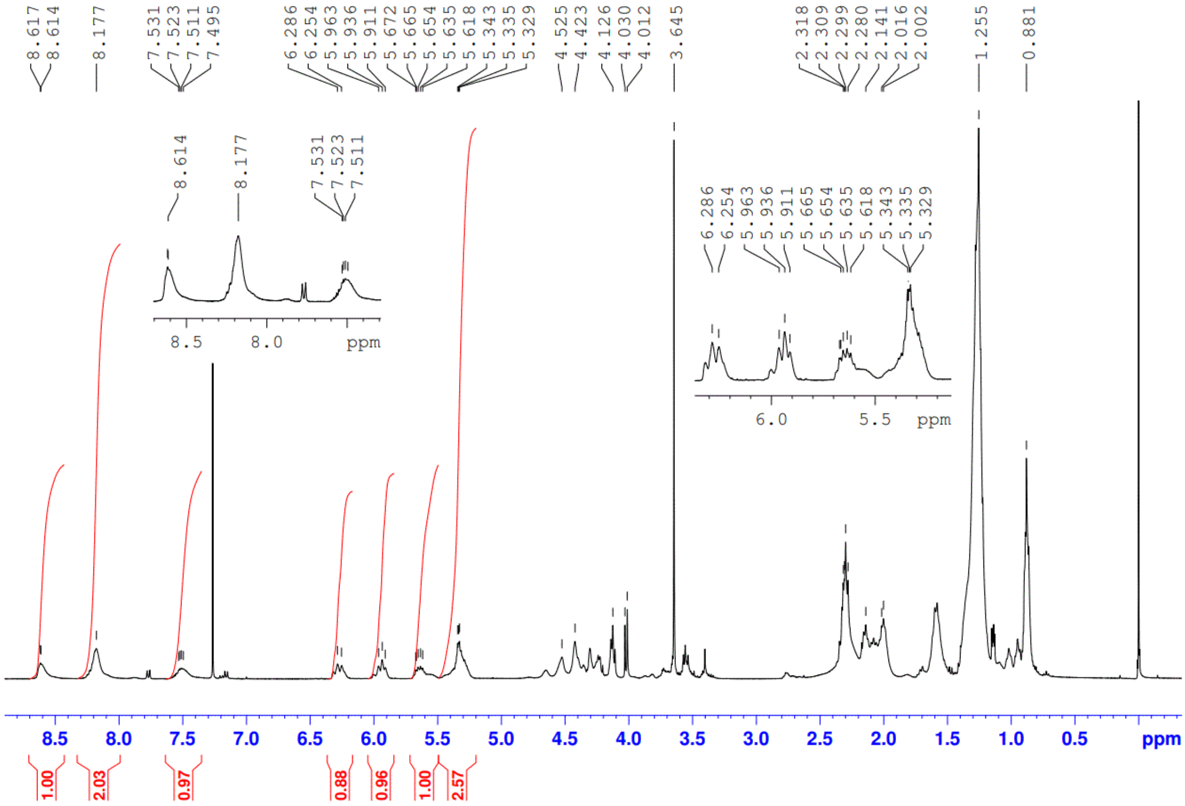


Figure 169: ^{1}H NMR spectra of emulsion MHE-1mix.

A.2: Crosslinkers

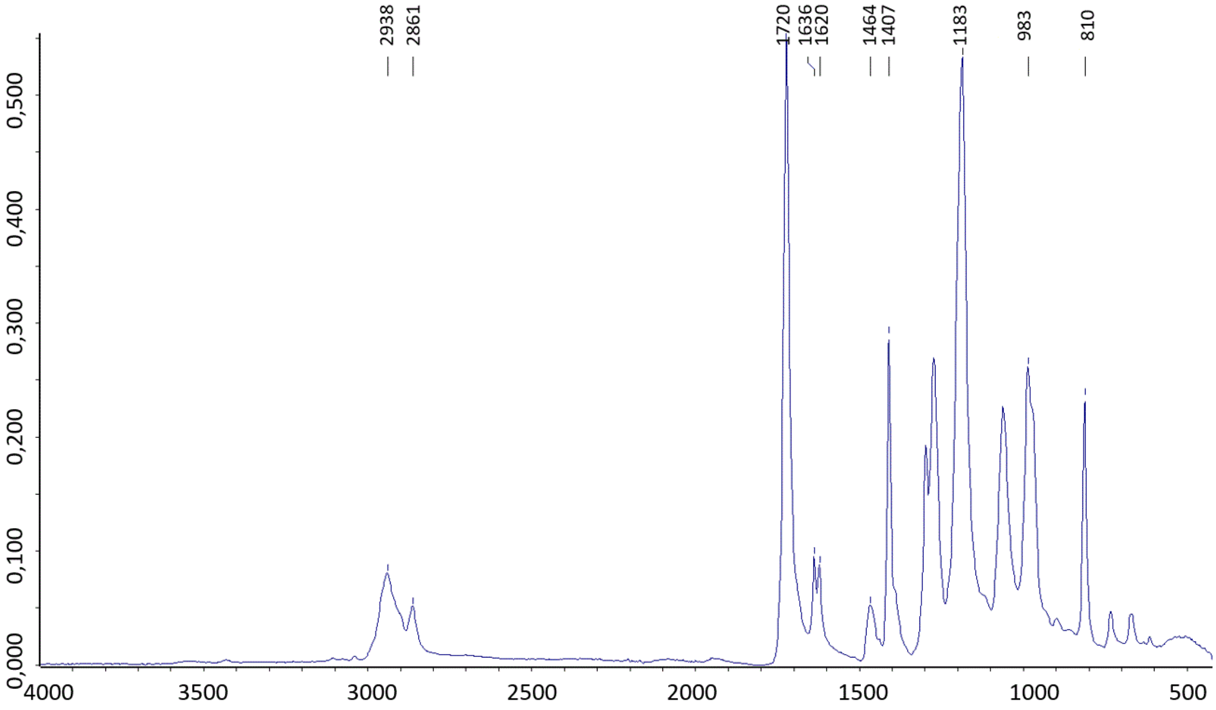


Figure 170: FTIR spectra of 1,6-hexanediol diacrylate (HD).

