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Environmental Stress Cracking of Interior Polymers used in the car

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Environmental Stress Cracking of Interior Polymers of a Car (PC/ABS and ABS)

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Abstract

The automotive industry is growing at a very rapid pace. Not long back, maybe 40 - 50 years, when owning a car was a luxury and today it is more of a necessities. In the past 20 years, automotive manufacturers have gone from making a simple basic vehicle to cars with all the latest features from large screen displays, music control system, navigation systems, autonomous driving and many more. With this advancement in technology in cars, there has been advancement in the materials used in the car to give them a more premium look as well as have solutions to the previous problems such as easy cleanability of stains, long service life and resistance to wear and tear.

Currently, in the interiors of the car, Acrylonitrile Butadiene Styrene and poly(carbonate) / Acrylonitrile Butadiene Styrene polymeric materials are used mostly except for the seating materials. These materials are used in the areas for example: instrument panels, tunnel consoles and door panels. The extensive use of these materials meant importance of addressing the issues related to these materials, including cracking under certain circumstances such as, when a part gets exposed to a chemical when it is under stress and cleanability issues.

This study aims to address the problem of the polymers used in the interior of the car - ABS and PC/ABS cracking due to environmental factors. This study proposes to introduce a low-cost test method to compare the polymeric materials and choose the best one for future purposes with the environmental circumstances in mind for materials to have a good service life.

During the thesis project, ABS and PC/ABS samples were tested for environmental stress cracking to compare the strained materials against PEG 400 and an assembly fluid chemicals. These tests were conducted at three different temperature levels. Differential Scanning Calorimetry (DSC) was used to verify the polymeric materials, samples were made of. Optical microscope and FTIR were employed to analyze the samples for crazes / cracks and degradation of material respectively.

The results obtained were that the chemicals used are highly aggressive for these materials and should be avoided. The materials when compared showed that polymeric blends of PC/ABS are more resistant to ABS materials

Keywords: ABS, PC/ABS, Environmental Stress Cracking (ESC), Interior Polymers, FTIR, DSC, Optical Microscope

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List of Acronyms and Abbreviations

This document requires readers to be familiar with terms and concepts related to Environmental Stress Cracking of Polymers. For clarity they are summarized with a short description of them before presenting them in next sections.

ABS	Acrylonitrile Butadiene Styrene Polymer
DMTA	Dynamic Mechanical Thermal Analysis
DPM	Dipropylene Glycol Methyl Ether
DSC	Differential Scanning Calorimetry
ESC	Environmental Stress Cracking
ESCR	Environmental Stress Cracking Resistance
FMCG	Fast - Moving Consumer Goods
FNCT	Full Notched Creep Test
FRP	Fibre Reinforced Polymers
FTIR	Fourier - Transform Infrared Spectroscopy
HDPE	High Density Polyethylene
HIPS	High Impact Polystyrene
HSP	Hansen's Solubility Parameter
ISO	International Standards Organization
MEK	Methyl Ethyl Ketone (Butanone)
MH	Micro Hardness
MVR	Melt Volume Flow Rate

NCTL	Single Point Notched Constant Tensile Load
PBT	Polybutylene Terephthalate
PC/ABS	Polycarbonate / Acrylonitrile Butadiene Styrene Polymer
PE	Polyethylene
PEEK	Poly (ether ether ketone)
PEG	Polyethylene Glycol
PEI	Polyethylenimine
PENT	Polyethylene Notched Tensile Test
PET	Polyethene Terephthalate
PMMA	Poly(methyl methacrylate)
POM	Poly(oxymethylene)
PP	Polypropylene
PPG	Polypropylene Glycol
PPO	Poly(p-phenylene oxide)
PUR	Polyurethane
PS	Polystyrene
PSF	Polysulfone
PVC	Poly (vinyl Chloride)
PVF	Poly (vinyl Fluoride)
RED	Relative Energy Difference
SAE	Society of Automotive Engineers
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscope
Tg	Glass Transition Temperature
VCC	Volvo Car Corporation

Chapter 1

Introduction

1.1 Background

Over the last few years, in the automotive industry, there has been a rise in the use of polymers in the car. With this rise, the problems occurring in these polymeric parts has also risen. Most common problems faced are of plastic parts failing and cracking. These factors include temperature they are exposed to, stresses applied on them, the chemicals which then come in contact with while manufacturing, assembly or accidentally spilled on them by customers, or a combination of them. These factors causes plastic parts to show crazes and cracks and fail under harsh circumstances.

Polymers are of huge importance in building a car as the most of the interior parts like glove box, dashboard, mats, seats, gearbox, door panels, etc. and some exterior parts also, like the bumpers, head and tail lamps are made of different polymers or composites. Today, they are also used for engine covers and fuel tank and many more areas in the car, which not only helps reduce the construction cost of the car, but also reduces the overall weight of the car , thus making the car more fuel efficient. Now stronger polymers like glass fibre composites, fibre reinforced polymers (FRPs) and Carbon fibres are being applied in the industry to make the materials stronger apart from being light in weight.