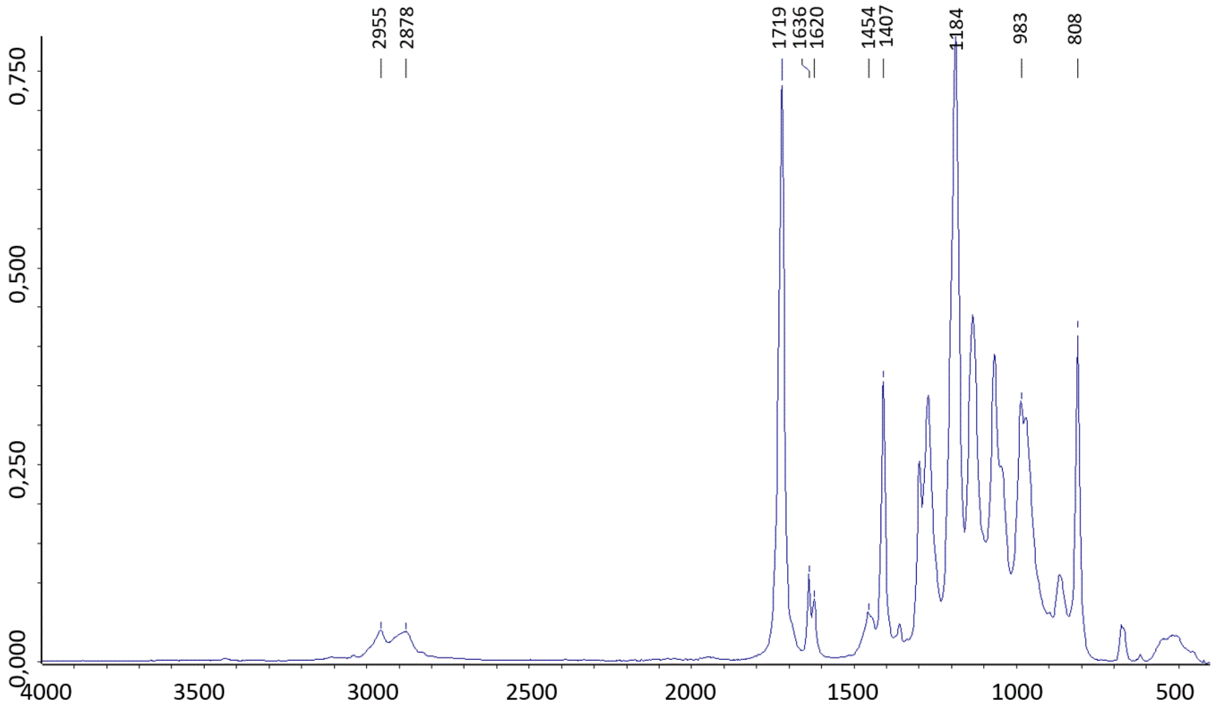


Figure 171: *FTIR spectra of di(ethylene glycol)diacrylate (DG).*

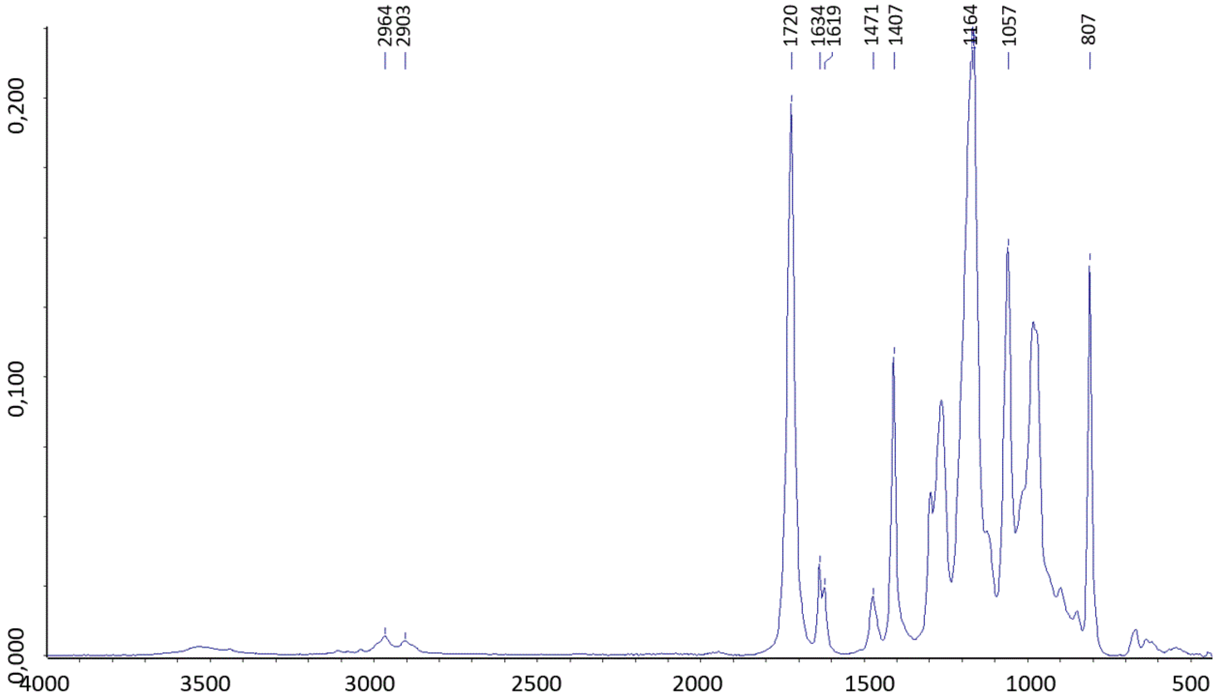


Figure 172: *FTIR spectra of pentaerythritol tetraacrylate (PT).*

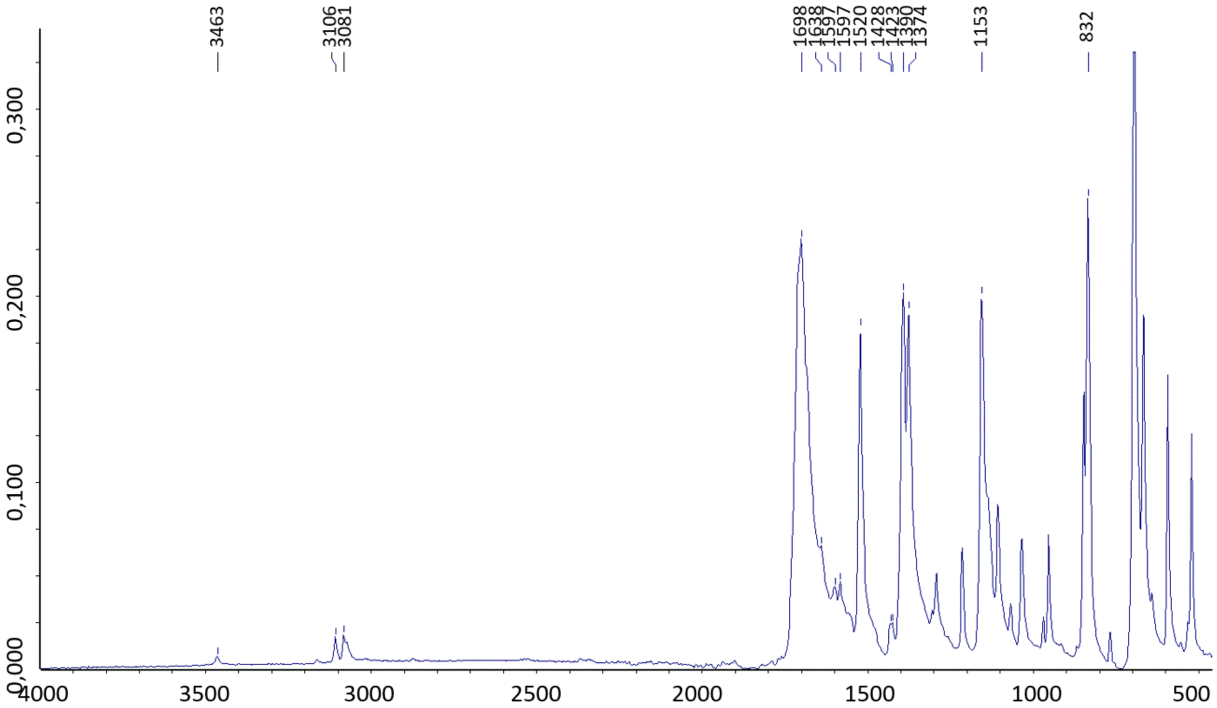


Figure 173: *FTIR spectra of N,N'-(1,4-phenylene)dimaleimide (pM).*

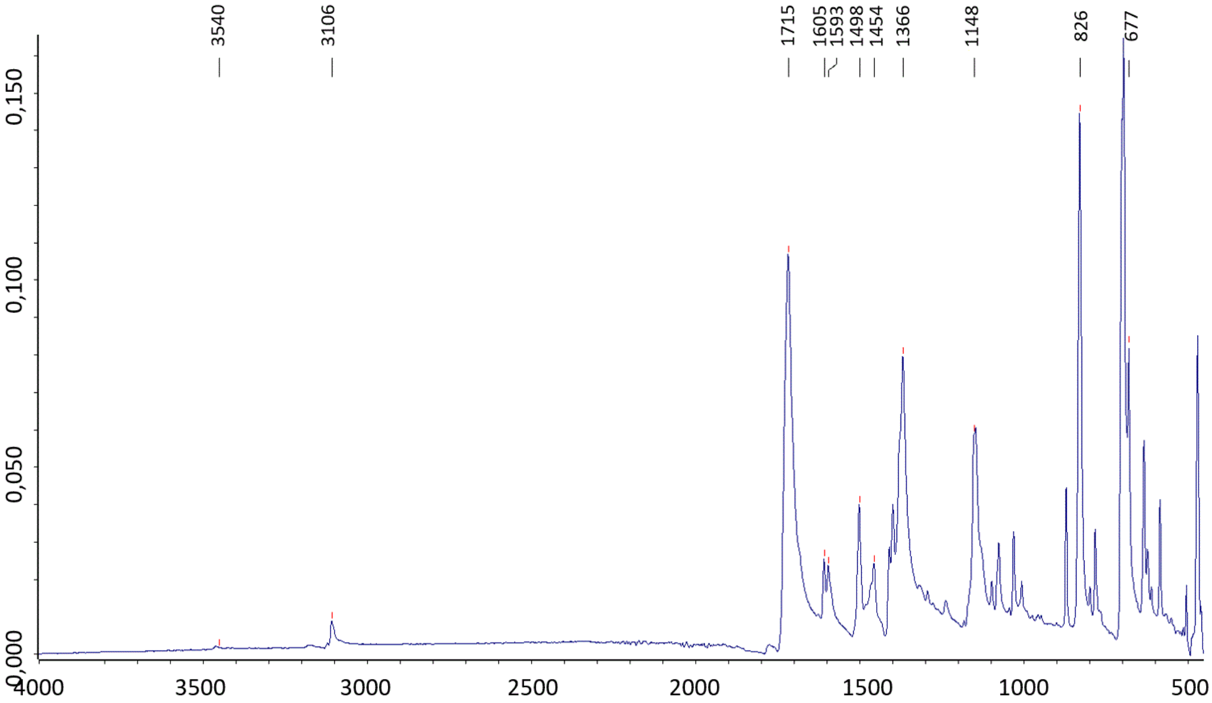


Figure 174: *FTIR spectra of N,N'-(1,3-phenylene)dimaleimide (mM).*

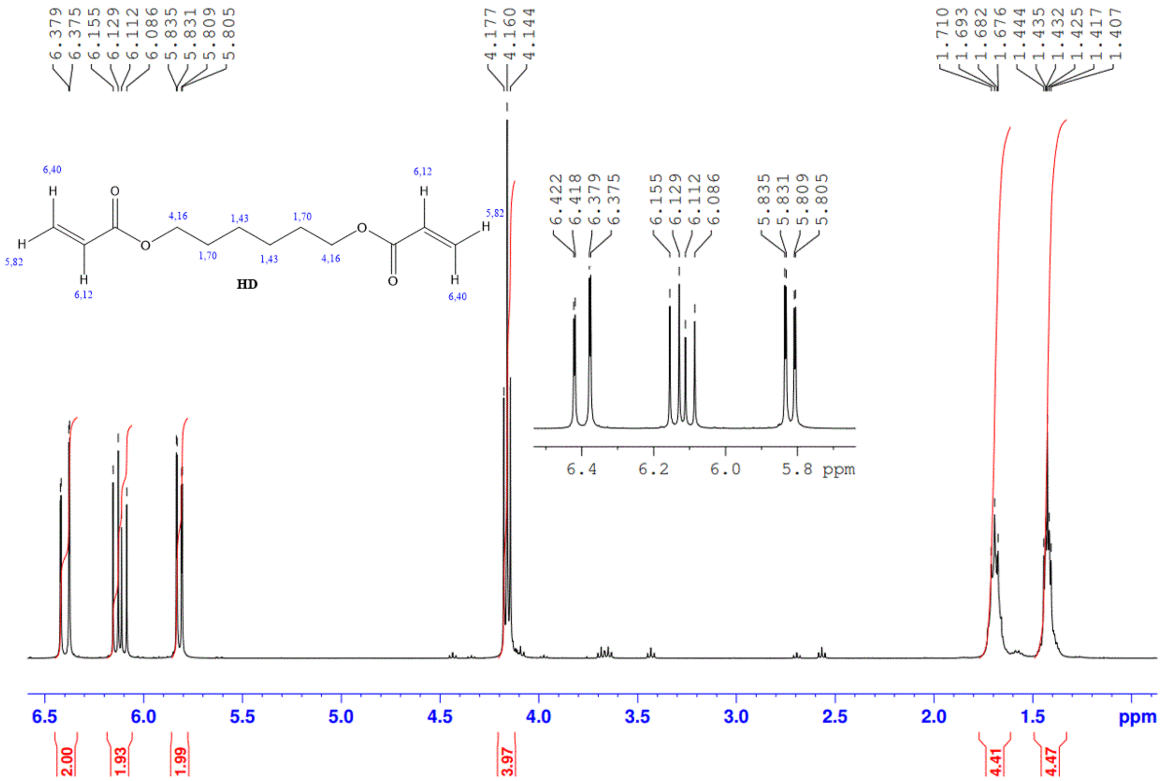


Figure 175: *^{1}H NMR spectra of 1,6-hexanediol diacrylate (HD).*

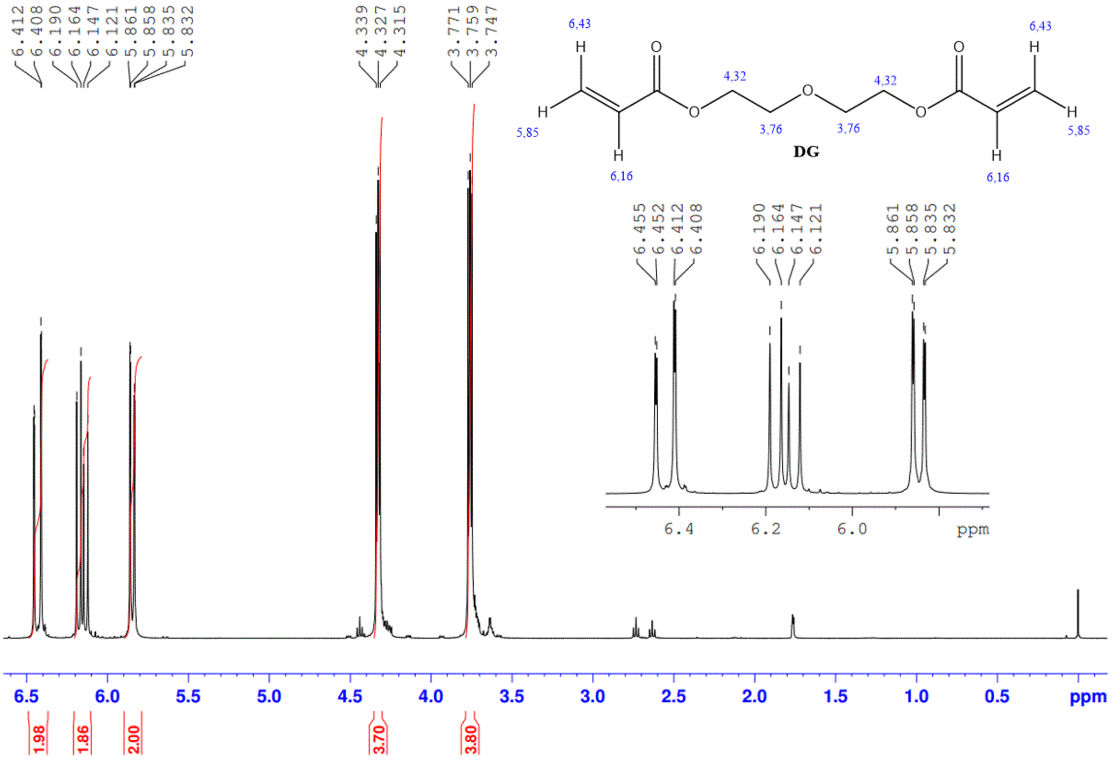


Figure 176: *^{1}H NMR spectra of di(ethylene glycol)diacrylate (DG).*

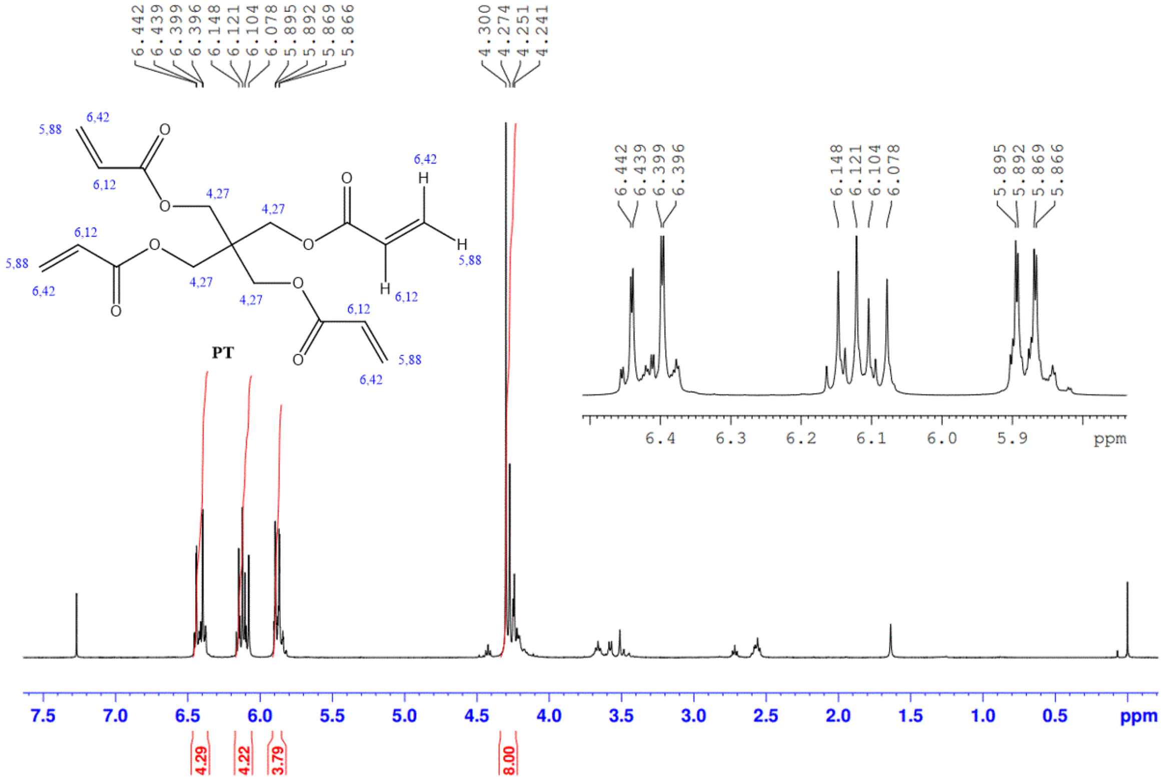


Figure 177: *^{1}H NMR spectra of pentaerythritol tetraacrylate (PT).*

B: Preliminary reactions

B.1.1 Preliminary emulsion reactions

The crosslinker was added to the alkyd post-emulsification in this set of experiments. Initially, different rations of emulsion and crosslinker HD were tested at different reaction times (

Table 19). Initially, the concentration was calculated based on the weight; however, in order to be comparable to the latter reactions, the concentration is also given based on the functionalities present.

Table 19: Emulsion and crosslinker amount in preliminary reactions. Concentration (c) in wt% and func% and total reaction time is given. The reactions were conducted at 80 °C unless otherwise noted.

	Emulsion		**Crosslinker**				
Exp.nr	**Weight (g)**	**Alkyd (mmol)**	**Weight (g)**	**Crosslinker (mmol)**	**c (func%)**	**c (wt%)**	**Reaction time (h)**
5	5.0168	1.0603	0.2483	HD (1.0974)	43.86	5	3
6	3.0292	0.6402	0.6034	HD (2.6667)	75.87	20	4
7	3.0025	0.6346	0.3154	HD (1.3939)	62.38	10	4
8	3.0051	0.6351	0.2093	HD (1.850)	52.37	7	5
9	3.0107	0.6363	0.3037	HD (1.3422)	61.42	10	8
10	3.0317	0.6407	0.4711	HD (2.0820)	71.04	15	4
11	2.9914	0.6322	0.1480	HD (0.6541)	1:0.78	5	4
12-13	Pure emulsion. Reaction time varied						
14*	3.0262	0.6396	0.4540	HD (2.0065)	70.31	15	72
15	5.0401	1.0652	0.0976	HD (0.4313)	23.41	2	23

16	4.0042	0.8463	0.1405	HD (0.6209)	35.64	3.5	12

	Emulsion			**Crosslinker**			
Exp.nr	**Weight (g)**	**Alkyd (mmol)**	**Weight (g)**	**Crosslinker (mmol)**	**c (func%)**	**c (wt%)**	**Reaction time (h)**
18	30.0221	6.3450	0.3082	HD (1.3621)	13.94	1	23
19	19.9850	4.2237	0.4000	HD (1.7678)	24.01	2	47
20	9.9895	2.1112	0.2076	HD (0.9175)	24.70	2	65
22	1.0199	0.2155	0.0204	HD (0.0902)	24.00	2	6
23**	2.0180	0.4265	0.0404	HD (0.1784)	23.99	2	52
24	10.0106	2.1157	0.2105	DG (0.9827)	25.96	2	46

*reaction was run at room temperature (RT)
**reaction was run in a hermetically sealed tube

The reactions mixtures were monitored with FTIR which showed a reduction in intensity for peaks at 3377 and 1635 cm^{-1}, regardless of the concentration of crosslinker (representative spectra in **Figure 178a**). Similar trends were observed when the reaction mixtures were stirred at room temperature (RT), although on a longer time scale compared to heating at 80 °C (representative spectra in **Figure 178b**) and for the pure emulsion (**Figure 178c**). The peaks at ~3380 and ~1635 cm^{-1} are attributed to the OH stretches and OH bends, respectively, originating from water present in the reaction mixture.[52]

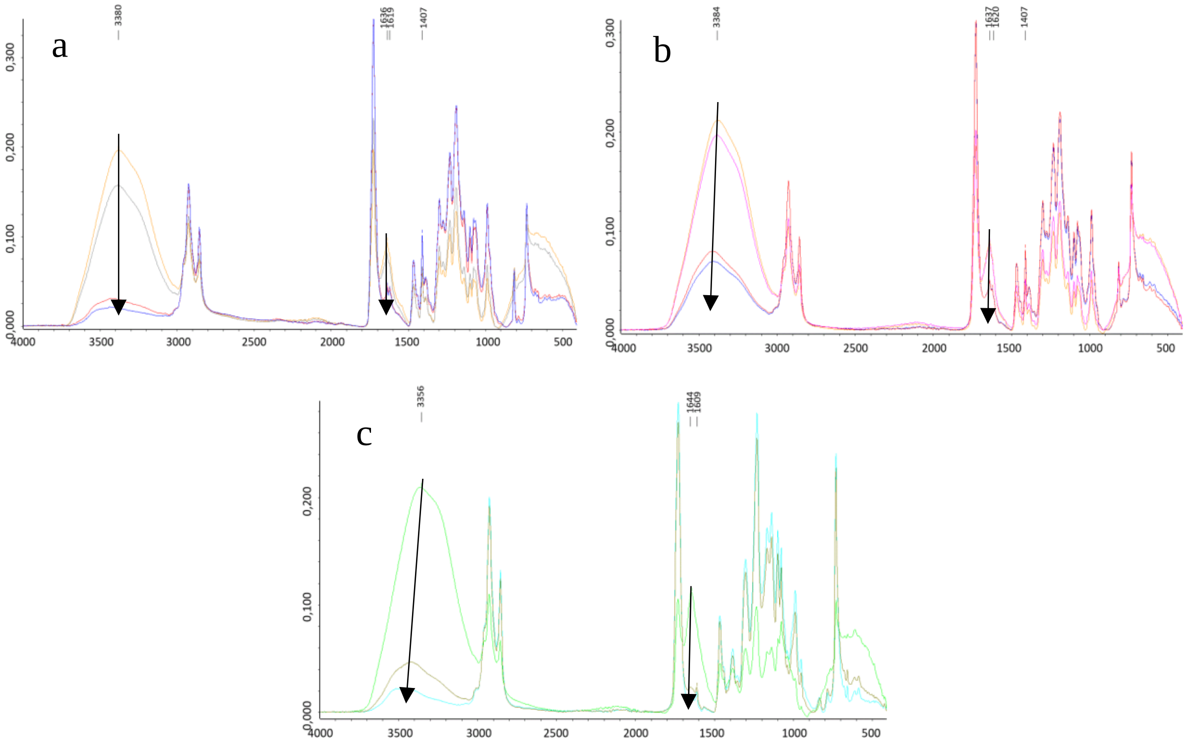


Figure 178: *FTIR spectra of* ***a)*** *emulsion with 20wt% 1,6-hexanediol diacrylate (HD) heated at 80 °C for t=0h, 0.5h, 2h and 2.5h,* ***b)*** *emulsion with 15wt% HD at room temperature (RT) for t=0h, 7h, 24h and 46h and* ***c)*** *emulsion heated at 80 °C for t=0h, 1.5h and 3h.*

Visual observations were also conducted for the reaction mixtures as this provides facile monitoring during polymerization reactions. Since the real-time GPC monitoring of the reaction is not available, visual confirmation of gel formation would yield important info in the reaction progress/termination. The mixtures changed from white to transparent, and, in some cases, gelation was observed. However, when the batch size was scaled up from 3-5 g to 20-30 g, the visual changes (**Table 20**) and changes in FTIR occurred after significantly larger reaction times (**Figure 179a** and **b**). It was assumed that all the initial observations were caused by the evaporation of water which was linked to the batch size. This is linked to the batch size and occurred more rapidly as the batch size was reduced, demonstrated by conducting several (Exp.nr 19, 20 and 22, **Table 19**) experiments in which all conditions were the same apart from the batch size. Having observed this, we opted to conduct the reaction in a hermetically sealed vial to prevent evaporation of water. Although some water appeared to have evaporated (**Figure 179c**) and some gel was formed around the magnet (**Table 20**), this happened to a much smaller extent than for the open systems. Another crosslinker (DG) was also employed under the same conditions to further confirm that the changes observed in FTIR were indeed not caused by reactions including the crosslinker (**Figure 179d**).

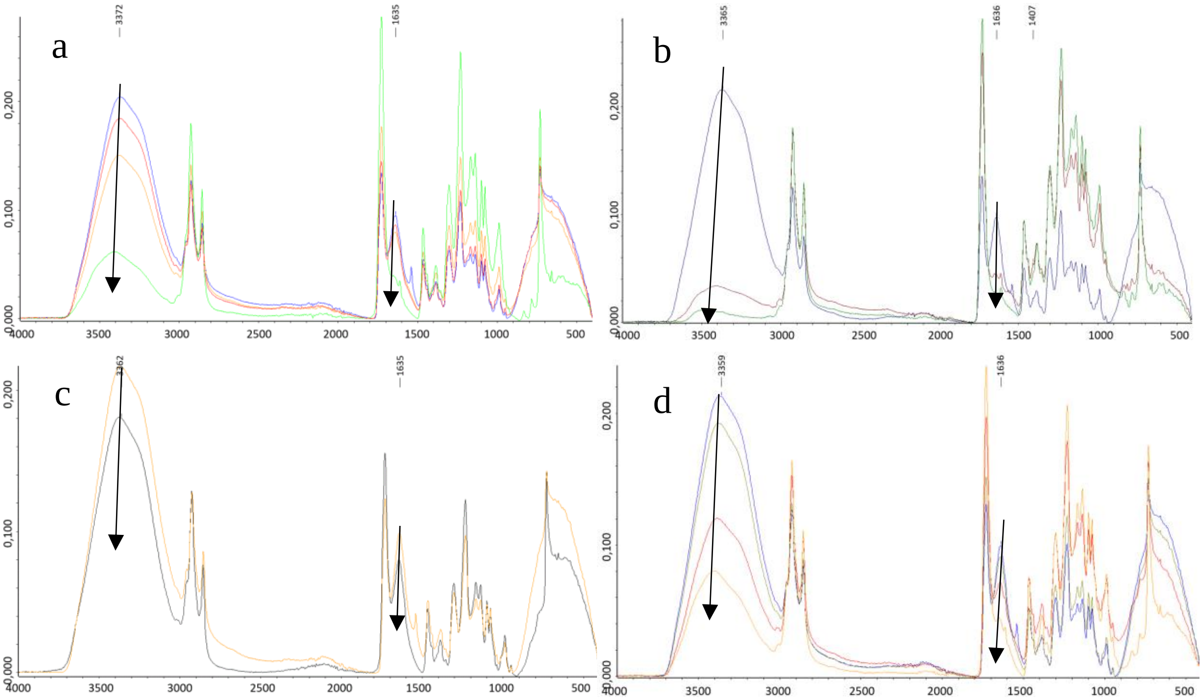


Figure 179: *FTIR spectra of emulsion with 2wt%* ***a)*** *1,6-hexanediol diacrylate (HD) heated at 80 °C for t=0h, 6h, 24h and 47h, using a larger batch size,* ***b)*** *HD heated at 80 °C for t=0h, 40 min and 6h, using a smaller batch size,* ***c)*** *HD heated at 80 °C in a hermetically sealed vial for t=0h and 52h and* ***d)*** *di(ethylene glycol)diacrylate (DG) heated at 80 °C for t=0h, 6h, 24h and 46h.*

Table 20: *Reaction time required to obtain a gel for varying batch sizes. The reaction mixtures contained 2wt% 1,6-hexanediol diacrylate (HD) and were heated at 80 °C.*

Reaction time	**1 g**	**5 g**	**10 g**	**20 g**	**2 g***
6h	Gel				
24h		Gel			
2d			Gel	Gel on magnet/ corners of vial	Gel on magnet

*reaction conducted in a hermetically sealed vial

B.1.2 1 and 2wt% 1,6-hexanediol diacrylate (HD)

Larger batches of reaction mixtures with 1 and 2wt% HD were prepared (Exp 18 and 19, **Table 19**) for further analysis. FTIR and the visual characteristics of the samples provided very basic and limited information about the crosslinking reactions. In order to further elucidate the reactions, ^{1}H NMR was employed as a characterization method that would provide quantitative as well as qualitative results on our samples. Initially, ^{1}H NMR was employed for some of the samples to track the water content after drying, but it can also be used to track the reaction progress through the peaks signal from the crosslinker, once a suitable peak is identified to normalize the spectra (**Figure 180**). For the reaction mixture of emulsion with 1wt% HD, a decrease in the vinylic peaks are observed after heating at 80 °C for t=24h compared to t=20 min.

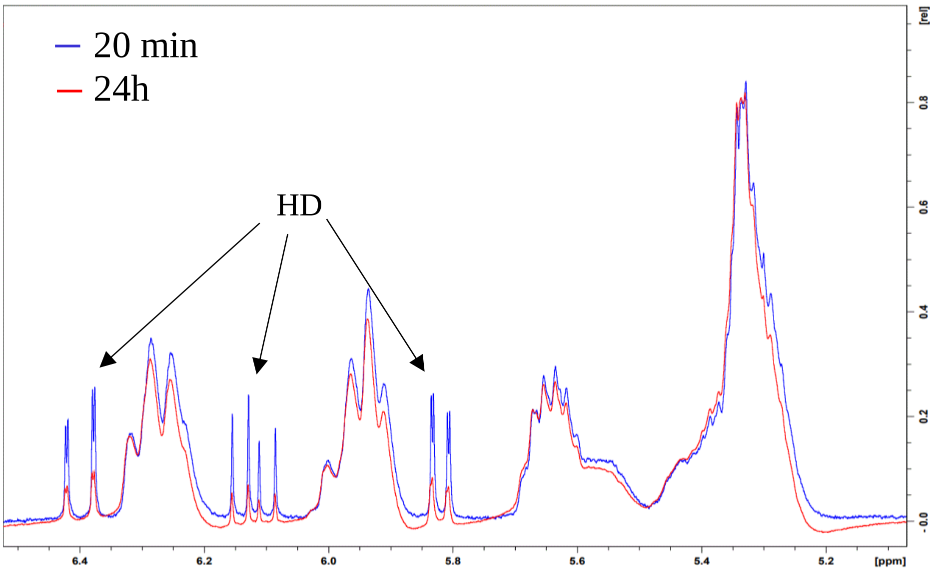


Figure 180: ^{1}H NMR spectra of emulsion with 1wt% 1,6-hexanediol diacrylate (HD) after heating at 80 °C for t=20 min (blue spectra) and 24h (red spectra). Peak at 8.61 ppm was used to normalize the spectra intensities.

GPC was also employed for all samples as a method which would indicate a successful polymerization reaction (**Figure 181**), using the conventional method. For both concentrations, the M_w was slightly increased compared to the initial emulsion. The molecular weight increased proportionally to the reaction time increased, although no large differences were observed, as may be expected for such a diverse mixture of compounds. The largest molecular weight was observed for the 1wt% HD mixture after heating at 80 °C for t=70 min, after which a slight decrease in molecular weight was observed. The molecular weight obtained for the 2wt% reaction mixture at t=8h was lower compared to the 1wt% HD mixture at t=70 min and 5h. It should be noted that GPC characterization is dependent on complete solubility and filtration of samples before measurement to protect the chromatography column. Given the crosslinking nature of the reaction, it may be hypothesized that only the lower molecular weight fractions were soluble and measured while the higher molecular weight fractions were filtered out. Some of the samples did not dissolve in THF, including 1wt% HD at t=23h and 2wt% HD at t=47h, and were therefore not measured. A more appropriate approach to SEC-GPC would be a DLS-capable instrumentation which was not available to us. It is worth noting, however, that GPC would provide definite information of the crosslinking reaction progress even though the actual molecular weight values obtained would be severely undercalculated.

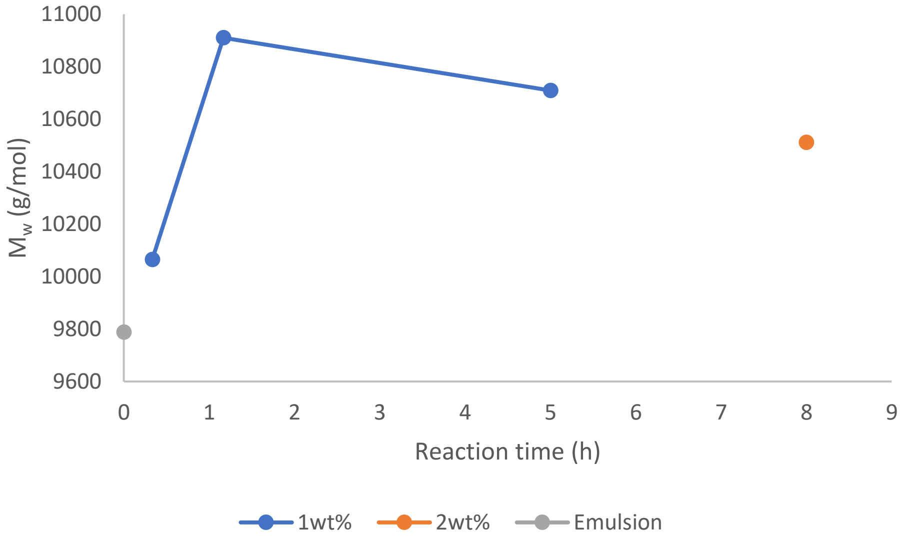


Figure 181: *Weight average molecular weight (M_w) of emulsion and emulsion with 1 or 2wt% 1,6-hexanediol diacrylate (HD) heated to 80 °C for t=20 min, 70 min and 5h and t=8h, respectively.*

Prior to the GPC measurements, the water was removed from the reaction mixtures. This involved exposing the reaction mixtures to oxygen from the atmosphere which might result in the reaction mixtures undergoing the autoxidation reaction. The reaction mixtures were dried under the same conditions regarding time and temperature which is expected to result in similar extents of autoxidation for all samples. This might not be the case as fewer unsaturated bond are expected to be present in the alkyd after a successful crosslinking reaction.

B.1.3 3.4.3 1, 3 and 5wt% 1,6-hexanediol diacrylate (HD)

To get a direct comparison between the effect of the concentration and reaction time, batches of different concentrations were prepared and samples were analyzed at the same reaction times (**Table 21**). Based on the increased molecular weight in the previous set of experiments, t=20, 70 and 150 min were chosen. Three concentrations of HD were tested, 1wt%, 3wt% and 5wt%.

Table 21: *Amount of emulsion and concentration (c) of crosslinker 1,6-hexanediol diacrylate (HD).*

	Emulsion		**Crosslinker HD**				
Exp.nr	**Weight (g)**	**Alkyd (mmol)**	**Weight (g)**	**HD (mmol)**	**c (func%)**	**c (wt%)**	**Reaction time (min)**
25	59.986	12.678	0.601	2.656	13.65	1	70
26	59.989	12.678	1.806	7.982	32.21	3	70
27	60.03	12.69	3.000	13.259	44.10	5	70
28	60.02	12.69	0.607	2.683	13.77	1	20
29	59.975	12.675	1.806	7.982	32.22	3	20
30	60.01	12.68	2.994	13.232	44.06	5	20
31	60.08	12.70	0.604	2.669	13.70	1	150
32	60.04	12.69	1.801	7.960	32.13	3	150
33	60.03	12.69	3.001	13.263	44.11	5	150

All the reaction mixtures were analyzed with FTIR prior to (**Figure 182a**) and after (**Figure 182b**) water had been removed. The resulting FTIR spectra are shown for the 5wt% HD mixture after t=150. This mixture contains the maximum values regarding concentration and reaction time and therefore, the largest differences are expected to be visible although the trends are expected to be apparent for the lower concentrations as well. While the peak at 1636 cm^{-1} overlaps with the signal from residual water, the spectra indicate that reaction might be possible to monitor through the peak at 1407 cm^{-1}. However, the baseline of the spectra is significantly affected by trace amounts of water, complication the reliable interpretation of the peak at 1407 cm^{-1}.

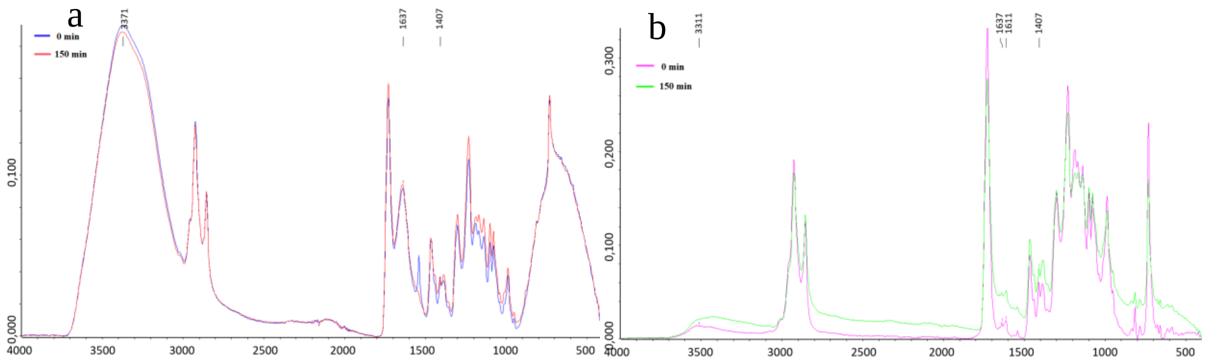


Figure 182: *FTIR spectra of emulsion with 5wt% 1,6-hexanediol diacrylate (HD) after heating at 80 °C for t=0h and 150 min,* ***a)*** *prior to removal of water and* ***b)*** *after removal of water.*

The FTIR spectra of the reaction mixture containing 5wt% were compared after heating for t=20 min, 70 min and 150 min (**Figure 183**) after the removal of water. No significant changes were observed in the FTIR spectra at 1636 or 1407 cm^{-1} which could indicate that the reaction times chosen are too close to one another.

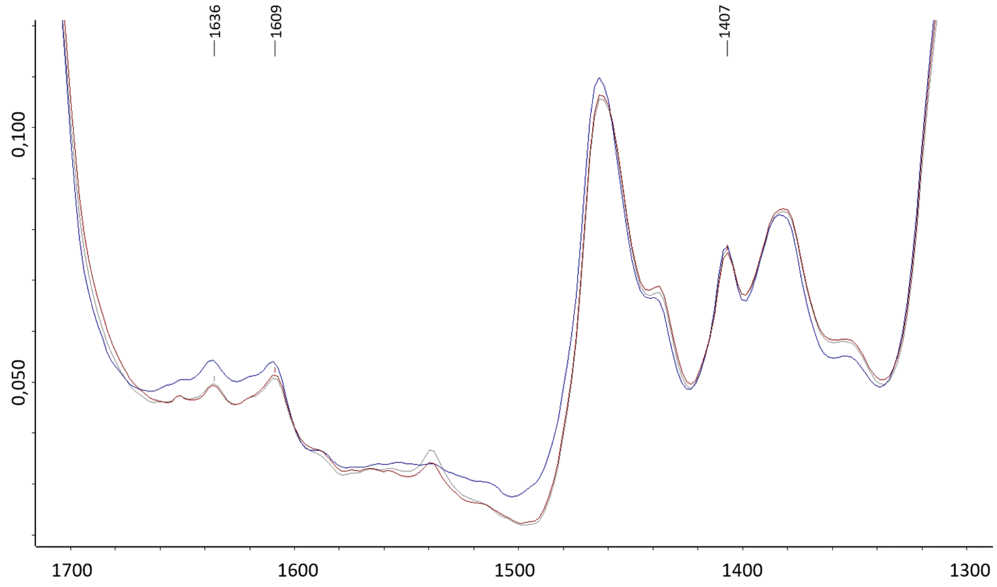


Figure 183: *FTIR spectra of emulsion and 5wt% 16-hexanediol diacrylate (HD) after heating at 80 °C for t=20 min, 70 min and 150 min.*

^{1}H NMR was measured for the samples with different concentrations of HD at t=70 min (**Figure 184**). The spectra show the presence of unreacted crosslinker in all samples, suggesting that the reaction should be run for a longer period or that the concentration should be lowered if the reaction should proceed until completion.

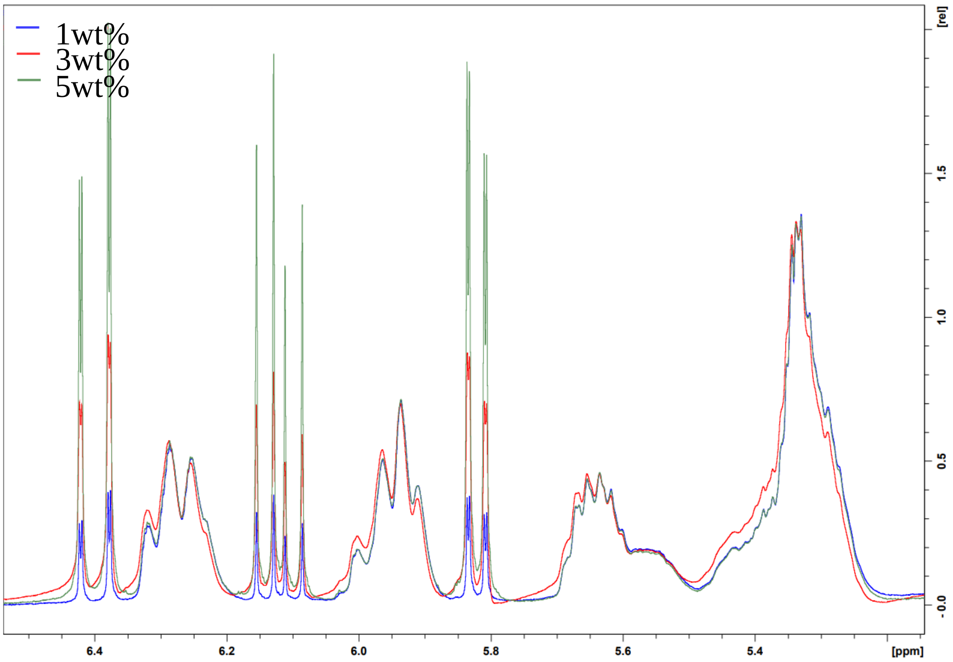


Figure 184: ^{1}H NMR spectra of emulsion with 1 (blue spectra), 3 (red spectra) and 5wt% (green spectra) 1,6-hexanediol diacrylate (HD) after heating at 80 °C for t=70 min. The integrals were normalized for peak at 8.61 ppm.

For the GPC measurements, conducted at Jotun AS, the conventional and absolute method were applied. The pure emulsion was used as a reference, however, without being exposed to heating at 80 °C like the crosslinker samples. Therefore, the following differences between the pure emulsion and emulsions with crosslinker could be caused by either the addition of crosslinker, heating or a combination of both. The results are presented in **Figure 185**, **Figure 186** and **Figure 187** where the M_w is lower for the reaction mixtures containing crosslinker compared the pure emulsion (**Figure 186**) while the M_z shows contradicting results for the two methods. For the conventional method, the M_z of all samples are lower or similar to the pure emulsion (**Figure 187a**). This could indicate that a competing reaction such as hydrolysis of the ester bond is occurring when the emulsion is subjected to heat. The decrease in the M_z for the mixtures with crosslinker could also be due to loss of solubility as high molecular weight polymers are formed. However, this is not observed in the absolute method, where the M_z in all reaction mixtures containing crosslinker are larger compared to the pure emulsion (**Figure 187b**). Unlike the conventional method, the absolute method clearly demonstrates that the addition of crosslinker and/or heat has a positive effect on the formation of high molecular weight polymers. However, due to the contradicting results for the two methods, there is no clear indication that the initial molecular weight is increased by the addition of crosslinker nor heating.

The molecular weight obtained at constant reaction times t=20, 70 or 150 min were compared to provide information of the impact of the crosslinker concentration. The M_n is inversely proportional to the concentration (**Figure 185**) which could reflect larger amounts of residual crosslinker present in the samples which initially contained higher concentrations. The same trend is evident for the M_w for most of the reaction mixtures (**Figure 186**) which might imply that there might be other factors affecting the molecular weight. This could be due to loss of solubility, resulting in the higher molecular weight polymers being filtered out or competing reactions such as hydrolysis. The conventional method (**Figure 187a**) indicates that the M_z is inversely proportional to the crosslinker concentrations at t=20 min while it is generally proportional to the concentration for longer reaction times. In order for the molecular weight to increase *via* crosslinking, the two functional groups in the crosslinker must first react. It may be hypothesized that only one of the functional groups are reacting initially, making hydrolysis the dominant reaction to affect the molecular weight. This could be due to the restriction of the relative movement of the crosslinker as one of the functional groups have reacted. However, if both functional groups react, this might counteract the molecular weight decrease caused by a competing reaction such as hydrolysis. The absolute method (**Figure 187b**) further demonstrates that the M_z is proportional to the crosslinker concentration, especially at t≥70 min. This indicates that the crosslinking density is increased by increasing the concentration, although t>20 min should be applied.

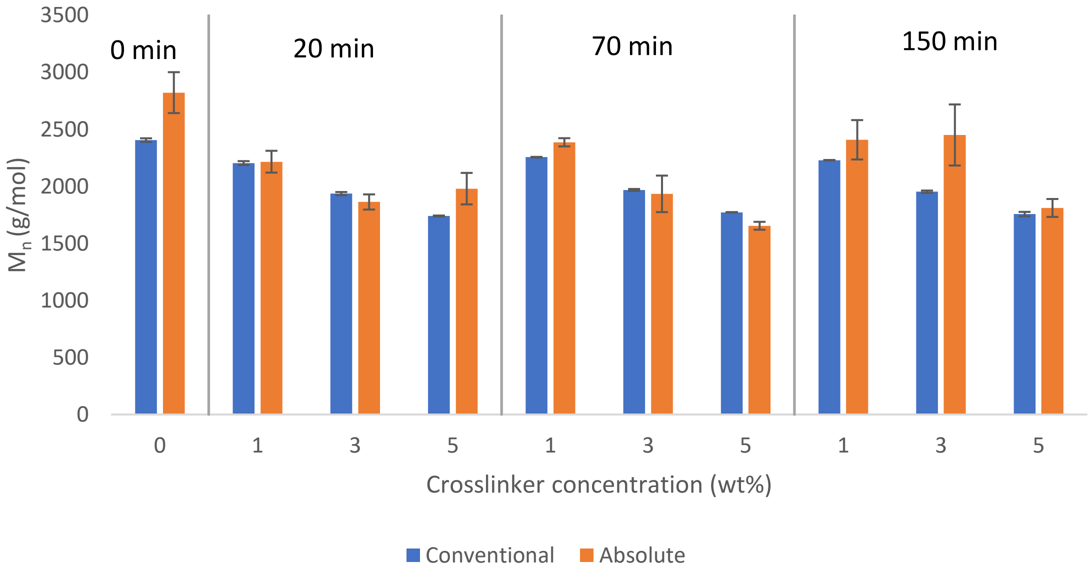


Figure 185: *Number average molecular weight (M_n) of emulsion and emulsion with 1, 3 or 5wt% 1,6-hexanediol diacrylate (HD) after heating at 80 °C for t=20 min, 70 min and 150 min using the conventional or absolute method.*

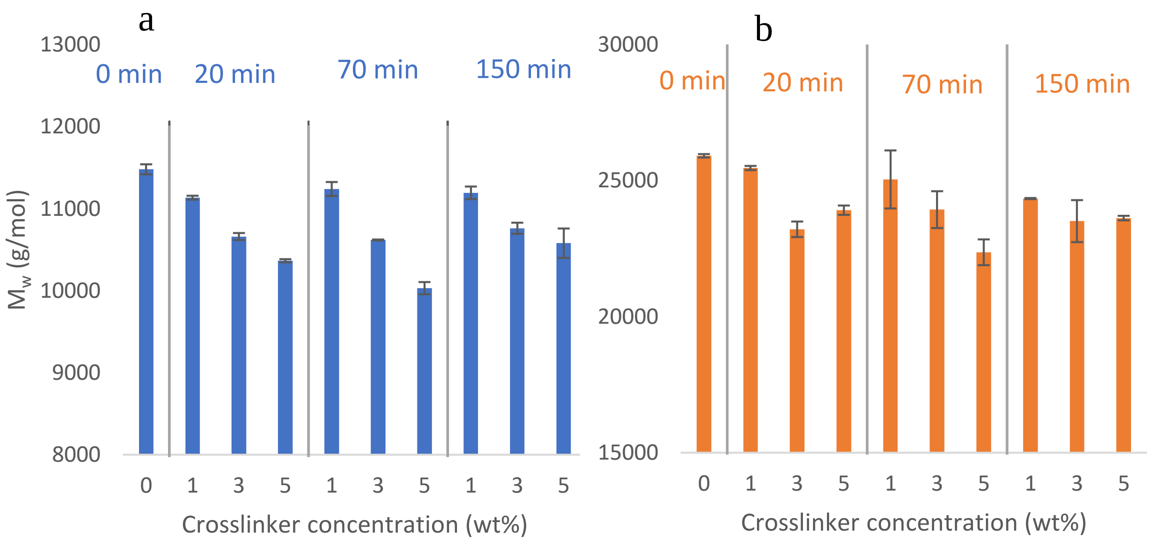


Figure 186: *Weight average molecular weight (M_w) of emulsion and emulsion with 1, 3 or 5wt% 1,6-hexanediol diacrylate (HD) after heating at 80 °C for t=20 min, 70 min and 150 min using the **a)** conventional and **b)** absolute method.*

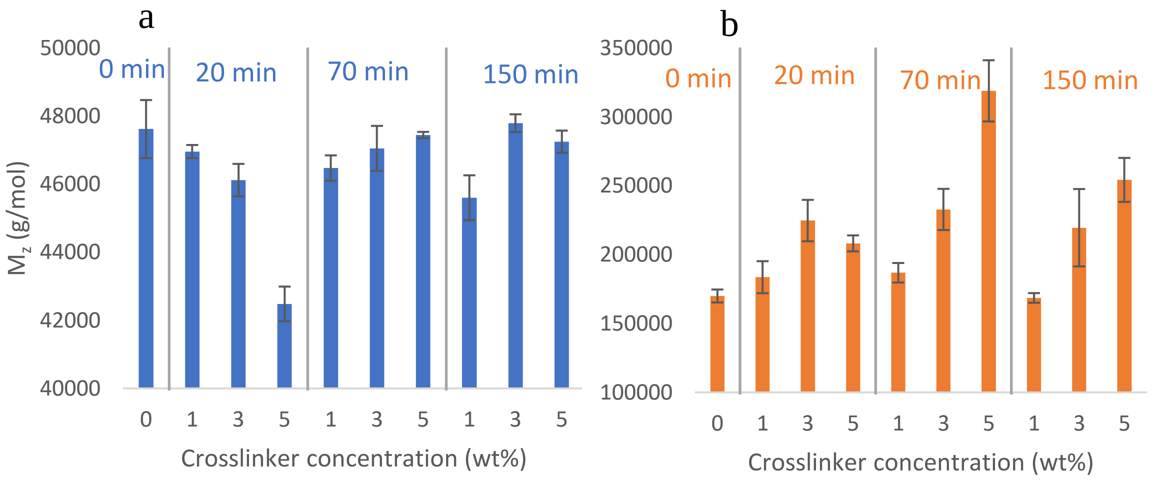


Figure 187: *Z-average molecular weight (M_z) of emulsion and emulsion with 1, 3 or 5wt% 1,6-hexanediol diacrylate (HD) after heating at 80 °C for t=20 min, 70 min and 150 min using the **a)** conventional and **b)** absolute method.*

The molecular weight at a constant crosslinker concentration was also compared to provide information about the impact of the reaction time. The M_n is generally proportional to the reaction time which could indicate successful incorporation of the crosslinker (**Figure 188**). This is evident in the 1 and 3wt% reaction mixtures but less pronounced for the 5wt% mixture which could be due to a larger amount of residual crosslinker in the higher concentration. Incoherent trends are observed between the reaction time and the M_w and M_z (**Figure 189** and **Figure 190**), making it difficult to establishing clear correlations. This might suggest that competing reactions are occurring simultaneously and the concentration appears to have an effect. For the reaction mixture with 1wt% HD, the M_z is inversely proportional to the reaction time. This could be due to the crosslinker concentration being too low to counteract competing reactions such as hydrolysis. For the 3wt% HD reaction mixture, the conventional method shows increases in both the M_w and M_z while no clear correlation can be observed with the absolute method. The M_w and M_z are generally proportional to the reaction time for the 5wt% reaction mixture. However, both methods show that the M_z obtained at t=70 min is similar or increased compared to t=150 min. This could indicate that the crosslinker has reacted fully within t=70 min, however, this contradicts the observations in the M_n. The observed trend could be a result of different rates for the crosslinking and hydrolysis reaction. The lack of coherence for the reaction mixture might also be due to the reaction times being too short.