There are variety of polymers and their composites used in this industry. The polymers range from polyethylene for packaging, to ABS and PC/ABS in the interior parts, then different kind of textiles for mats or poly(vinyl chloride) (PVC) for non - leather seats. PMMA and PC are also used for making head and tail lamps because of the optical properties of amorphous polymers like PMMA. FRPs and carbon fibres are nowadays used in the exterior parts or the side pillars of the cars to give them more strength. Other commonly used polymers are polyurethane (PUR) in the form of foams in the seats, polyesters in various textile parts of the car, polypropylene (PP) for engine covers, fuel tanks and many other polymers in different areas.

1.2 Problem description

In the recent years, the car industry has been moving at a fast pace towards the use of polymers and lightweight composites, transitioning from metals and alloys which are heavier. On one side they reduce the weight, cost and increase the fuel economy, but on the other side polymers or composites / compounds of different polymers can be countless, which makes it difficult to know exact properties of each material and their interactions with every type of chemical beforehand from theory. Thus, many times the tests conducted give totally new results by trial and error method based on the type of polymer or composites with different composition.

The polymer can fail and crack when they come in contact with chemical that they are sensitive to and in different conditions like temperature and over a certain period of time when there is stress applied. These cracked polymeric parts cannot then be used, so they add to the waste cost, but also, it can destroy the material if many parts start to crack. The strength, and the appearance and thus value of the object is reduced. Therefore, there is a need to address this problem and avoid or solve the problem of cracks and failure in the material for its long life.

During the assembling of a car, a part made of PC/ABS cracked overnight when it came in contact with the assembly aid chemical, where there was stress applied on the material. The materials was sent for investigation of the cracks to the laboratory. After the investigation was complete, it was found that the material failed and cracked due to environmental stress cracking with the combination of chemical and stress applied on it. Changing the process aid chemical and conditions reduced the failure of the material. It was still important to study about the root causes for it, the material and chemicals which could be avoided and the ones that could be used as well as the conditions under which the materials fail, also measuring the time to failure. This would help understand the problem in depth and eventually help in solving the issue.



Figure 1.1: ESC occurred in a part of a car

1.3 Purpose

This thesis project evaluates how different factors such as stress applied, temperature and chemicals affect a polymeric material which are used in the interiors of the car (ABS or PC/ABS) and how much time it takes for these materials, under certain test conditions, to crack or have crazes in them and fail. The purpose of the thesis project is to study *Environmental Stress Cracking* of ABS and PC/ABS and qualitatively analyze them under microscopy to compare the materials under fixed conditions and with the selected chemicals at the chosen conditions of temperature and stress and strain applied on the materials. This study can then help to check which material or grade of polymer could be a better alternative out of all these for manufacturing of the car parts.

Chapter 2

Theory

2.1 What is Environmental Stress Cracking?

Environmental Stress Cracking (ESC) is a phenomenon observed in materials - metals and polymers when the crack, crazes or embrittlement initiates and propagates in the material prematurely due to a combination of various factors which include the type of material, the stress applied on the material, the chemicals with which the material is in contact, the temperature of the environment [1].

ESC of plastics is a concept observed in thermoplastic polymers especially in amorphous polymers, for example - Polycarbonate (PC), Polymethylmethacrylate (PMMA), PPO, Acrylonitrile Butadiene Styrene (ABS), Polystyrene (PS), etc. Although, it can also occur in crystalline polymers like Polyethylene (PE) but in general, higher the crystallinity of polymers, the more resistant to ESC are the materials [2]. The amorphous polymers are more vulnerable to environmental stress cracking than semi-crystalline polymers because of the structure of amorphous polymers. Amorphous polymers have more free volume as compared to the more ordered structure of semi-crystalline. ESC accounts for 15 - 30 % of plastic component failure [3]. Because of its severity, it is also termed as "Plastic Killer" [3]. Therefore, study of ESC is important for the selection of better materials, usage of chemicals and environmental conditions compatible with the material selected.

ESC process in polymers is a very complicated process because of involvement of various factors which influence the process. These factors include stress on the material which can be external stress and / or residual stress, type of chemical solvent which comes in contact with the material, morphology of the material, the environmental conditions like temperature at which the material experiences the above factors and the duration for which these factors have an impact on the material. Thus, the synergistic effect of these all factors causes Environmental Stress Cracking and makes this phenomenon complicated [4].