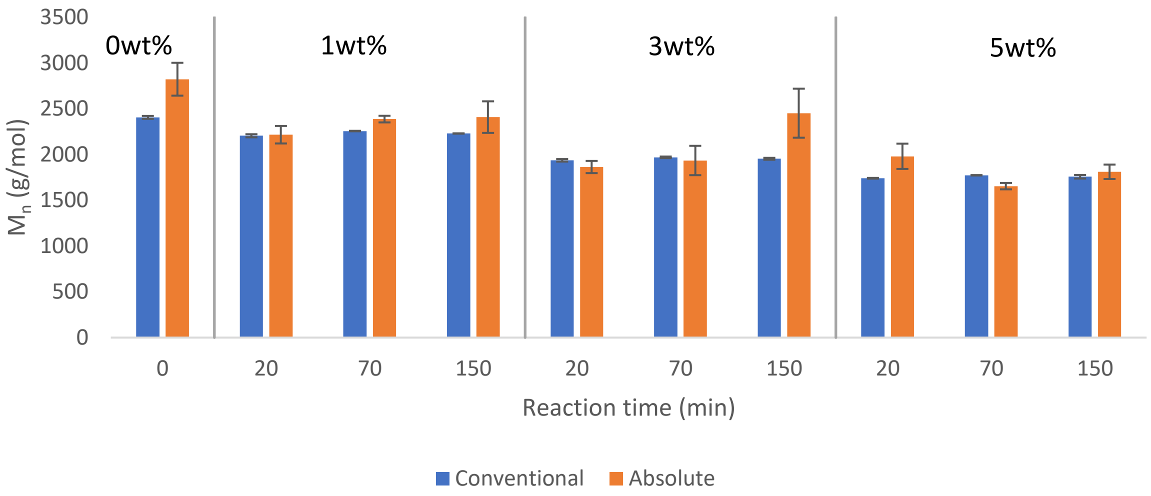


Figure 188: *Number average molecular weight (M_n) of emulsion and emulsion with 1, 3 and 5wt% 1,6-hexanediol diacrylate (HD) after heating at 80 °C for t=20 min, 70 min and 150 min using the conventional or absolute method.*

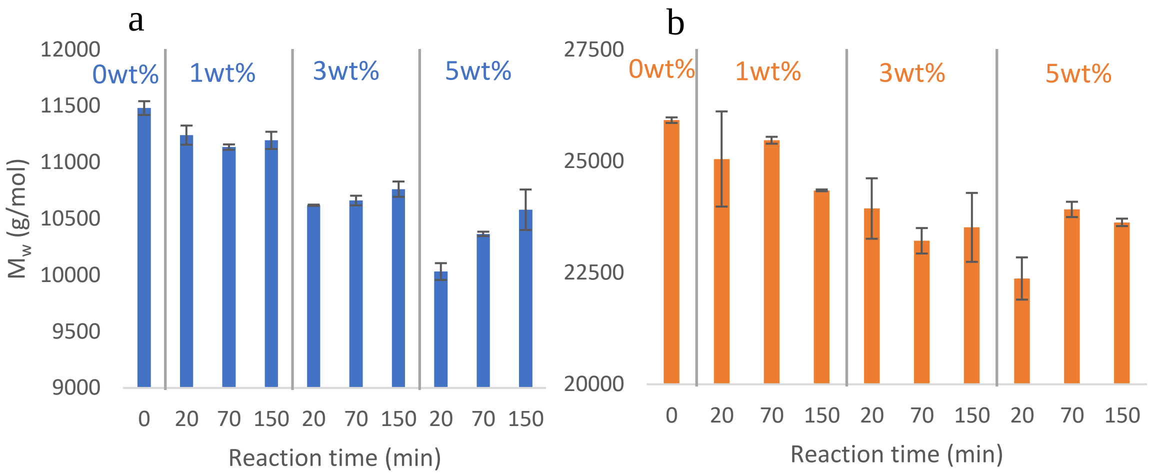


Figure 189: *Weight average molecular weight (M_w) of emulsion and emulsion with 1, 3 or 5wt% 1,6-hexanediol diacrylate (HD) after heating at 80 °C for t=20 min, 70 min and 150 min using the* ***a)*** *conventional and* ***b)*** *absolute method.*

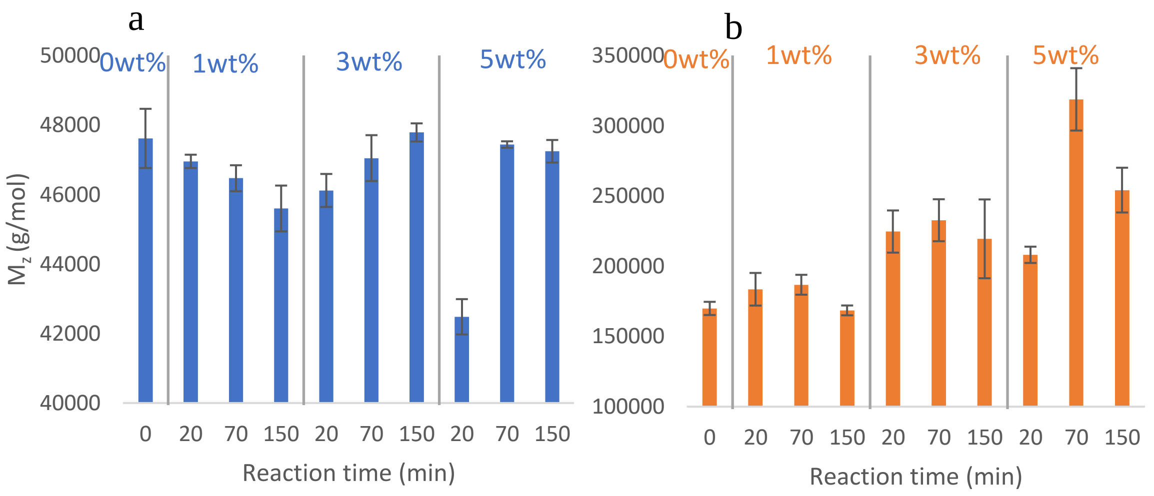


Figure 190: *Z-average molecular weight (M_z) of emulsion and emulsion with 1, 3 or 5wt% 1,6-hexanediol diacrylate (HD) after heating at 80 °C for t=20 min, 70 min and 150 min using the* ***a)*** *conventional and* ***b)*** *absolute method.*

Moving on to a link between reactions and practical applications, the reaction mixtures were incorporated into paint formulations, and the properties of the resulting thin films were measured, including the pendulum hardness. The pendulum hardness is proportional to the crosslinker concentration, resulting in the hardest film formed for the reaction mixture containing 5wt% HD, regardless of reaction time (**Figure 191-Figure 193**). The increase in hardness could be due to increased molecular weight, proving the crosslinking reaction successful. The increase in hardness might also be due to the addition of unsaturated acrylate species which can contribute to the autoxidation reaction. [4, 12, 20] There is no clear correlation between the reaction time and hardness which could indicate that the reaction times were too close to one another. It could also be due to the reaction progressing (most likely at a lower reaction rate) at RT, as the reaction mixtures were stored prior to making the paint formulations.

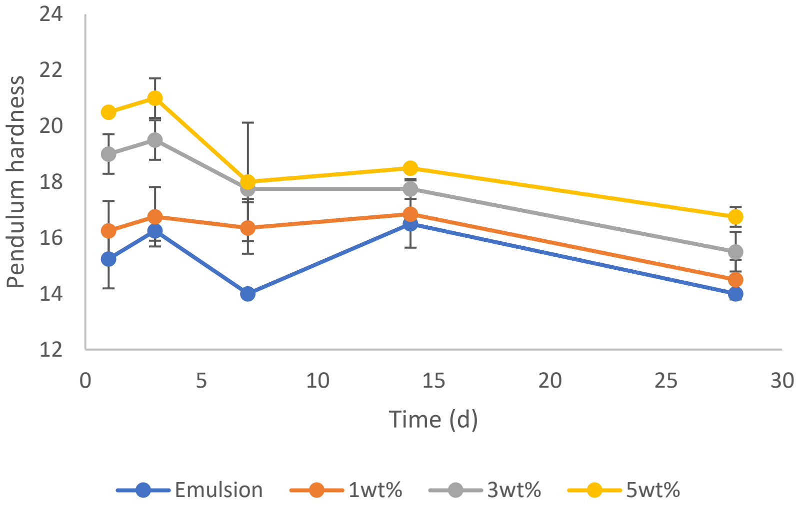


Figure 191: *Pendulum hardness for emulsion and emulsion with 1, 3 or 5wt% 1,6-hexanediol diacrylate (HD) after heating at 80 °C for t=20 min.*

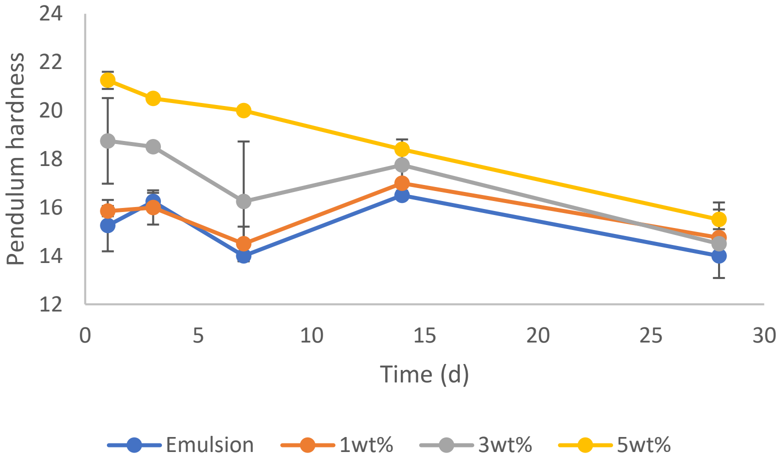


Figure 192: *Pendulum hardness for emulsion and emulsion with 1, 3 or 5wt% 1,6-hexanediol diacrylate (HD) after heating at 80 °C for t=70 min.*

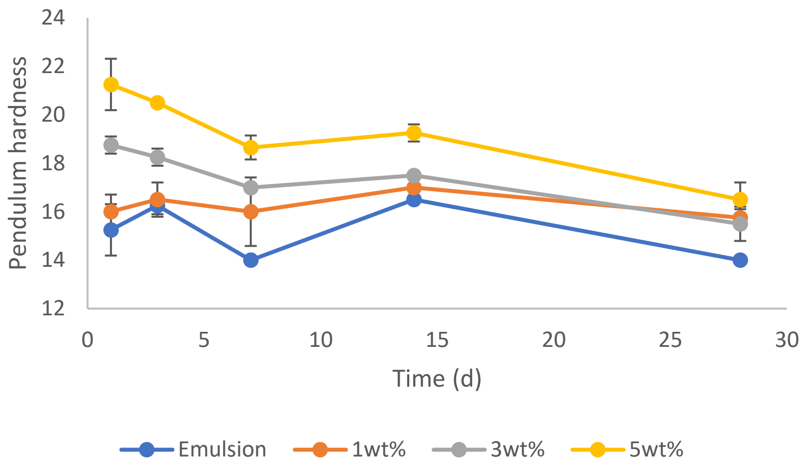


Figure 193: *Pendulum hardness for emulsion and emulsion with 1, 3 or 5wt% 1,6-hexanediol diacrylate (HD) after heating at 80 °C for t=150 min.*

The glass transition temperature (T_g) was measured for the thin films after curing for t>1 month (**Figure 194**). All samples containing crosslinker, regardless of reaction time, show a slightly increased T_g compared to the pure emulsion. For the reaction mixtures heated for t=20 min and 70 min, the T_g increases with increasing crosslinker concentration (**Figure 194a**) while the opposite is observed for t=150 min. Generally, the differences in the T_g for the different reaction mixtures are quite small and could explain the lack of coherency in the results.

The general trend shows that the T_g is inversely proportional to the reaction time (**Figure 194b**). This is counter intuitive to our expectations because the crosslinking density is expected to increase proportionally to the reaction time, resulting in an increase in the T_g. As was the case with the pendulum hardness measurements, these observations could be due to the reaction time being too short to provide adequate differences, although an increase in molecular weight was indicated by the GPC measurements.

The T_g measurements were carried out after the autoxidation reaction had occurred. The autoxidation reaction involves crosslinking between the polymer chains and increases the molecular weight which could “mask” the effect of the crosslinking reaction. This could explain the small differences in the T_g between the reaction mixtures. The T_g measurements were therefore also carried out for the emulsion after removal of water but prior to the autoxidation process. However, the resulting spectra were complex, showing several slopes/curves, making it very difficult to establish the true T_g. The behavior could be due to the presence of solvents (water, xylene) which could alter the T_g significantly. Although the samples were dried using a desiccator and vacuum for long periods prior to the measurement, water can remain trapped inside the polymer matrix. Thin films were formed on top of some of the samples during the drying process, most likely due to the autoxidation process with the environment. This could further limit the removal of water from the samples. Further drying was limited, as the reaction mixture might react with oxygen by exposing them to the atmosphere or further crosslink if heat was introduced. This would disguise the effect of the crosslinker. The lowest temperature scan range was -80 °C, and the T_g would therefore not be visible if it lies below this temperature. Unreacted, residual crosslinker could also alter the spectra.

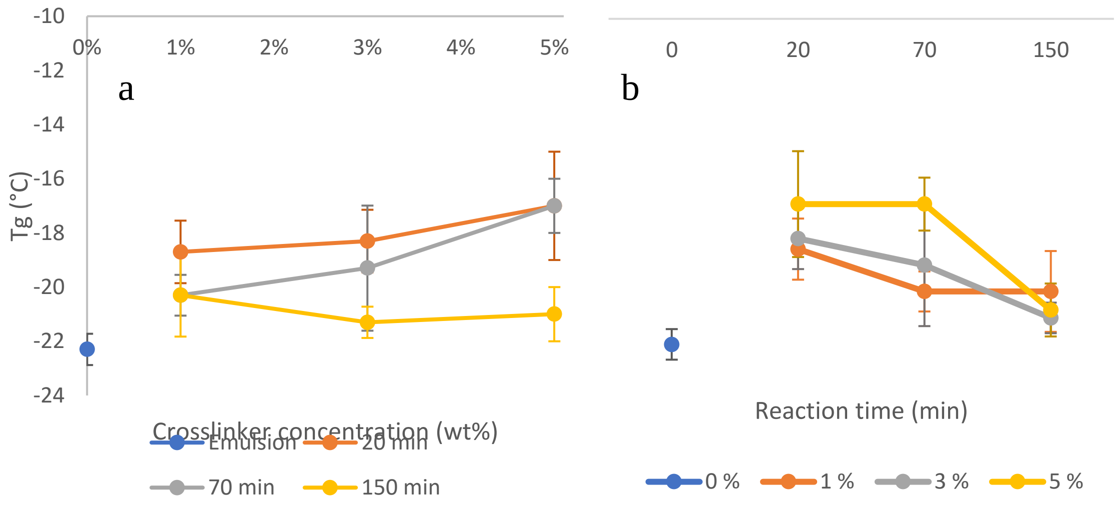


Figure 194: *T_gs for emulsion and emulsion with 1, 3 or 5wt% 1,6-hexanediol diacrylate (HD) heated at 80 °C for t=20 min, 70 min or 150 min.*

The results from the different methods are summarized in **Table 22**. As previously discussed, the reaction mixtures were compared to the pure emulsion which had not been subjected to heating. Therefore, the observations might be caused by the introduction of crosslinker, heat or a combination of both. Very few of the methods provided definite answers concerning the crosslinker concentration or reaction time. This could, as mentioned previously, be due to competing reactions or the reaction times being too short. It should be noted that the increase in molecular weight is mainly based on the observations in the M_z as this is expected to reflect the high molecular weight polymers and the effect of residual crosslinker should be diminished.

Table 22: Effect of adding crosslinker and subjecting the mixture to heating at 80 °C, increasing reaction time and crosslinker concentration, based on experiments with emulsion containing 1, 3 or 5wt% 1,6-hexanediol diacrylate (HD) after heating at 80 °C for t=20 min, 70 min and 150 min.

	Adding crosslinker/heat	Increasing reaction time	Increasing crosslinker concentration
FTIR	Inconclusive	Inconclusive	Inconclusive
Molecular weight*	Inconclusive	↑**	↑***
Pendulum hardness	↑	Inconclusive	↑
DSC	↑	↓	Inconclusive

*analyzed at Jotun AS, including the absolute and conventional method
**except for the 1wt% reaction mixtures
***except for the t=20 min reaction mixtures

B.1.4 1 and 3wt% N,N'-(1,4-phenylene)dimaleimide (pM)

The same conditions were applied to a system using a different crosslinker, pM (**Table 23**). Using the guidelines from the previous experiments, the longest reaction time (150 min) and highest concentration (5wt%) were discontinued, due to the small differences. However, the crosslinker's solubility in the emulsion proved somewhat challenging. As the use of different solvents, is not intended for industrial use by Jotun AS, in order to bypass this problem and create smooth films, the larger solid particles were removed from the mixture. This could potentially lead to a decrease in accuracy with regard to the GPC results, as the amount of crosslinker present might vary between each sample.

Table 23: Amount of emulsion and concentration (c) of crosslinker N,N'-(1,4-phenylene)dimaleimide (pM) and reaction time.

	Emulsion		Crosslinker pM				
Exp.nr	**Weight (g)**	**Alkyd (mmol)**	**Weight (g)**	**pM (mmol)**	**c (func%)**	**c (wt%)**	**Reaction time (min)**
34	60.02	12.68	0.602	2.244	11.78	1	20
35	59.993	12.679	0.600	2.237	11.75	1	70
36	60.01	12.68	1.801	6.715	28.55	3	70
37	59.995	12.680	1.801	6.715	28.56	3	20

Some of the analysis methods were discontinued as they did not provide definite answers in the previous set of reactions. The samples were initially characterized with GPC using the absolute method. As was observed with the HD crosslinker in the previous experiments, the M_n and M_w is larger for the pure emulsion compared to the samples containing crosslinker (**Figure 195** and **Figure 196**). The M_z is larger for the emulsion compared to the reaction mixtures with crosslinker at lower reaction times (t=20 min), suggesting that no high molecular weight polymers were synthesized within short reaction times (t≤20 min). The decrease in molecular weight could be caused by competing reactions such as hydrolysis of the ester bond which might disguise the occurrence of the crosslinking reaction. High molecular weight polymers might have adhered to the solid crosslinker and been removed with it. For the reaction mixture with 3wt% pM heated for t=70 min, the M_z is slightly larger than for the pure emulsion, indicating that the crosslinking reaction occurred to some extent.

The molecular weight increases proportionally to the reaction time for both reaction mixtures 1wt% and 3wt% (**Figure 195-Figure 197**). Increasing the crosslinker concentration increases the M_w while no significant differences are observed in the M_n and M_z. The largest M_z is obtained for the reaction mixture with the highest crosslinker concentration and longest reaction time which could indicate that the increase in both are beneficial for the reaction. For some of the reaction mixtures, the molecular weight for the parallels are quite large, which could be a result of varying concentrations of crosslinker due to the removal of crosslinker. This might explain why no clear correlation can be established between the concentration and molecular weight. It could also be due to the reaction time being too short for the crosslinker to fully react, resulting in similar amounts of the crosslinker reacting in both the 1 and 3wt% crosslinker reaction mixtures.

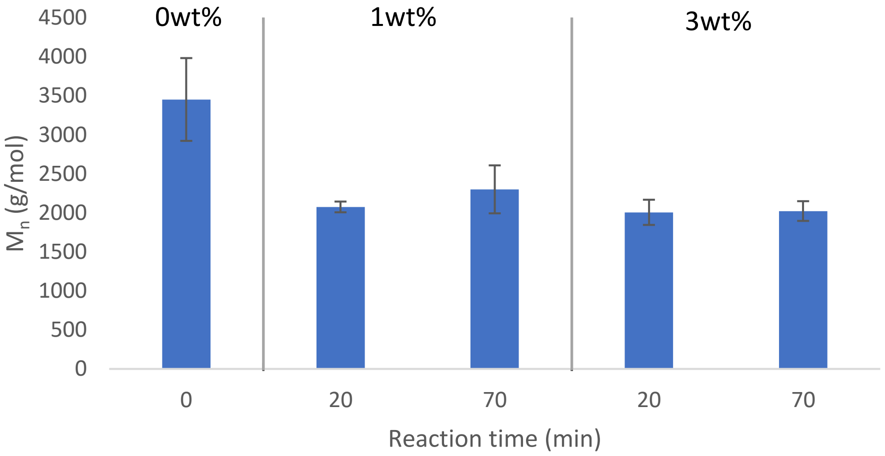


Figure 195: *Number average molecular weight (M_n) for emulsion and emulsion with 0, 1, and 3wt% N,N'-(1,4-phenylene)dimaleimide (pM) after heating at 80 °C for t=20 min and 70 min.*

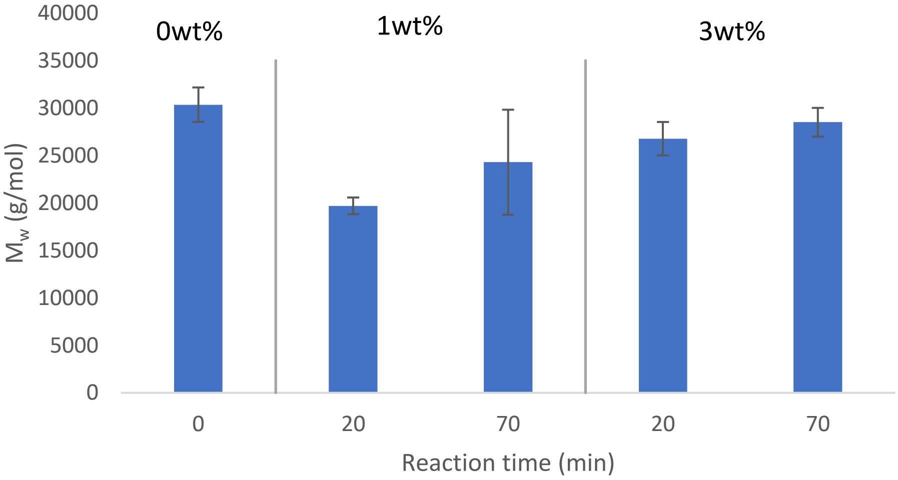


Figure 196: *Weight average molecular weight (M_w) for emulsion and emulsion with 0, 1, and 3wt% N,N'-(1,4-phenylene)dimaleimide (pM) after heating at 80 °C for t=20 min and 70 min.*

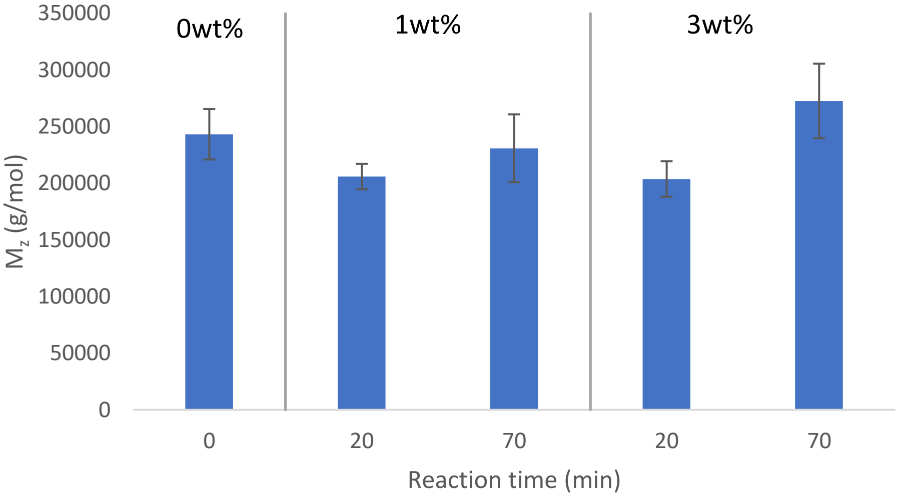


Figure 197: *Z-average molecular weight (M_z) for emulsion and emulsion with 0, 1, and 3wt% N,N'-(1,4-phenylene)dimaleimide (pM) after heating at 80 °C for t=20 min and 70 min.*

As with the HD reaction mixtures, the reaction mixtures were applied in paint formulations to form thin films and the hardness was measured (**Figure 198**). The reaction mixtures with low crosslinker concentrations form films with similar hardness as the emulsion while the mixtures with higher concentrations form softer films. The reaction time does not seem to affect the hardness of the films.

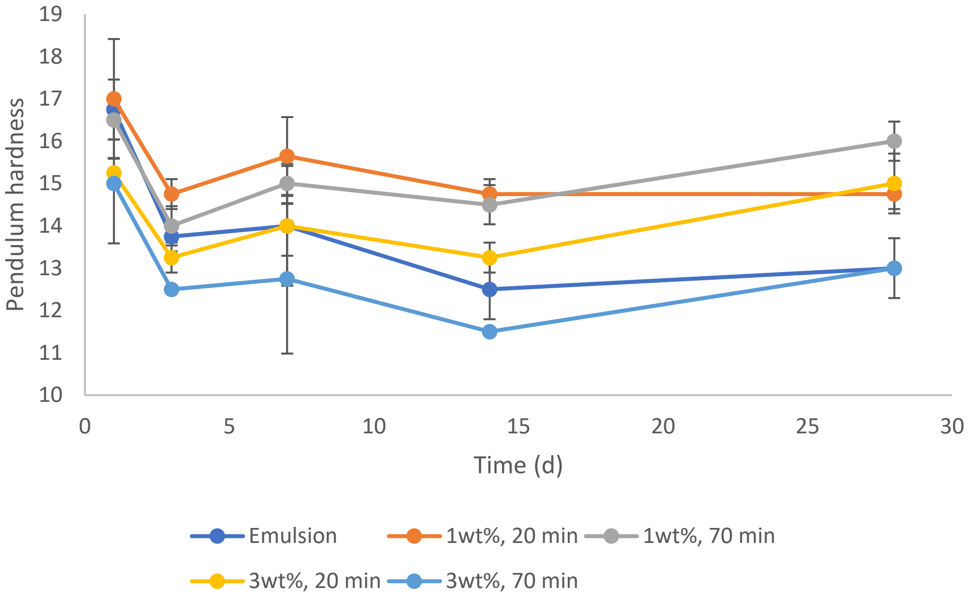


Figure 198: *Pendulum hardness for emulsion, and emulsions with 1 and 3wt% N,N'-(1,4-phenylene)dimaleimide (pM) after heating at 80 °C for t=20 min and 70 min.*

The effect of the crosslinker, reaction time and crosslinker concentration are summarized in **Table 24**. As can be observed, most of the methods used for the analysis are inconclusive. For this set of samples, no methods provide any definite proof of a successful crosslinking reaction.

Table 24: *Effect of adding crosslinker and subjecting the mixture to heating at 80 °C, increasing reaction time and crosslinker concentration, based on experiments with emulsion containing 1 or 3wt% N,N'-(1,4-phenylene)dimaleimide (pM) after heating at 80 °C for t=20 min and 70 min.*

	Adding crosslinker/heat	Increasing reaction time	Increasing crosslinker concentration
FTIR	Inconclusive	Inconclusive	Inconclusive
Molecular weight*	Inconclusive	↑	Inconclusive
Pendulum hardness	Inconclusive	Inconclusive	↑

*analyzed at Jotun AS, using the absolute method

B.1.5 Preliminary alkyd reactions

There were no clear indications to whether the crosslinking reactions had been successful due to the many incoherent results obtained from the preliminary emulsion reactions. This prompted us into an alternate route of approaching the problem at hand. The most obvious choice was simplify the reaction system in order to first understand the reaction progress and through a more facile monitoring, identify the issues and then see if these parameters would apply to the industrially produced material. In order to simplify the system and obtain a clearer indication on the crosslinking reaction, the pure alkyd, pre-emulsification, with crosslinker was used to facilitate the model reaction. The concentrations were increased to 10wt% (**Table 25**) compared to for the emulsion reactions, as this was expected to result in more pronounced differences. FTIR was used to monitor the reactions.

For the crosslinker to react with the conjugated fatty acid in the alkyd after emulsification, the crosslinker would have to travel through the water phase and enter the micelles. Adding the crosslinker directly to the alkyd was expected to increase the concentration of the crosslinker in the vicinity of the reactive sites on the alkyd, hence increasing the reaction rate.

One concern in the previous emulsion reactions was whether the drying procedure would affect the reaction mixtures. The drying procedure included exposing the samples to oxygen in the atmosphere which could result in the reaction mixtures undergoing autoxidation reactions to varying extents. This concern was bypassed in this set of experiments by performing the reactions in the pure alkyd without the presence of water, hence avoiding the drying procedure.

For the following experiments, alkyd MH-5mix or emulsion MHE-1mix were applied. Their properties compared to the previously applied alkyd/emulsions are shown in **Table 4** and **Table 5**.

Table 25: Amount of alkyd and concentration (c) of crosslinkers pentaerythritol tetraacrylate (PT) and N,N'-(1,4-phenylene)dimaleimide (pM). The total reaction time is given.

	Alkyd			**Crosslinker**			
Exp.nr	**Weight (g)**	**Alkyd (mmol)**	**cFA (mmol)**	**Crosslinker (mmol)**	**Weight (g)**	**c (func%)**	**Reaction time (h)**
J01	137.45	56.494	149.69	PT (39.02)	13.75	51.05	2
J02	100.29	41.221	109.22	mM* (37.13)	9.96	40.48	7
J03	11.02	4.529	12.00	PT (3.07)	1.08	50.53	32
J04	11.20	4.603	12.197	mM (4.36)	1.17	41.70	32

*mM was intended dissolved in 59,89 g di(propylene glycol) methyl ether (DPM)

For the reaction mixture containing 51,05func% PT heated for t=2h, no changes were observed in FTIR (**Figure 199**), indicating that the reaction time was too short for a reaction to occur.

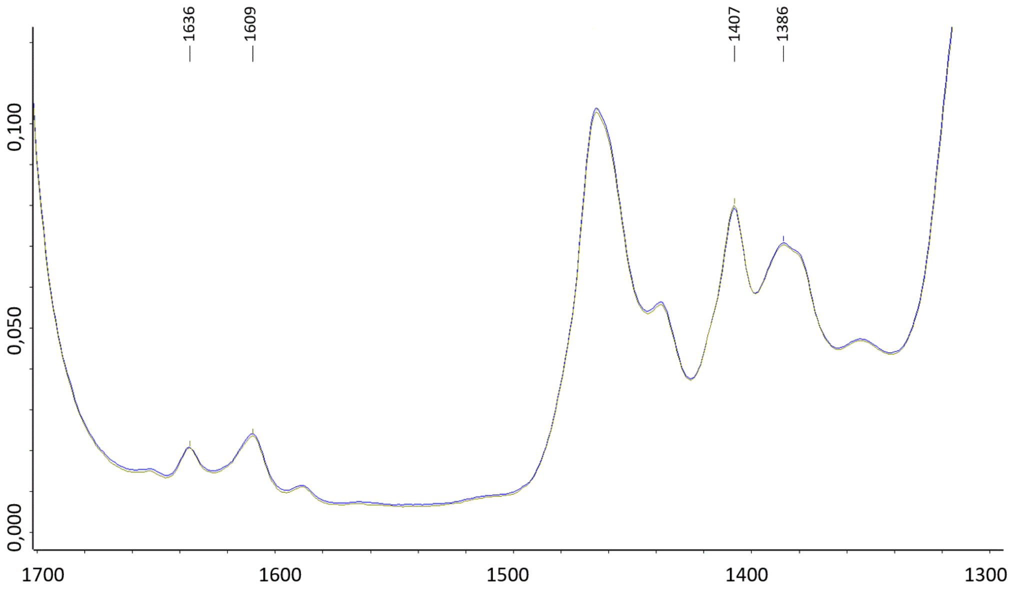


Figure 199: *FTIR spectra of emulsion with 51,05func% pentaerythritol tetraacrylate (PT) after heating at 80 °C for t=0h and 2h.*

It had previously been observed that pM did not successfully dissolve in the alkyd nor in the emulsion, and the same was observed for mM. It was not completely dissolved in di(propylene glycol) methyl ether (DPM) either. The mixture was added in 40.48func% to the alkyd and gelation was observed after t=7h. Characteristic peaks from the crosslinker were observed in FTIR and seemed to intensify throughout the reaction (**Figure 200**). This could be due to the crosslinker gradually dissolving. However, this provided no indication of whether a reaction was occurring.

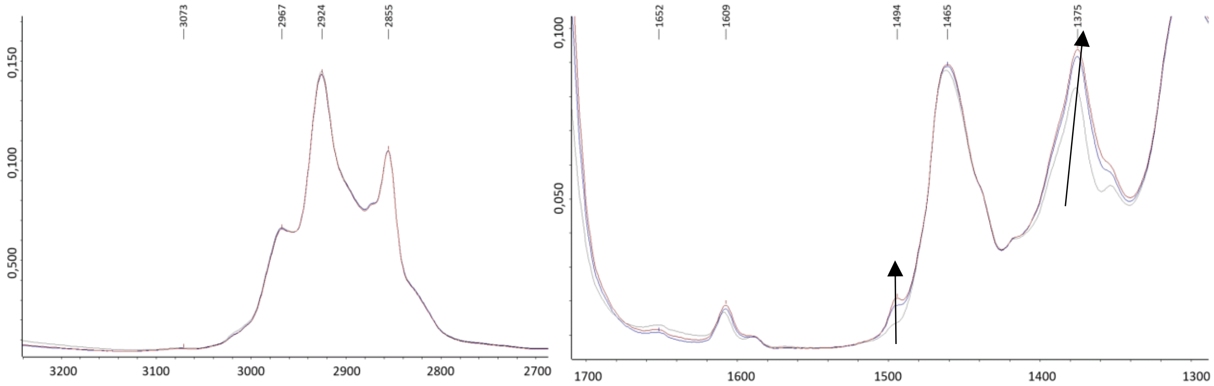


Figure 200: *FTIR spectra of emulsion with 40,48func% N,N'-(1,3-phenylene)dimaleimide (mM) after heating at 80 °C for t=0h, 3h and 7h.*

Two mixtures containing alkyd and 10wt% PT or mM (J03 and J04) were heated to 80 °C for t=16h. In difference from the previous experiments (J01 and J02), the reaction mixtures were not subjected to mechanical stirring. After t=16h, a viscosity change was observed for the PT mixture while gelation was observed in the mixture with mM. The formation of the gel indicated a higher reactivity for the mM mixture. After t=32h, gelation was also observed in the mixture with PT. As the reaction progresses, decreases can be observed in the alkene peaks from the acrylate at 1636 and 1407 cm^{-1} (**Figure 201**) which can be associated with the Diels-Alder reaction occurring. GPC, using the conventional method, show an increase in molecular weight (**Figure 203**). The chromatogram shows that the crosslinker was consumed as the reaction progressed (**Figure 202**).

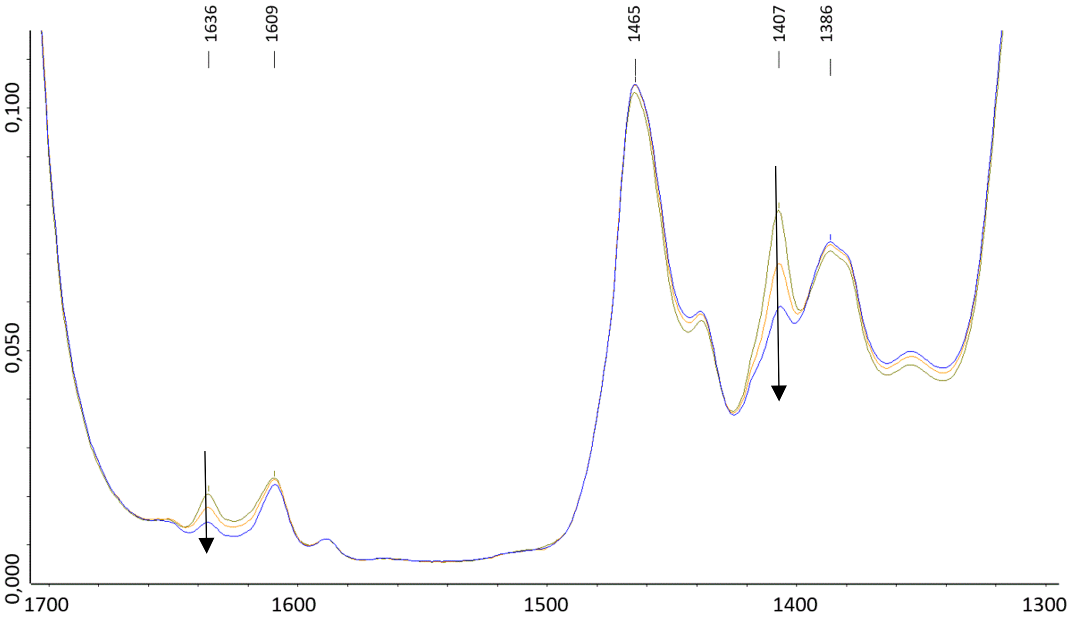


Figure 201: *FTIR spectra of alkyd and 10wt% pentaerythritol tetraacrylate (PT) after heating at 80 °C for t=0h, 16h and 32h.*

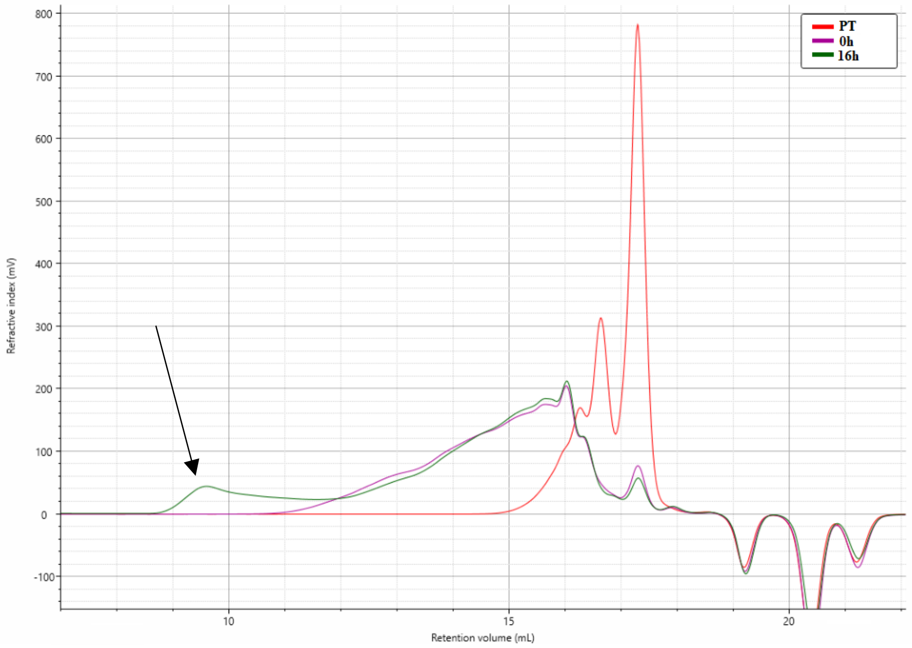


Figure 202: *GPC chromatogram of pentaerythritol tetraacrylate (PT) (red) and alkyd with 10wt% PT after heating at 80 °C for t=0h (purple) and 16h (green).*

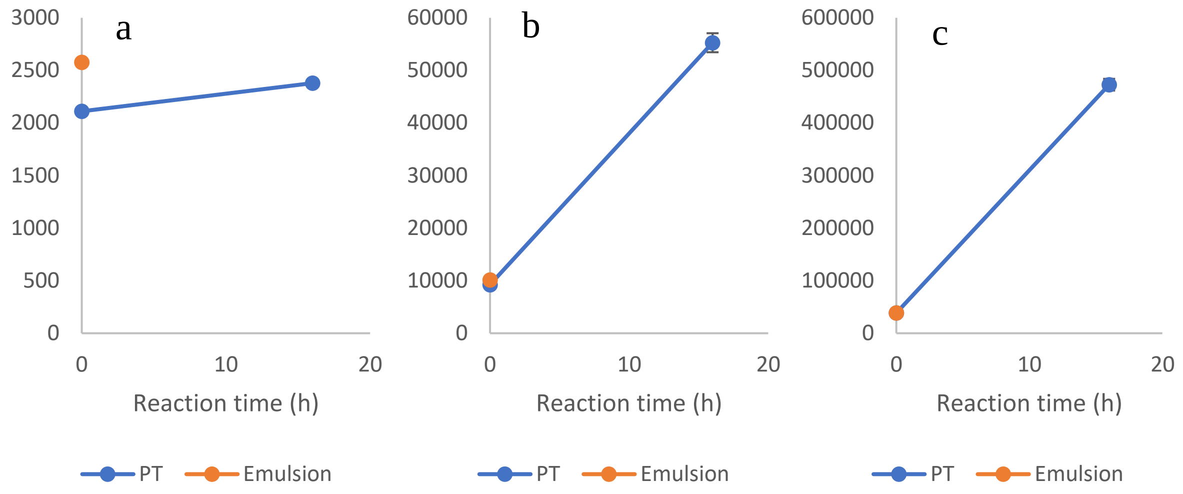


Figure 203: a) *Number average molecular weight (M_n),* ***b)*** *weight average molecular weight (M_w) and* ***c)*** *z-average molecular weight (M_z) of emulsion and emulsion with 10wt% pentaerythritol tetraacrylate (PT) after heating at 80 °C for t=0h and 16h.*

As observed previously in the FTIR for the mM mixture, characteristic peaks from the crosslinker appeared during the reaction time (**Figure 204b**). A small decrease in the 3005 cm^{-1} from the =CH stretches in the alkyd can be observed (**Figure 204a**). It should be noted that the difference in intensity of this peak is relatively small which makes it challenging to track the reaction based on solely on this peak. A decrease in the molecular weight was observed as the reaction mixture was heated (**Figure 206**); however, the difference in intensity for the spectra could indicate poor solubility for the t=16h mixture (**Figure 205**). Additionally, solid aggregates were observed. Although the molecular weight could not be decided accurately due to the loss of analysis of the high molecular weight polymers, the aggregation indicates that they were indeed formed. The GPC analysis should be carried out after shorter reaction times in order to get accurate molecular weight results.