2.1.1 Characteristics of ESC

Some characteristics which proves the ESC phenomenon are that ESC of materials is caused by action of chemicals, stress, temperature and aging time on the materials, all or some in a cumulative way which accelerates the cracking process. And the cracks in the material experiencing ESC occurs as brittle fracture and in the elastic region before the material reaches the yield point. That is, the stress applied during this time is lower than the stress of the material at yield point. Most of the times chemicals which cause ESC of materials are secondary chemicals, that is, the chemicals which are used with the materials after their manufacturing [1].

Another characteristic of ESC is that the polymeric material doesn't undergo chemical changes like new bonds formation or change in morphology in the material when the chemical attacks the material. There is only breaking of the existing bonds due to which fracture of material occurs. Also amorphous polymers are more susceptible to Environmental Stress Cracking than crystalline polymers because of greater free volume in amorphous polymers. Thus Environmental Stress Cracking Resistance (ESCR) is directly proportional to degree of crystallinity. ESCR is also directly proportional to the molecular weight of the chemical attacking the polymer because larger the chemical, more difficult it is for it to enter the free volume of the material [1].

The tensile stress applied on the material generally creates molecular disentanglements which lead to ESC. Thus, the material will not experience ESC when compressive stress is applied [1].

Regarding chemicals which causes ESC, fluids with moderate hydrogen bonding like organic fluids (aromatic hydrocarbons, halogenated hydrocarbons, ethers, ketones, aldehydes, esters, etc.) are more likely to be severe stress cracking agents than non hydrogen bonded fluids like aliphatic hydrocarbons and highly hydrogen bonded compounds like water or alcohol due to the solubility compatibility of the compounds with the materials [1]. Fluids are most aggressive at temperature near their boiling point and thus liquid nitrogen which has a boiling point of $-196\text{ }^{\circ}\text{C}$ is a stress cracking fluid for many plastics [1].

The figure below shows the stress vs. strain curve (Hooke's law) for polymers where the first straight diagonal line represents the elastic region. In this region, stress applied on the material is proportional to the strain experienced on the material. Here, when the stress is released, the material gets back to the original shape to what it was when there was no stress applied. Then after a certain stress, there comes a point, when the material gets permanently strained and cannot get back to its original shape after relaxation of stress. This point is called the yield point. Further, increasing the stress, the strain on the material increases till a point, where crack develops in the material and eventually breaks. That is the point of necking and ultimately fracture stress.

So, according to the theory of ESC, the stress applied on the material should be below yield point and preferably in the lower or the middle part of the elastic region.

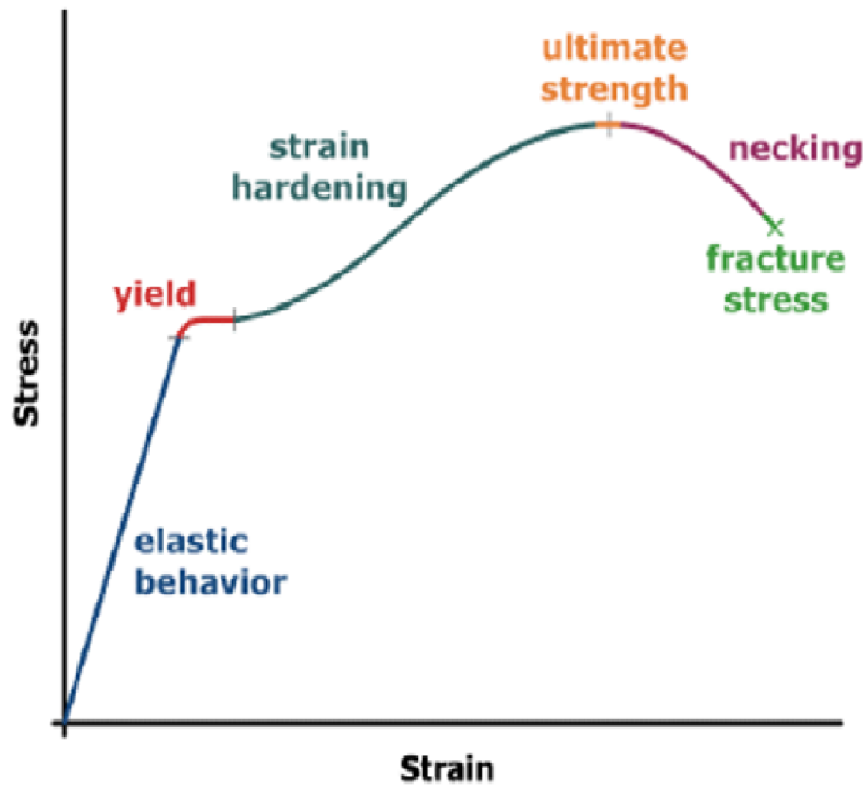


Figure 2.1: Hooke's Law (stress vs. strain curve) for polymers [5]

2.1.2 Examples of ESC

The effect of Environmental stress cracking of plastics can be little, and it can have adverse effects on the materials which can be really dangerous. Some examples of ESC in real life are as follows:-

a) Motorcycle helmets which were produced from injection moulded PC experienced cracks, the reason found for this was the adhesives from the stickers pasted on the helmets and this can prove to be dangerous [1].



Figure 2.2: Cracked Helmet
[6]

b) Polyvinyl Chloride (PVC) pipes failed when they were fixed at the cement bonded joints because of the solvents present in the cement [1].



Figure 2.3: Cracked Pipe due to stress and fluid

c) Babies feeding bottles made from PC cracked when they came in contact with insect spray [1].

d) Polyethylene packaging has failed in the past due to the silicone oil on o-seal [1].

e) ABS appliance consoled have undergone ESC because of the migration of platicizer from PVC wire insulation [1].

f) Plastics have cracked under stress when they have come in contact with the vapors of rust inhibitor which were used on the metal parts kept close to the plastic parts. [1]

g) Automotive polymer parts made from ABS and PC/ABS have cracked under stress when they have come in contact with fluids which are used during the construction of the car or the chemicals used by the customers [1].

There are many more examples of ESC and some of them can be reduced using different ways which will be discussed later in the chapter.



Figure 2.4: Cracked Material
[7]

2.2 Sources or Factors of ESC

Generally, when stress is applied on the polymeric material, it follows Hooke's law and is initially in the elastic region where, the material regains its shape and size after the stress applied is removed. At certain stress, the material reaches a yield point after which there is a transition from elastic region to plastic region and in this region the material does not regain its original shape and size when the stress is removed. There

is a permanent deformation in this region. Finally, the material undergoes breakage or ductile fracture.

But, due to some factors the cracking and crazing in the material occurs in the elastic region, before the material reaches its yield point. These factors accelerate the cracking / crazing of the material. And this is Environmental Stress Cracking. The factors or the sources due to which the material experiences ESC are as follows:-

2.2.1 Type of Material

Rate of ESC depends on the type of material being used. As mentioned above amorphous polymers are more vulnerable to stress cracking than semi-crystalline or crystalline polymers because of the greater free volume in amorphous polymers compared to semi-crystalline or crystalline polymers which are more ordered and thus tightly packed. This helps in slowing down the ESC because then the chemical agents can not be absorbed easily in the material and also stress to be applied for the material to fail is greater. Also, increasing the crosslinking of the materials will decrease the risk of materials failing because it reduces the voids or the free space in the material and also because it's difficult to disentangle the material, making it stiffer [3].

The material with higher levels of crystallinity and higher specific gravity has more resistance to environmental stress cracking.

Within the material selected, the resistance of ESC reduces with decrease in the molecular weight of the material. The reason for this is that with increase in molecular weight of the resin of the plastic material selected, the entanglements increase in the material [3].

The type of the material selected also affects the rate of ESC because of their compatibility with the chemicals which are in contact with them and also different materials have different stress levels to reach their respective yield point.

2.2.2 Chemical agent

In Environmental Stress Cracking of plastics, the fluids do not chemically attack and degrade the plastic by processes like oxidation, hydrolysis, etc. that lead to chemical modification. Instead, the fluids in ESC, promote cracking through physical processes, that is, fluids are absorbed within the free space (micro-yielded or stress dilated zones) which plasticizes the polymer and in turn decreases the yield strength. The greater is the concentration of the fluid, lower is the yield strength. Thus, these fluids only embrittle the plastic in presence of stress [1].

As mentioned earlier in 2.1.1, fluids that have moderate level of hydrogen bonding are more aggressive to materials in ESC than chemicals with extreme levels of hydrogen bonding. Thus chemicals like organic esters, ketones, aldehydes, aromatic hydrocarbons are more severe than organic alcohols and aliphatic hydrocarbons. The reason for this

could be the solubility compatibility between the material and the chemical and also the size of the molecule.

Lower molecular weight chemicals are more aggressive towards the material during ESC than high molecular weight chemicals because it's easier for smaller sized molecules to permeate into the molecular structure of polymer than larger molecules. Therefore, for example, silicone oil is a more severe ESC agent than silicone grease [3].

Most fluids have a tendency to get absorbed in plastics and open up the voids more, making it more susceptible to cracking compared to air. The fluids can be classified as mild, moderate and severe. Chemical agents that are absorbed by a plastic in a short period by simply immersing the plastic in that chemical may come under severe ESC agent category. These chemicals have high solubility or compatibility with the materials. For example, MEK is absorbed rapidly by PMMA decreasing the strength and hardness. This can also be studied by solubility parameters theory and finding the solubility parameters of the chemical with the material. But that doesn't mean that all chemicals which have high solubility are severe stress cracking agents. For example, DPM is a severe ESC agent for ABS, but not when immersed simply for a short period without stress applied. Moderate ESC agents are those which lead to cracking of the material when the material is immersed in the chemical with stress applied. The chemicals can be highly compatible but the material will only break when stress is applied. Then apart from compatibility of the chemical with the material, cracking also depends on the level of stress or strain applied. The remaining chemicals would be classified as mild ESC agents because, mild category is difficult to interpret because the reduction in time span by same time by a fluid can be dangerous for one material, and can be fine for one [1].