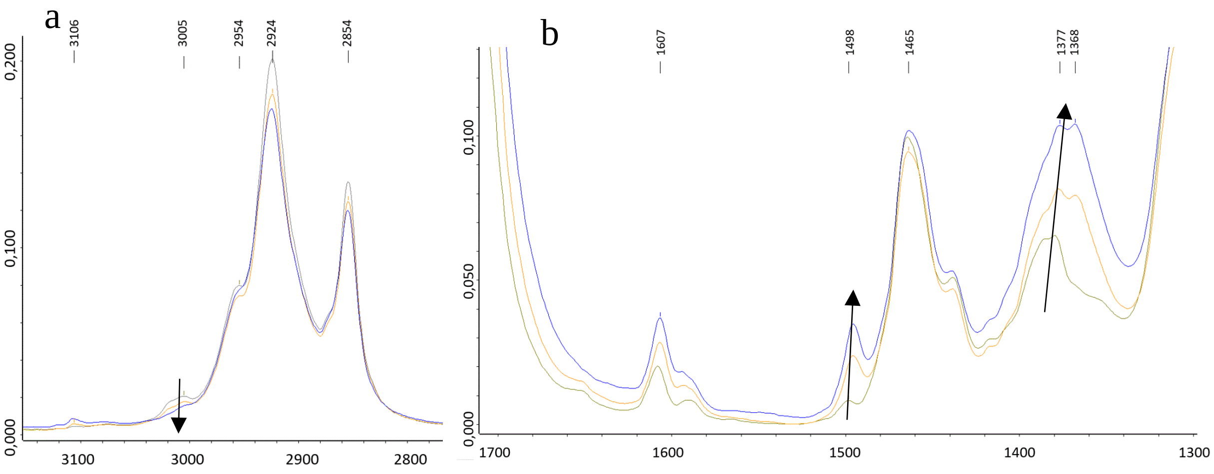


Figure 204: *FTIR spectra of alkyd and 10wt% N,N'-(1,3-phenylene)dimaleimide (mM) after heating at 80 °C for t=0h, 16h and 32h.*

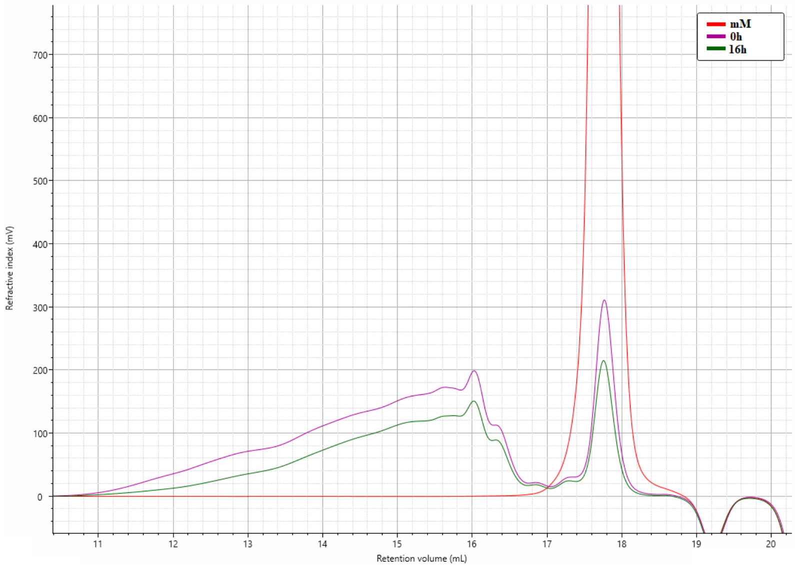


Figure 205: *GPC chromatogram of N,N'-(1,3-phenylene)dimaleimide (mM) (red) and alkyd with 10func% mM after heating at 80 °C for t=0h (purple) and 16h (green).*

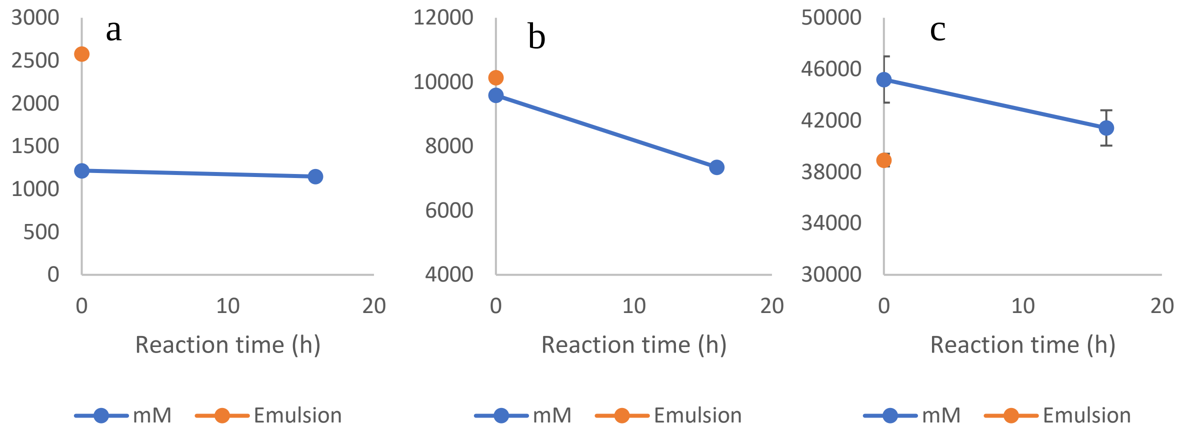


Figure 206: ***a)*** *Number average molecular weight (M_n),* ***b)*** *weight average molecular weight (M_w) and* ***c)*** *z-average molecular weight (M_z) of emulsion and emulsion with 10wt% N,N'(1,3-phenylene)dimaleimide (mM) after heating at 80 °C for t=0h and 16h.*

The aggregated polymers were washed with THF, dried, and measured with FTIR. The FTIR spectra of the aggregates were compared to the spectra of the dissolved polymer, both obtained after evaporation of the solvent (**Figure 207**). The aggregated polymers showed a larger decrease in the 3005 cm^{-1} peak which could indicate that the Diels-Alder reaction had occurred to a larger extent. This fraction of the reaction mixture is therefore expected to have an increased molecular weight compared to the fraction which dissolved. However, this could not be confirmed by GPC due to the solubility.

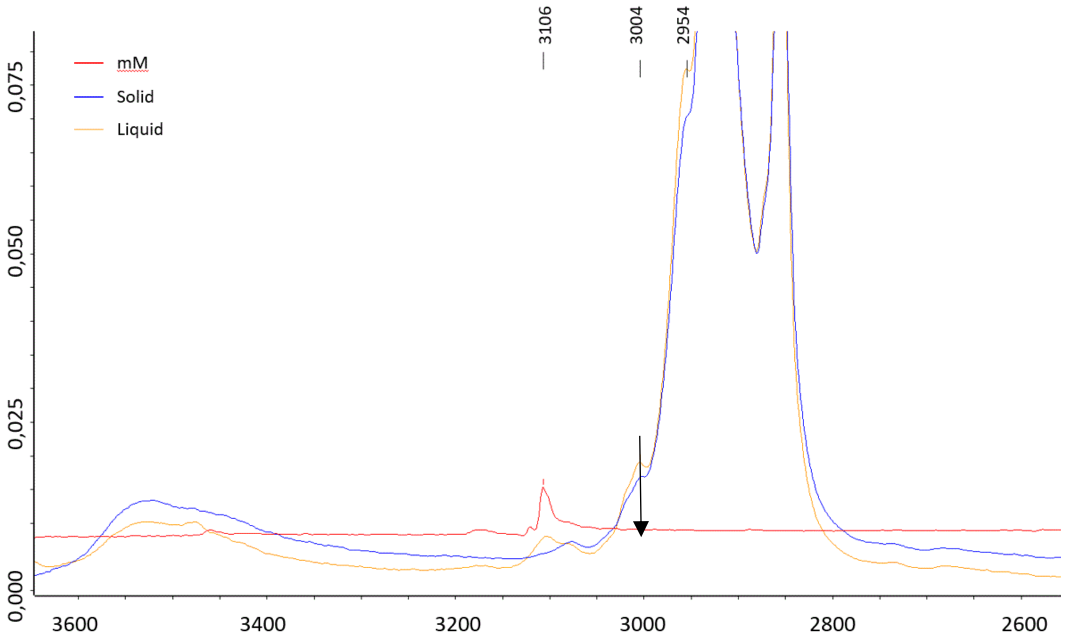


Figure 207: *FTIR spectra of crosslinker N,N'-(1,3-phenylene)dimaleimide (mM) and alkyd with 10wt% mM after heating at 80 °C for t=16h dissolved in THF and the aggregate formed.*

FTIR was measured for the initial reaction mixtures of PT and mM, prior to heating but after storing in RT for t=30d (**Figure 208** and **Figure 209**, respectively). No significant differences were observed for the PT mixture. Small differences can be observed for the mM mixture, especially after t=30d. This indicates that if the reaction progresses at RT, the rate is significantly reduced.

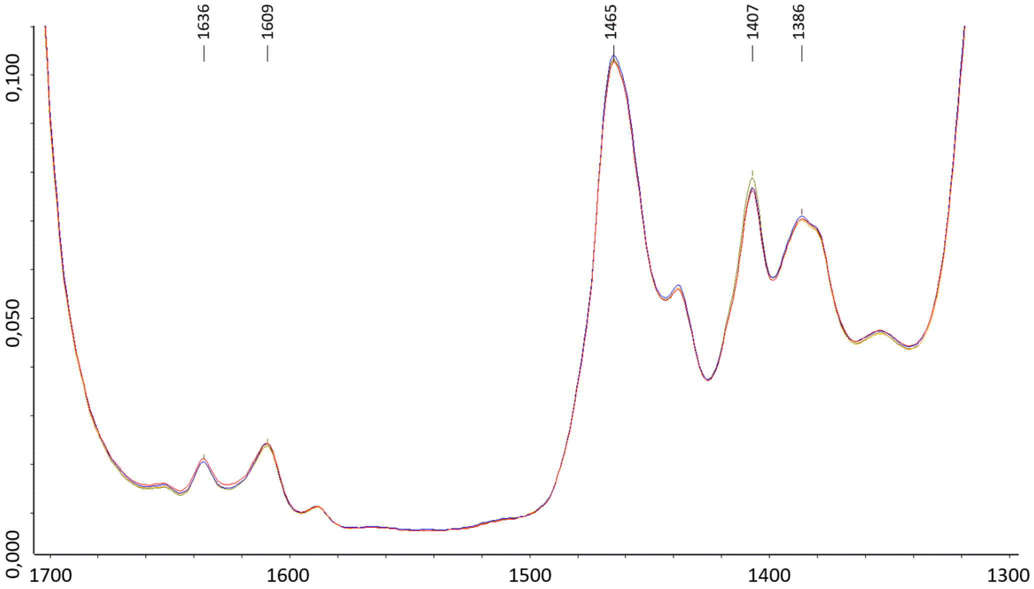


Figure 208: *FTIR spectra of alkyd with 10wt% pentaerythritol tetraacrylate (PT) after storing in room temperature (RT) for t=0h, 3d, 10d and 30d.*

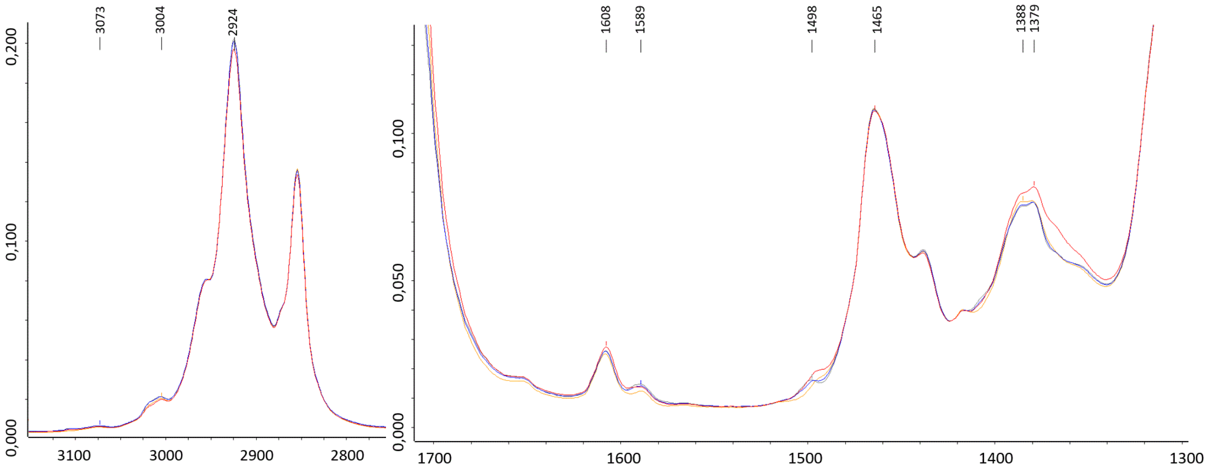


Figure 209: *FTIR spectra of alkyd with 10wt% N,N'-(1,3-phenylene)dimaleimide (mM) after storing in room temperature (RT) for t=0h, 3d, 10d and 30d.*

In order to investigate whether the changes observed in the visual properties i.e. viscosity and FTIR were contributed to reactions including the crosslinker or solely in the alkyd, pure alkyd was subjected to heating under the same conditions for t=2 weeks. A possible side reaction could be for the unsaturated groups in the alkyd to react with oxygen from the air. One of the vials was exposed to oxygen while the other was flashed with N_2. However, no changes were observed in either vial based on FTIR (**Figure 210** and **Figure 211**).

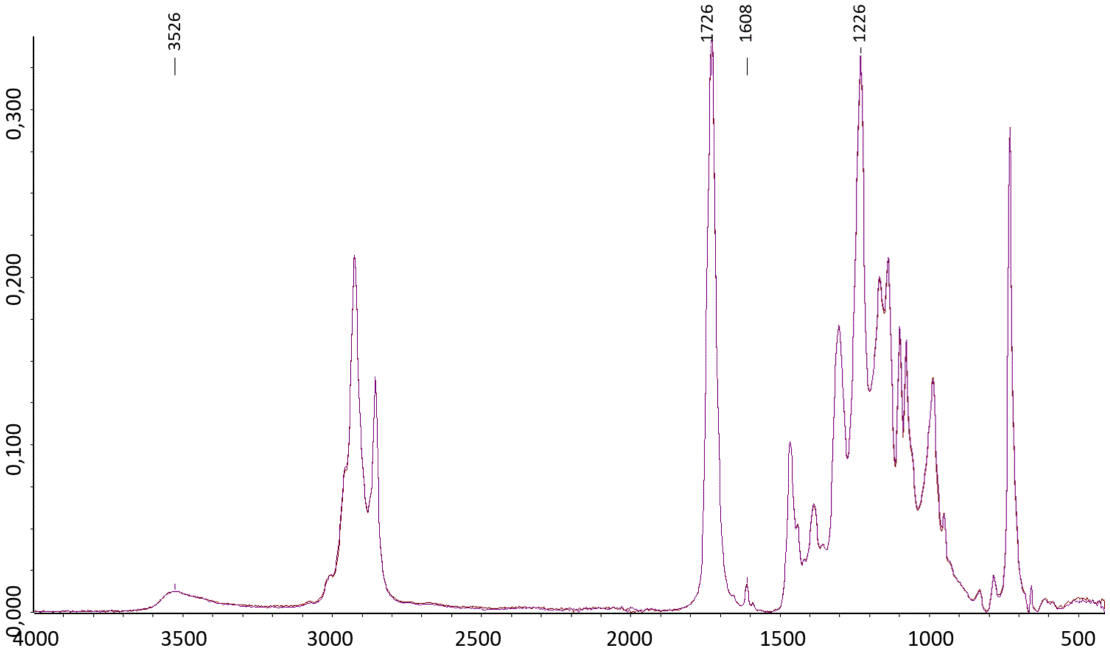


Figure 210: *FTIR spectra of alkyd flashed with nitrogen and heated at 80 °C for t=0h and 2 weeks.*

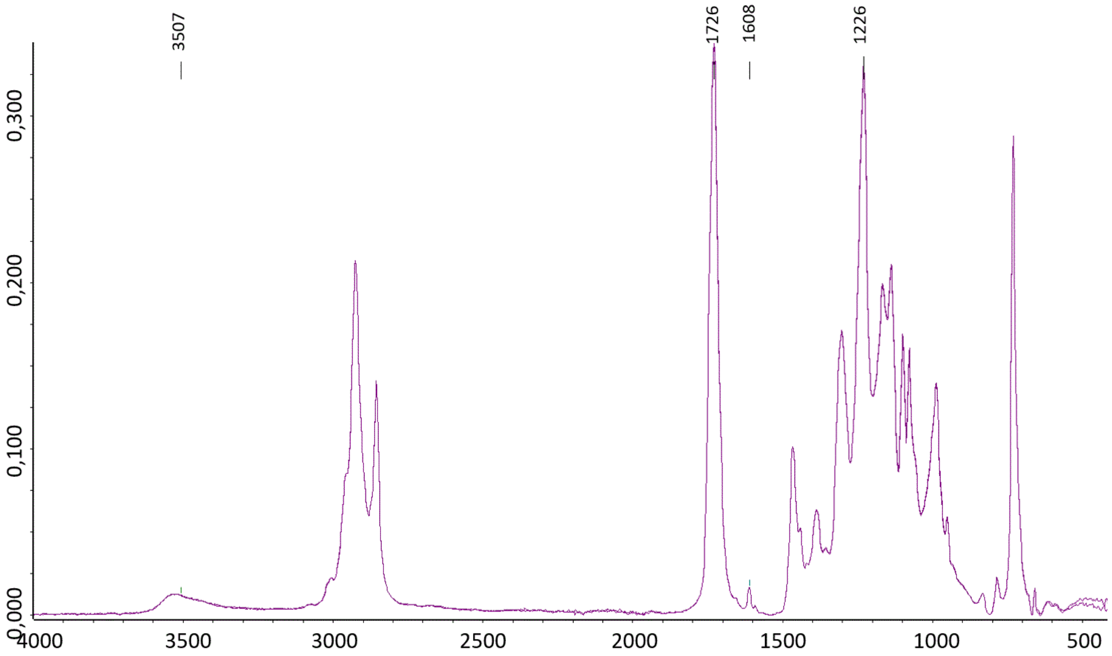


Figure 211: *FTIR spectra of alkyd heated at 80 °C for t=0h and 2 weeks*

Comparing the results obtained from the different analysis methods with the alkyd without crosslinker indicates that the changes observed are indeed a result of the addition of crosslinker (**Table 26**) and not a result of exposing the alkyd to heating. Although the reaction mixtures contained varying amounts of reactive species, comparisons of the crosslinkers can still be made. The visual changes in mM obtained at shorter reaction times combined with the loss of solubility suggests a higher reactivity compared to PT. This set of experiments also suggests that the reaction progression for alkyd reactions can be qualitatively monitored through FTIR for the PT reaction mixture while the mM reaction mixture proves more challenging. GPC measurements should be carried out while the reaction mixtures are completely soluble which may be achieved at lower reaction times, especially for the mM reaction mixtures. For the PT mixture, FTIR indicates that t>2h should be employed for this concentration.