There have been studies done by for example Bernier and Kambour which shows the proportionality of the magnitude of the stress cracking with solubility parameters of the chemicals with the material [2].

Also, chemicals can be classified as primary fluid and secondary fluids for ESC. Primary fluids are those fluids that are used while manufacturing or processing of the material. Whereas, secondary fluids are those which are used by the customers after the product is ready like paints, adhesives, lubricants, etc. Since the compatibility of primary fluids with the material has been studied beforehand so as to select the right material and fluid, there are less chances of failure by primary fluids compared to secondary ones.

2.2.3 Stress applied

A ductile polymer which is stressed will fail ultimately via static fatigue or creep rupture. The time for failure will increase as the levels of stress applied is decreased but at lowers levels of stress, the cracking process can be accelerated by other factors like attack by chemicals, temperature, etc. So, when high stress is applied, high density of locally yielded sites are generated which grow and multiply and finally coalesce

and crack with time. Thus, with or without other factors, the material will undergo early ductile failure under high stress, whereas, when under low stress, material will experience a slow or late brittle failure [1].

Taking other factors into consideration, and the effect they might have on the stress applied and consequently on ESC, it can be observed that, yield stress and yield strain of the material decrease when the temperature is increased and at T_g , both becomes zero. Yield stress also increases with strain rate. Yield stress is proportional to annealing and inversely proportional to plasticization [1].

For cracks to develop in the material, type of stress is also important. When tensile stress is applied, the material will tend to undergo cracking, but on the other hand, if compression stress is applied, there will be no cracks or crazes developed on the material. Because, these tensile stress will create molecular disentanglements which will lead to ESC failure, whereas, compressive stress can subject the material to mechanical failure, but that failure would not be accounted as Environmental Stress Cracking [3].

Also, there are two types of stresses which contribute towards ESC. Firstly, external stresses, which are applied externally on the material due to some loads on the material or stretching of the material. The other one is, residual stress, which is the type of stress present in the material due to manufacturing process. Both of these stresses combine to have a cumulative effect of ESC on the material [3].

2.2.4 Temperature

The effect of temperature on materials for ESC is complex. When material is subject to annealing temperature, the free volume of the material decreases which in turn increases the resistance to the stress cracking. But increasing the temperature further, the material will undergo thermal degradation due to acceleration in viscoelastic processes which cause yielding and cracking [1].

According to D. C. Wright [1], increasing the temperature, the stress and strain rate that initiates ESC would decrease, thus accelerating the cracking process in the material.

2.2.5 Aging of the material

According to D. C. Wright in his book Environmental Stress Cracking of Plastics, 'physical aging due to densification of the material with time has similar effect as of annealing. It decreases free volume and thus increases the stress cracking resistance. Aging develops with time at a rate that increases with temperature.' [1]

Physical aging has a close relation with temperature. Sub- T_g annealing, that is, annealing that takes place below glass transition temperature (T_g) can accelerate the physical aging process by increasing the annealing temperature and/or annealing time. When physical aging of the polymer is compared between aging at room temperature

and aging at sub-T_g annealing, sub-T_g annealing will increase the testing time for the material to show cracks or crazes. But sub-T_g annealing also leads to some changes in micro-structure like increase in number of inter-chain locking sites, which may take longer to develop at room temperature aging. The increase in these entanglements will increase Environmental Stress Cracking Resistance (ESCR) [4].

Environmental Stress Cracking is not caused by a single factor. But the synergistic effect of these factors contribute towards the stress cracking phenomenon. Cyclic loading also contribute to ESC apart from other factors and it can accelerate the fracture in the polymeric material. But apart from that, when chemicals which are compatible with the material are in contact with the material at certain stress and strain levels and temperature will have an effect on the material according to the material's morphology. Thus, deducing effect of individual factors for cracking is easier than deducing the cumulative effect of all the factors, because then it will be a complex and tedious scenario. Therefore, there cannot be a trend for all the factors acting at once on the material to check environmental stress cracking.

2.3 Mechanism of Environmental Stress Cracking

Environmental Stress Cracking is a phenomenon in which the factors discussed above in section 2.2 acts in a cumulative way, having their own individual effects which adds up and ends up cracking or fracturing the material. But the concept of environmental stress cracking of polymers is slightly different from polymer degradation or plastic deformation / yielding or even creep rupture.

With respect to ESC, bulk properties of the material for example stiffness and strength are not affected and only the surface in contact is affected, not the whole material. The cracks which occur when the material undergoes ESC initiates at localized area of stress concentration like design corners, notch defects, surface scratch or crack occurring from the start.

Creep rupture is defined as cracking of a plastic material as a response to stress that occurs through disentanglement of polymer chains overcoming inter-molecular forces like van der Waals forces, hydrogen bonding between polymer chains. Creep rupture of polymeric materials is also influenced by temperature, cyclic loading, fatigue, stress concentration, etc. These factors have a proportional effect of the creep rupture of the material. The same factors also have an influence on ESC of the material. Creep rupture can also be seen as stress cracking of plastic in presence of air and in absence of chemical. In ESC, chemical agent permeates into the molecular structure interfering with the inter-molecular forces bonding the polymer chains, therefore accelerating the polymer disentanglement. This reduces the energy to crack the polymer. Chemical accelerates the stress cracking, thus both of them - creep rupture and ESC are parallel

failure mechanisms.

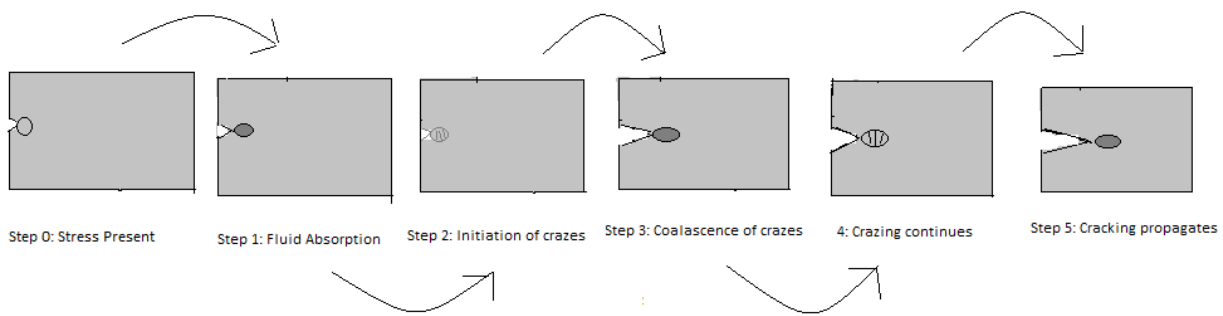
In plastic deformation failure of the materials, the material undergoes increase in stress until it reaches yield point of the material and the material transits from brittle or elastic region to ductile or plastic region and with further stress applied, the material deforms permanently before fracturing, whereas, in the case of ESC, the stress applied on the material is always under the yield stress and the material experiences brittle fracture after a long time or due to additional factors like chemicals, temperature variation or cyclic loading to name a few.

According to the theory of polymer degradation, the polymeric material when under stress or influence of factors like temperature or chemical degrades chemically and the polymeric bonds break. But in ESC, as mentioned earlier, the bonds of the material do not break or the material doesn't degrade chemically (no chemical reaction between polymer and chemical), here the secondary linkages between polymers break or disentangles due to free volumes being attacked by the chemicals and thus disentangling of linkages occurs eventually causing cracking or crazing of the material. In ESC, mechanical stress causes minute cracks and then these minute cracks propagate under harsh environmental conditions which finally lead to cracking of the whole material.

Environmental Stress Cracking of polymers takes place through chemical agent entering the free volume with the action of other environmental conditions and disentangling the linkages between the molecules, which gives rise to a crack and eventually a continuous crack growth occurs which leads to step wise progressive mechanism of cracking and failure depending on the different factors discussed in sec 2.2 [3].

In ESC, liquids or chemical agents diffuse into polymers which cause swelling and in turn lead to chain mobility. This results in decrease of yield stress and glass transition temperature (T_g) causing plasticization of the material leading to crazing at lower stress and strain. The liquid or the chemical agent reduces the energy required to create new surfaces in polymer by wetting the polymer surface and hence aiding the void formation, which can be important in the early stages of craze formation.

The figure below shows a description of the mechanism of ESC in five different steps. Where in the first step, the fluid gets adsorbed in the free space of the material which causes swelling of the void space and thus crazes initiates. Then different crazes which are formed coalesce and eventually lead to crack in the material.



of ESC.png

Figure 2.5: Mechanism of ESC
[3]

2.4 Importance of study of ESC

Environmental Stress Cracking of Materials is a very hot topic today because of the various industries experiencing this problem which makes their products short lived and the industries also face economical problems due to this apart from the reputation which goes down to the regular complaints they get from their customers. That's why a lot of work is done in this area.