Table 26: *Summary of results for the preliminary alkyd reactions, including FTIR, GPC and visual changes (i.e. viscosity). No changes are denoted by 0.*

	PT	**mM**	**No crosslinker**
FTIR	↓	Inconclusive	0
Molecular weight*	↑	Inconclusive	N/A
Visual changes	↑	↑	0

*analyzed by Jotun AS, using the conventional method

C: Supporting NMR to the fatty acid study

C.1 Fatty acid mixture

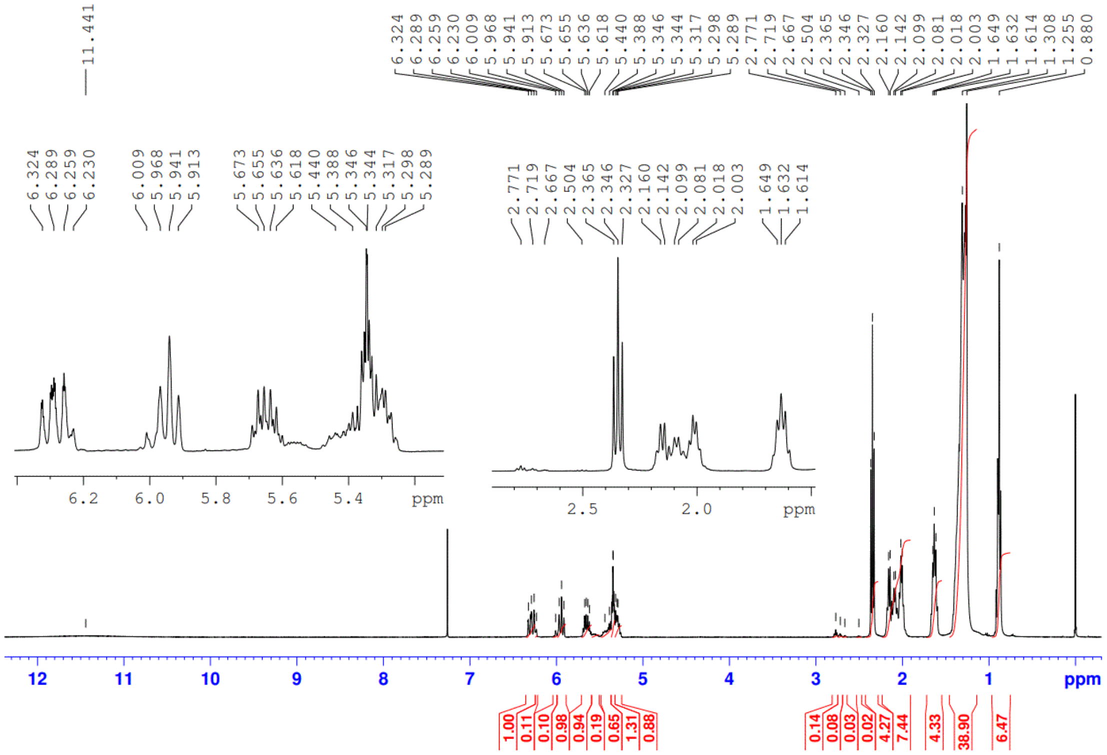


Figure 212: *^{1}H NMR spectra of the fatty acid mixture.*

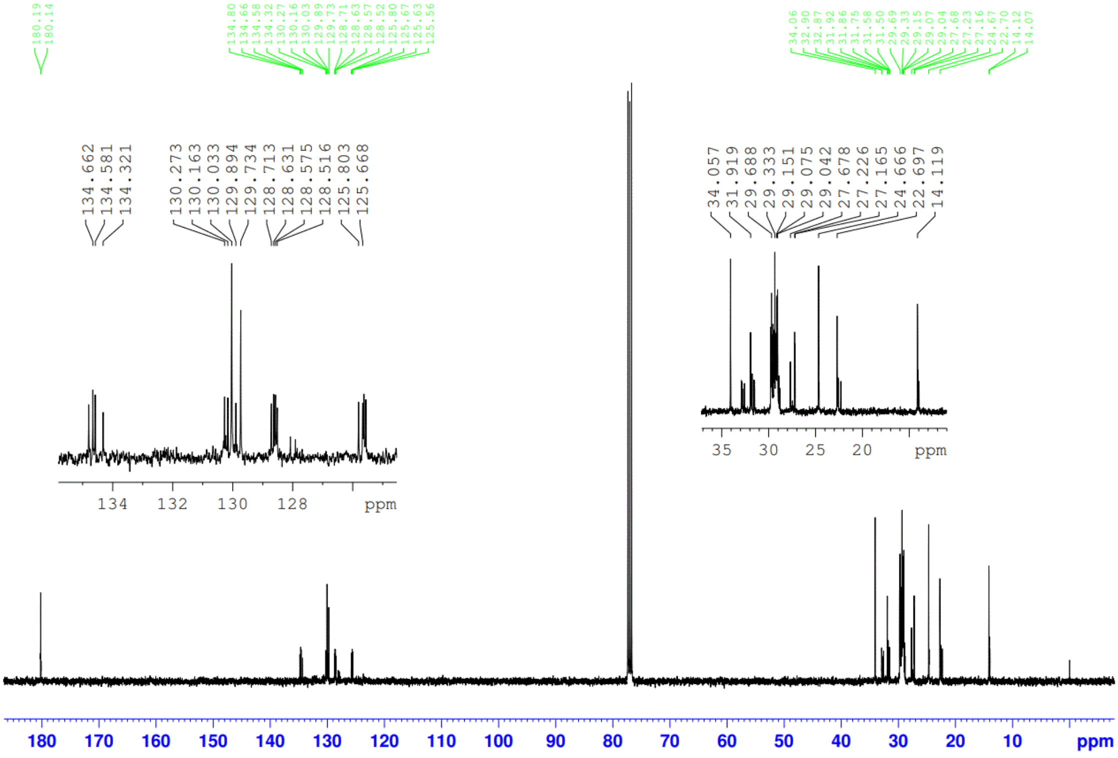


Figure 213: *^{13}C NMR spectra of the fatty acid mixture.*

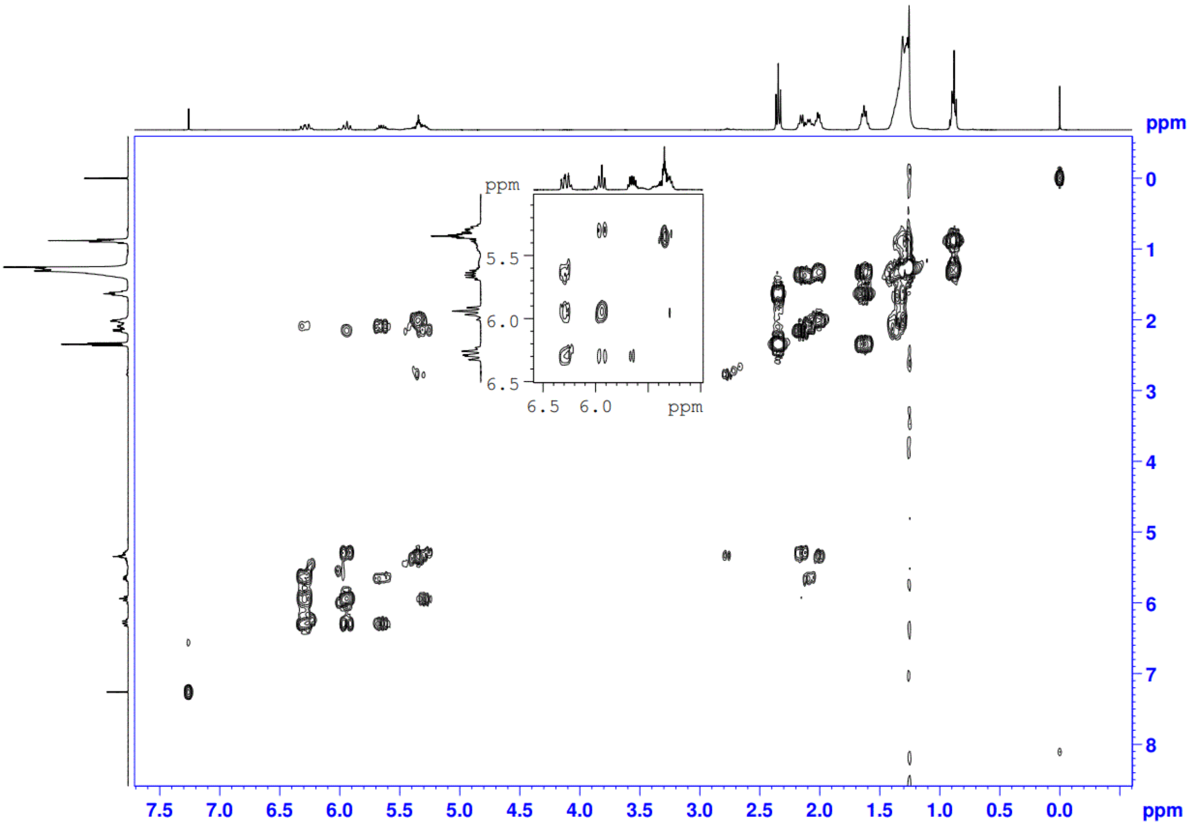


Figure 214: COSY NMR spectra of the fatty acid mixture.

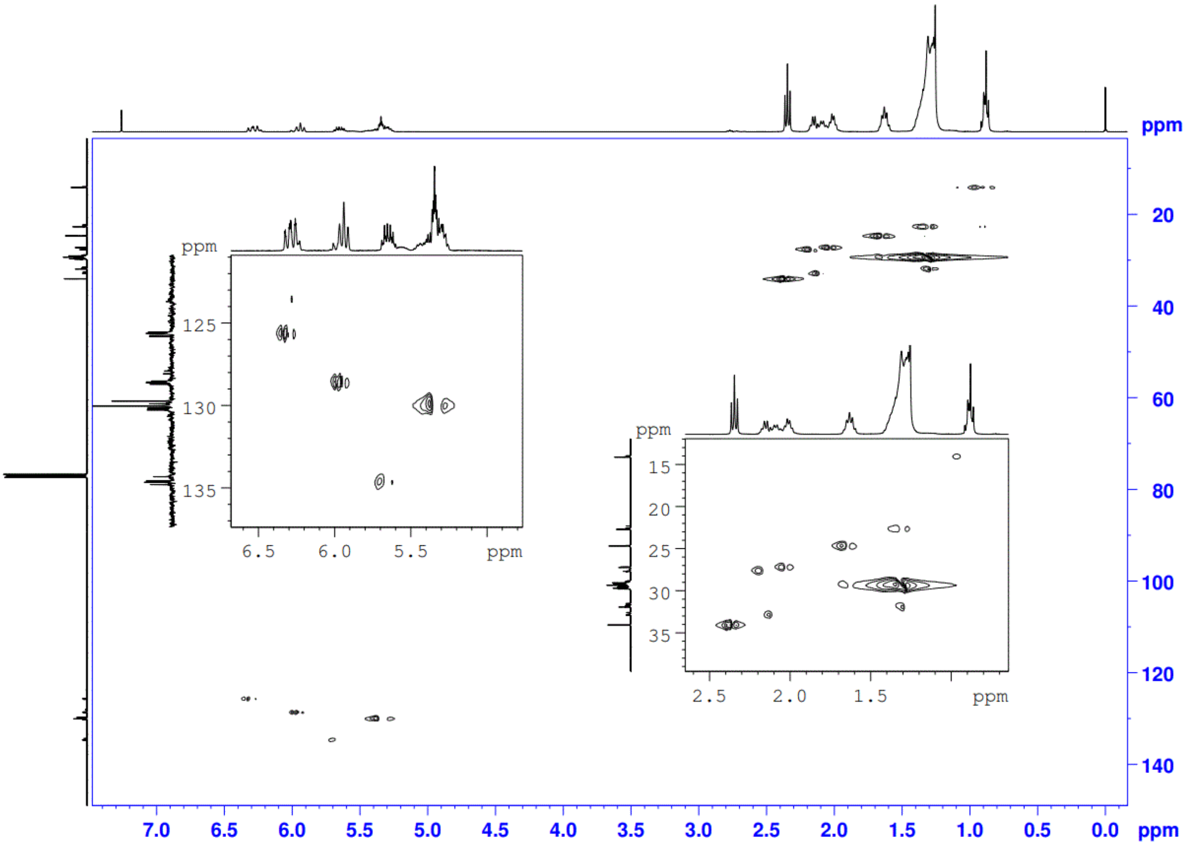


Figure 215: HSQC NMR spectra of the fatty acid mixture.

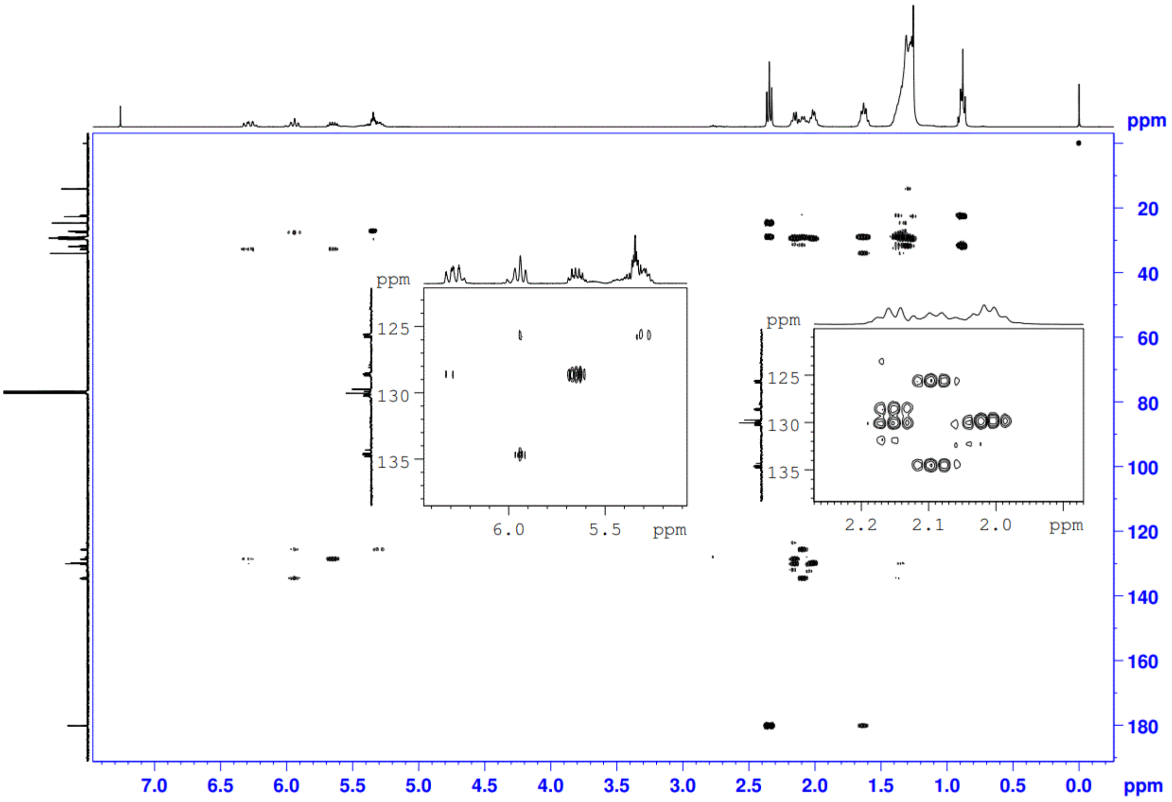


Figure 216: *HMBC NMR spectra of the fatty acid mixture.*

Table 27: *NMR shifts for the fatty acid structure associated with the carboxylic acid.*

^{1}H shift	HSQC	COSY	HMBC
1.63	34.67	1.3/2.35	180.19/34.06/29
2.35	34.06	1.63	180.19/29/24.65

Table 28: *NMR shifts for the most prominent unsaturated fatty acids.*

^{1}H shift	HSQC	COSY	HMBC
2.01	27.2	5.34/1.3	28.9/130
2.10	32.8	5.65/5.37w/6.28w/1.36	28.9/125.7/134.5
2.15	27.7	5.94/5.29/1.3	28.9/128.9/129.6
5.29	129.6	5.94/2.15/2.15	125.7/27.6w/29.5w
5.34	129.3	2.01/2.8	27.17/29.7w
5.65	134.8	6.29/2.10	128.8/32.8/29.5w
5.94	128.8	6.29/5.29/2.15	134.6/125.7/27.6
6.29	125.7	5.94/5.65/2.10	130/128.8/32.8

C.2 Fatty acid reactions

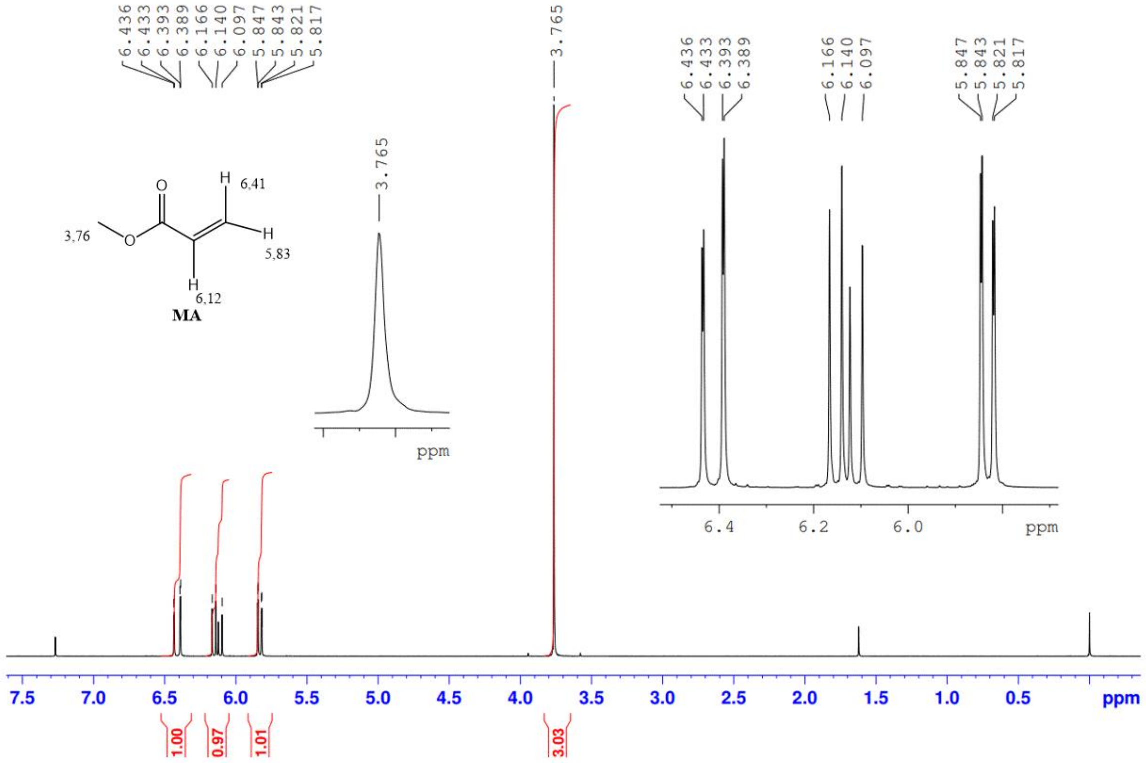


Figure 217: *^{1}H NMR spectra of methyl acrylate (MA).*

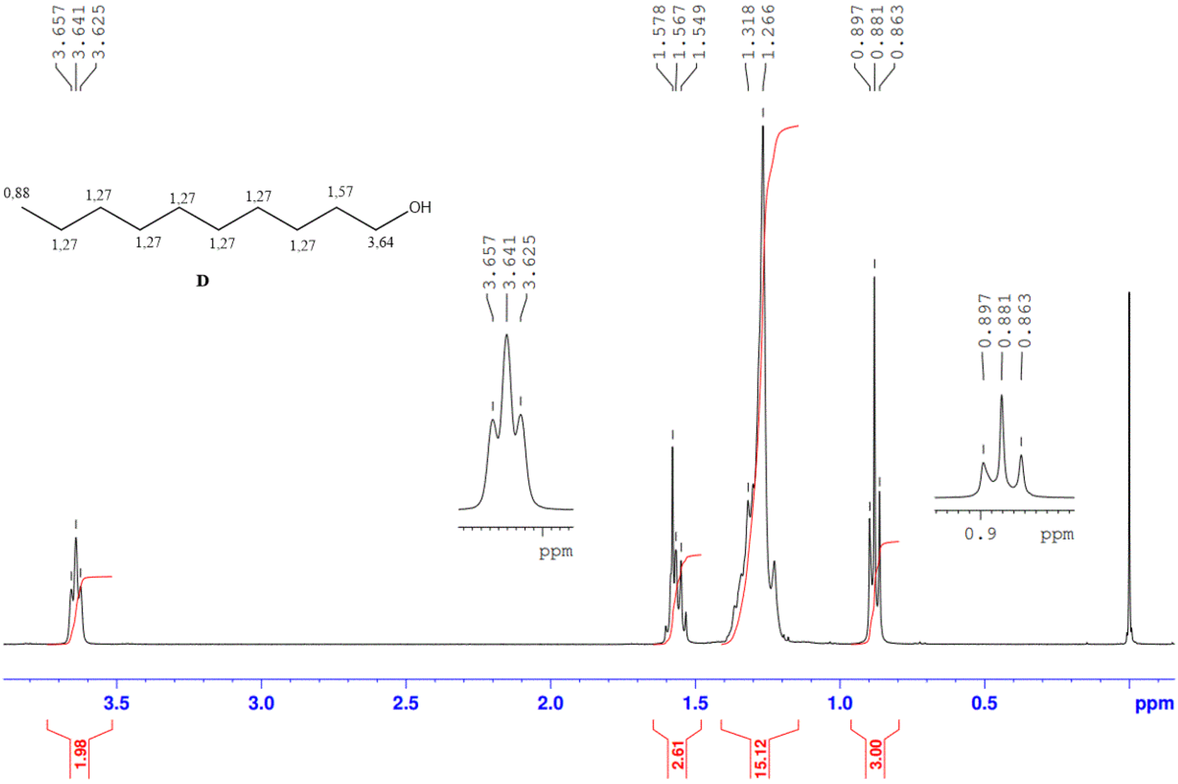


Figure 218: *^{1}H NMR spectra of decanol (D).*

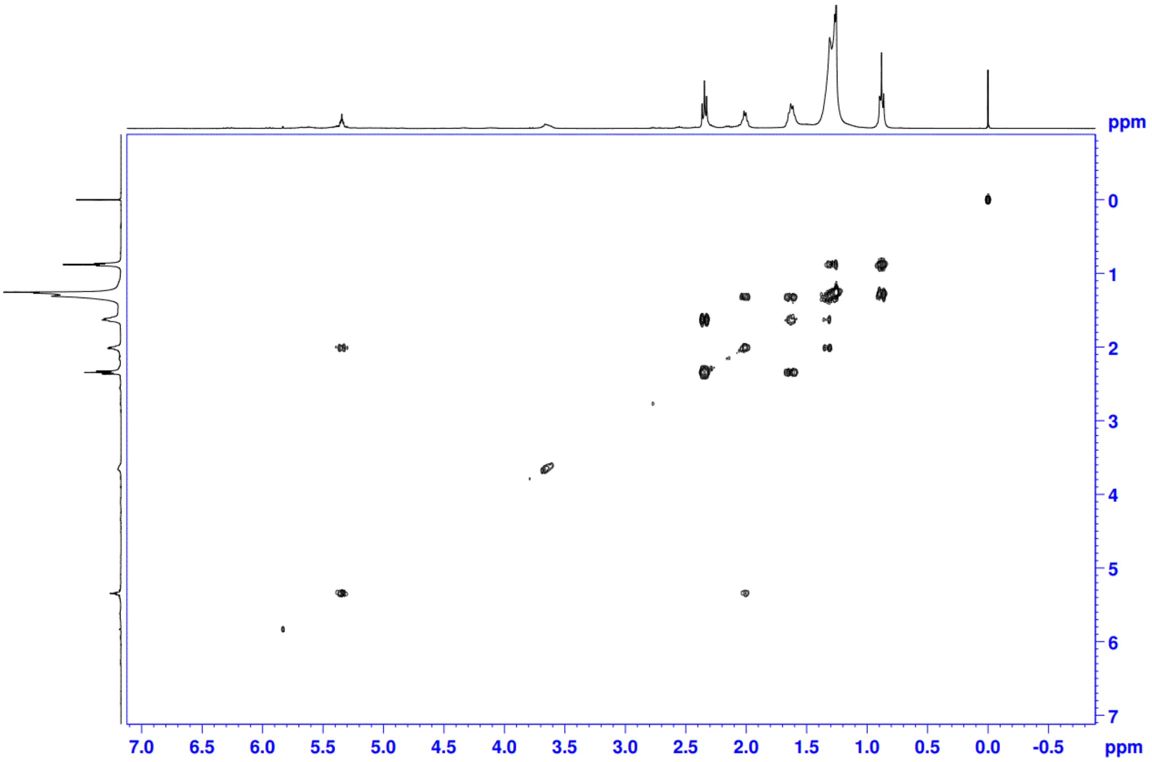


Figure 219: *COSY NMR spectra for the reaction mixture consisting of the fatty acid mixture and methyl acrylate (MA) at t=70h.*