Since most of the industries (if not all) work with materials, be it metals or polymers, they have the issue of stress cracking at some point and to resolve this a lot of research is going on currently on this subject. Stress Cracking has been the reason for 15 - 25 % of all plastic failures [3]. The topic of Environmental Stress Cracking of polymers has almost now been researched for 40 - 50 years. But since the research on this is vast and extensive due to infinite number of materials, with infinitely different chemicals at various environmental conditions, the research cannot be deduced from the results gathered till now, because every combination of chemical, material and environmental condition would have a different effect than others.

Different materials have different applications and can be used in various industries to produce a variety of products. During manufacturing of these products or even the use of these materials by customers, there can be use of different chemical agents at unknown conditions which can fracture the material. Thus, it is important to know which fluids can be used during manufacturing and during the end use by customers with the information of other conditions at which the material will not fail.

Aerospace, automotive, packaging industry are among few industries which get affected by the cracking of their polymeric materials. These industries are specifically important in this respect because of the wide use of amorphous polymers in the products.

Some other industries which can be affected by these cracking of polymeric materials could be the toy industries, sports industries, FMCG industries, medical industries, etc. Since the topic of thesis is ESC of interior polymers specifically ABS and PC/ABS used in the car, the following is a discussion of ESC in the automotive industry.



in a glass (PMMA).png

Figure 2.6: ESC in PMMA glass
[8]



Figure 2.7: Cracked Cover
[9]

2.4.1 ESC in Automotive Industry

Thermoplastic materials are extensively used in automotive components like door handles, dashboards, interior trims, seats, gear boxes, instrument panels, tunnel consoles, etc. Interiors of automotive are especially surrounded by a lot of plastic materials used for decorative to structural to functional purposes. For these components, extensive testing is done to find the right material which can be used for each component and this material selection depends on the end use conditions of these components when assembled together in a car or even while assembling, so that these materials shouldn't fail in even the extreme scenarios. Therefore, there are various tests developed for each part to link the test as close as possible to the reality. These tests include aging tests and mechanical tests to name a few.

One of the important things while testing these components is also to check the compatibility with different chemicals, lubricants, processing aids, etc. so that those fluids can be used which do not cause any harm to the material, or to use those materials which are resistant to the risk of failing when coming in contact with these chemicals. The chemicals can range from sunscreen to drinks like coffee which can be spilled over in the car by customers. Examples of lubricants can be different oils and polishes used to remove scratches or make the materials shine. And different assembly aids, acids, soaps for cleaning could be some probable processing aids. These fluids could cause damage to the material. The use of different fluids at certain environmental conditions and at point on material where the stress is applied already can break the materials. The limitation in this case is that there are a lot of chemicals which can come in contact with these materials, thus for sake of simplicity, obvious or the most commonly used chemicals are tested or else, the testing of the material won't end. Another problem with respect to this is that there are no standard chemicals defined and therefore, it is free for the different industries to select different chemicals which they think could be important for the tests.

Automotive components are often made of amorphous polymers like ABS, PC, composites of different ratios of PC and ABS, semi-crystalline polymers like POM, PMMA, HDPE and PP. These all polymers are susceptible to Environmental Stress Cracking (ESC). For example, interior parts like Instrument panels, tunnel consoles, etc. are made of ABS or PC/ABS and exterior parts like tail and head lamps are made of PC or PMMA. This cracking can be observed without chemicals (in presence of air), but chemicals accelerate the cracking process. Although the results from different tests to study ESC cannot be quantified, a trend could be observed, which also could be helpful to select best combinations of material and chemical at the applicable conditions according to applications. Also, PC is known to be highly sensitive with respect to ESC [10].

According to the paper **SAE'11** [11], sunscreen contains various chemicals which can cause cracking in PC. These chemicals could be aromatic esters, ketones, amines

found in the sunscreen used. The authors of this paper also thought that the degradation or cracking occurs through swelling followed by craze formation or softening and finally chain scission at elevated temperatures. They also observed that amorphous thermoplastic polyesters were better ESC resistant materials when compared to PC at higher stress levels and for various cleaning agents. According to the authors, sunscreen permeates through the paint which acts as a barrier layer to the polymeric materials, and the reason for the failure of these polymeric materials could be due to this diffusion.



Figure 2.8: ESC in car radiator pipe
[12]



Figure 2.9: ESC in car

2.5 Environmental Stress Cracking Resistance (ESCR)

Environmental Stress Cracking Resistance is an ability of the materials to resist fracture or cracking process to attain materials with longer life and better properties. ESCR can ensure reduction in the cost of wastage, production and repair of the products due to the failures in these materials.