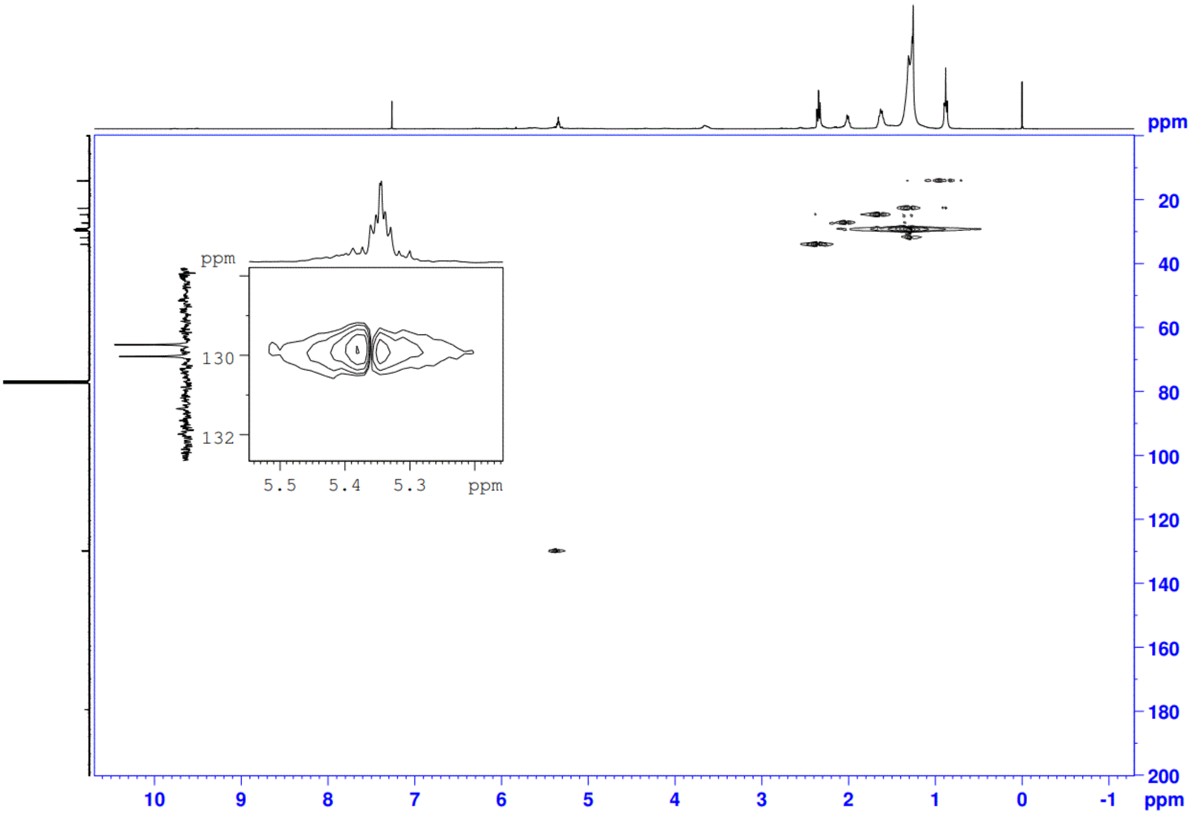


Figure 220: *HSQC NMR spectra for the reaction mixture consisting of the fatty acid mixture and methyl acrylate (MA) at t=70h.*

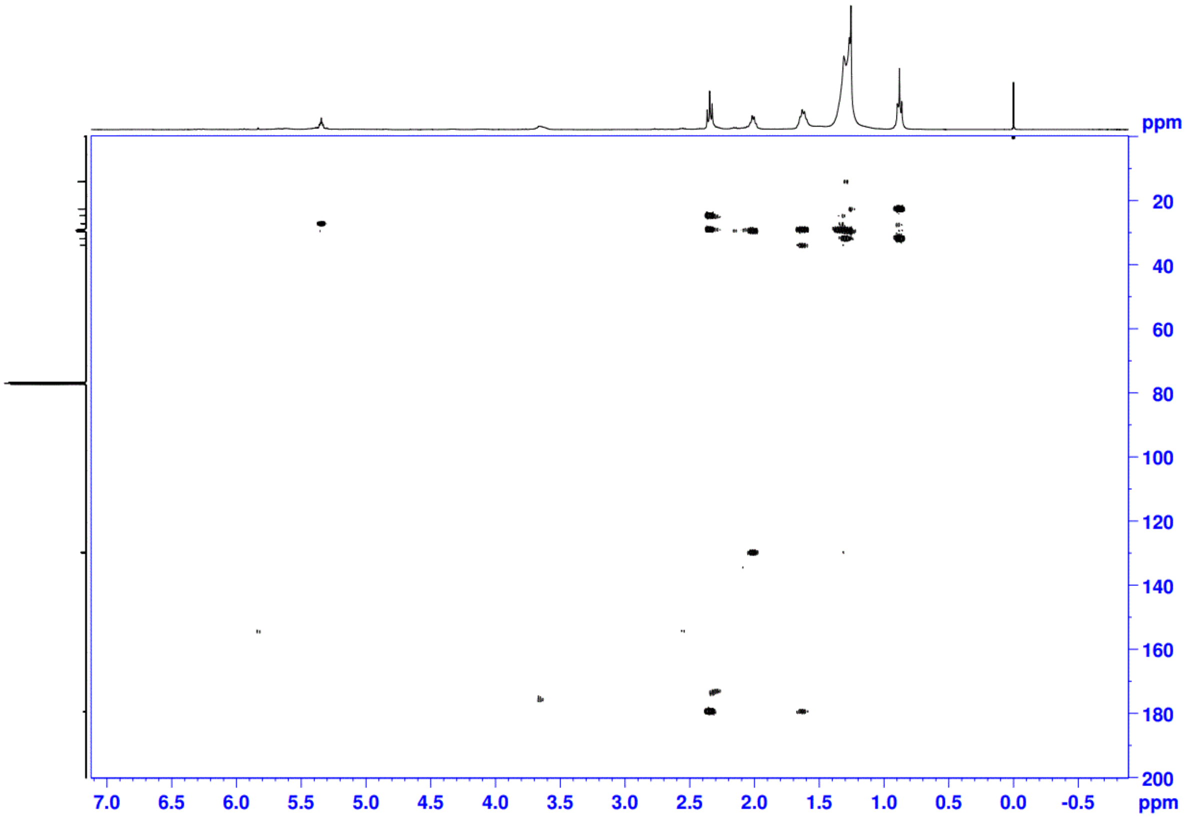
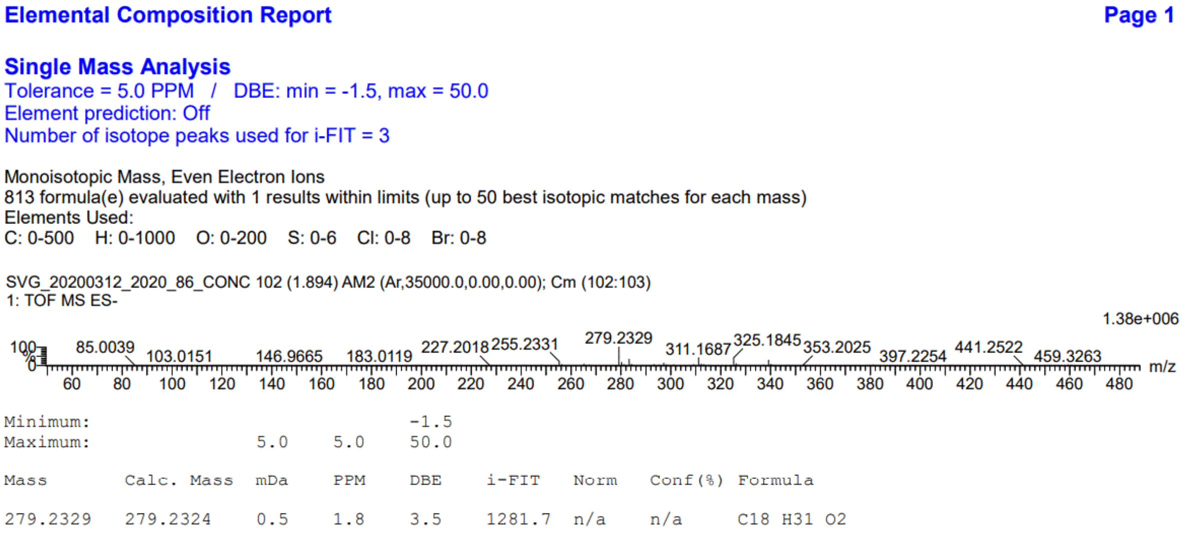


Figure 221: *HMBC NMR spectra for the reaction mixture consisting of the fatty acid mixture and methyl acrylate (MA) at t=70h.*

D: MS



Elemental Composition Report **Page 1**

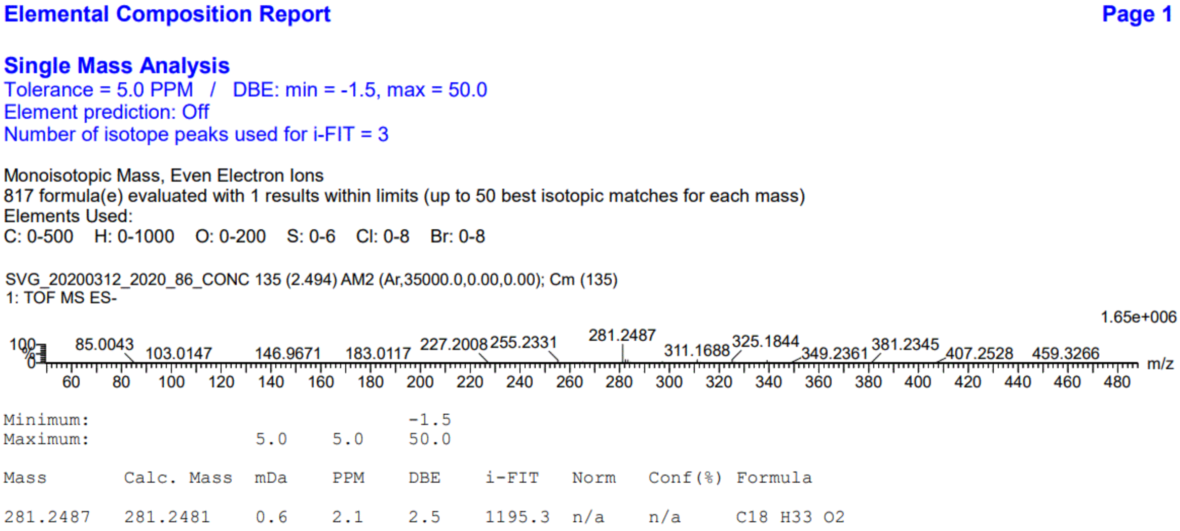
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
813 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 S: 0-6 Cl: 0-8 Br: 0-8

SVG_20200312_2020_86_CONC 102 (1.894) AM2 (Ar,35000.0,0.00,0.00); Cm (102:103)
1: TOF MS ES-

```
Minimum:                              -1.5
Maximum:                  5.0    5.0   50.0

Mass        Calc. Mass  mDa    PPM    DBE    i-FIT   Norm   Conf(%) Formula

279.2329    279.2324    0.5    1.8    3.5    1281.7  n/a    n/a     C18 H31 O2
```

Figure 222: Elemental composition of fatty acid 1. Signal was detected in negative mode as M-H.



Elemental Composition Report **Page 1**

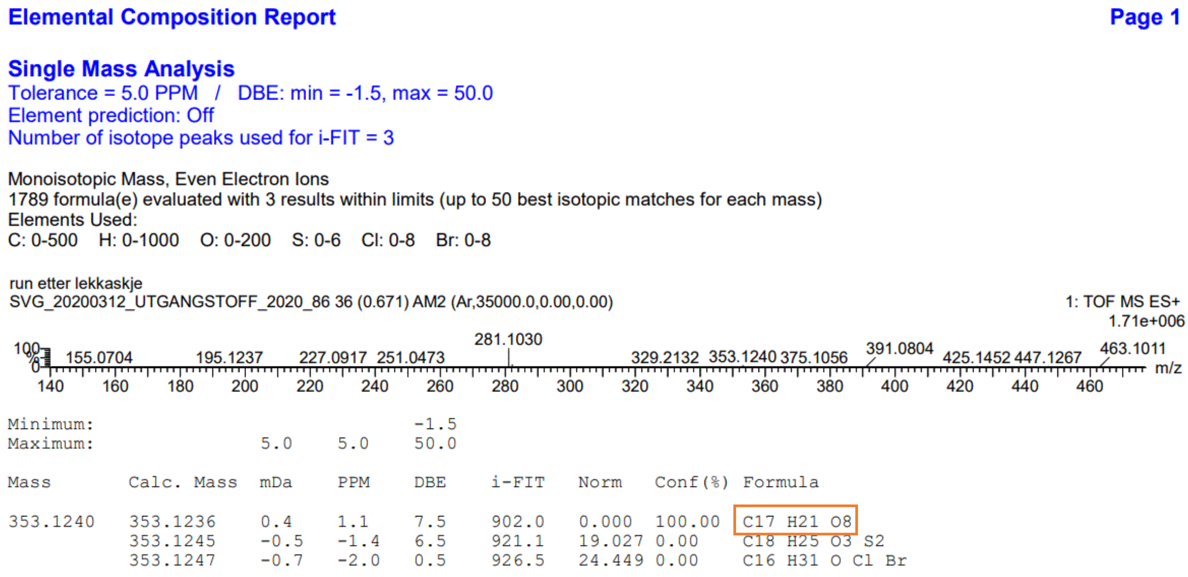
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
817 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-500 H: 0-1000 O: 0-200 S: 0-6 Cl: 0-8 Br: 0-8

SVG_20200312_2020_86_CONC 135 (2.494) AM2 (Ar,35000.0,0.00,0.00); Cm (135)
1: TOF MS ES-

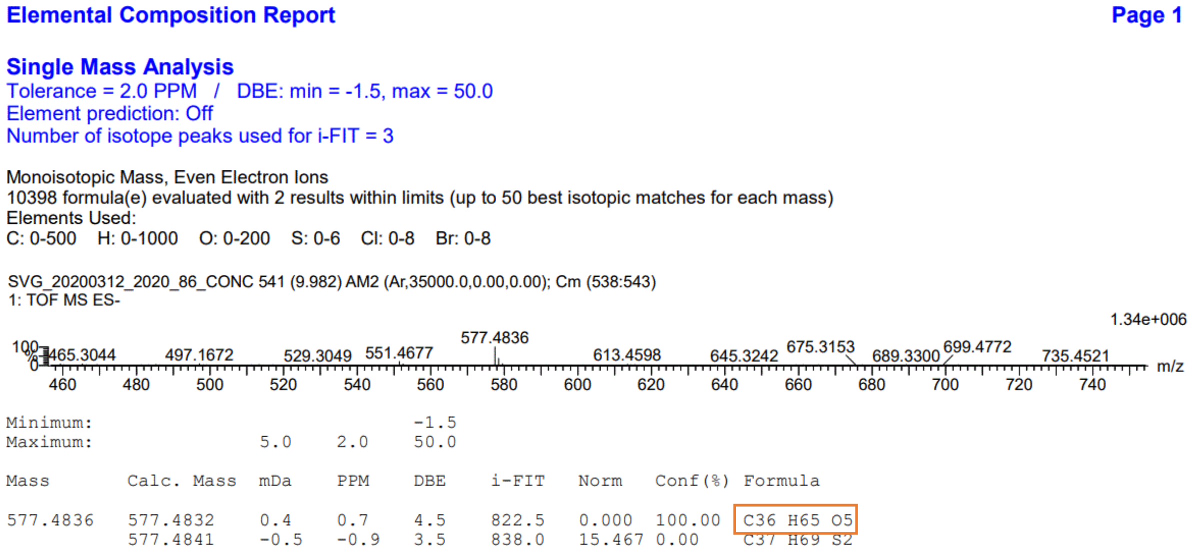
```
Minimum:                              -1.5
Maximum:                  5.0    5.0   50.0

Mass        Calc. Mass  mDa    PPM    DBE    i-FIT   Norm   Conf(%) Formula

281.2487    281.2481    0.6    2.1    2.5    1195.3  n/a    n/a     C18 H33 O2
```

Figure 223: Elemental composition of fatty acid 2. Signal was detected in negative mode as M-H.



```
Elemental Composition Report                                                    Page 1

Single Mass Analysis
Tolerance = 5.0 PPM   /   DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1789 formula(e) evaluated with 3 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-500    H: 0-1000    O: 0-200    S: 0-6    Cl: 0-8    Br: 0-8

run etter lekkaskje
SVG_20200312_UTGANGSTOFF_2020_86 36 (0.671) AM2 (Ar,35000.0,0.00,0.00)            1: TOF MS ES+
                                                                                    1.71e+006

Minimum:                          -1.5
Maximum:          5.0      5.0    50.0

Mass       Calc. Mass   mDa    PPM    DBE    i-FIT   Norm    Conf(%) Formula

353.1240   353.1236     0.4    1.1    7.5    902.0   0.000   100.00  C17 H21 O8
           353.1245     -0.5   -1.4   6.5    921.1   19.027  0.00    C18 H25 O3 S2
           353.1247     -0.7   -2.0   0.5    926.5   24.449  0.00    C16 H31 O Cl Br
```

Figure 224: *Elemental composition of pentaeryhtritol tetraacrylate (PT). Signal was detected in positive mode as M+H.*



```
Elemental Composition Report                                                    Page 1

Single Mass Analysis
Tolerance = 2.0 PPM   /   DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
10398 formula(e) evaluated with 2 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-500    H: 0-1000    O: 0-200    S: 0-6    Cl: 0-8    Br: 0-8

SVG_20200312_2020_86_CONC 541 (9.982) AM2 (Ar,35000.0,0.00,0.00); Cm (538:543)
1: TOF MS ES-
                                                                                    1.34e+006

Minimum:                          -1.5
Maximum:          5.0      2.0    50.0

Mass       Calc. Mass   mDa    PPM    DBE    i-FIT   Norm    Conf(%) Formula

577.4836   577.4832     0.4    0.7    4.5    822.5   0.000   100.00  C36 H65 O5
           577.4841     -0.5   -0.9   3.5    838.0   15.467  0.00    C37 H69 S2
```

Figure 225: *Elemental composition of reaction mixture with fatty acid and pentaerythritol tetraacrylate (PT). Signal was detected in negative mode as M-H.*

Maren Hauknes Ranheim

Crosslinking of Polyesters in Emulsion Droplets

NTNU
Norwegian University of
Science and Technology