There can be several approaches that can be taken to reduce Environmental Stress Cracking. Some of them are as follows [2]:-

1. Environmental Stress Cracking can be reduced by choosing appropriate polymeric material according to the environment in which they will be applied. That means, choosing a material which can withstand the chemicals which will be used or other factors like temperature and stress which will be applied.
2. Polymer morphology, molecular weight and its distribution also has an important effect on ESC resistance. Increasing the molecular weight of the polymer could increase the environmental stress cracking resistance [13]. And in general, narrow molecular weight distributed polymers have poorer ESCR compared to broader molecular weight distributed polymers when other variables are constant. Also, a general rule of thumb is that, with increase in branching of the polymer, there is an increase in the ESCR of the polymer. Therefore, as density decreases, ESCR increases [14].
3. Another approach can be choosing a chemical during assembling or manufacturing of the material that won't initiate the cracking process in the material. This can also be measured by Hansen's solubility parameter calculation (described later) to check the compatibility between chemical and the material. Increasing the difference between solubility parameter of polymer and chemical will increase ESCR. Another method to check the compatibility between fluids and the polymer could be by use of various standard test methods. These test methods will be discussed later. Apart from this, chemical concentration may also affect stress cracking of the material. Chemical concentration in general may be directly proportional to the rate of stress cracking [14].
4. There are also evidences showing that higher the test environment temperature, the faster is ESC rate and hence lower temperature levels are better for ESCR [14].
5. Decreasing stress applied on the material decreases the rate of ESC of the material. [14]
6. Crosslinked or crystalline polymers can provide better resistance to environmental stress cracking than glassy / amorphous polymers.

7. Environmental Stress Cracking Resistance can be increased by employing polymer blends. Adding crystalline polymers to amorphous polymers in a proper ratio can increase ESCR. According to L. M. Robeson [2], ESCR was increased for miscible blend of amorphous PEI with crystalline PEEK compared to pure PEI. Similarly, improvement in ESCR was seen when crystalline and miscible Polyvinyl Fluoride (PVF) was added to amorphous PMMA. In automotive application polymer blends have shown improvement in resistance to cracking when exposed to gasoline, oil, and other lubricants. Some examples of polymer blends used in automotive industry are Noryl GTX (PPO/nylon 6,6), Xenoy (PC/PBT), Germax (PPO/PBT), Triax (ABS/nylon 6), Elemid (ABS/nylon 6,6), fiberglass reinforced PSF/PET and many more. Also, amorphous polymer blends like PC/ABS are also used to increase the cracking resistance.
8. Another technique to increase ESCR can be the application of fibre reinforcement in the materials. Fiber reinforcements can bridge the cracks and crazes which can develop on the surfaces and can help in preventing easy propagation of these cracks. Example of this was seen in fiber reinforced polystyrene (PS) requiring more stress in presence of acetone to crack compared to PS with no fiber reinforcement according to L. M. Robeson. Another example is fiber reinforced PSF being a better material compared to other materials in automotive industry for spring loaded safety interlock device. Also according to M. N. Bureau, et. al. when accommodating glass fibers in the materials, the lower cooling rate will lead to fibers being free of amorphous phase and thus having higher crystallinity [15].
9. Impact modification mostly with rubber can increase ESCR of the material because, rubber impact modified material can withstand higher stress and more chemicals. But rubber particle size has an important influence on the ESCR of the material. Material with larger rubber particles has better ESCR properties than materials with smaller rubber particles but to an extent, after which increasing the size of rubber particles decrease the ESCR. The limit in size observed was 6 micrometer. Due to rubber modification, there is decrease in modulus and thus decrease in surface stress at constant strain compared to materials without rubber modification. And rubber modification also helps in stabilizing the surface crazing that may have occurred. There have been evidences of rubber modification increasing ESCR in polystyrene (PS), ABS, PC, etc. Adding thermoplastic polyurethanes or hydrogenated styrene-butadiene-styrene block copolymer to PC has also been seen to improve ESCR and impact strength [2].
10. Different parameters of manufacturing process can also have various effects on ESCR of the material. The design of the material, injection moulding, whether the material has sharp edges or not, temperature of manufacturing process, injection

molding cycle time, rate of quenching, etc. are some variables effecting the ESCR of the material. For example, if the material has sharp edges, there is a higher probability of that material to show cracks because those sharp edges could initiate and propagate cracks faster. Processing temperature and molding pressure also can affect the ESCR of the material. Due to these variables, there can be changes in the crystal morphology and surface defects and thus affecting ESC [16].

11. There is also evidence which shows that lower the melt volume - flow rate (MVR) value, the more resistant is the material. Base oil viscosity also has an effect on the ESC of the material. [10]
12. Polymers with more chain entanglements have better ESC resistance. The number of chain entanglements is influenced by chain length. Larger chains have more entanglement than shorter chains. Also, less mobile chains would take longer to be disentangled. Polymer with larger chain having better ESCR also confirms that higher molecular weight polymer has increased ESCR [17].
13. According to J. J. Cheng et. al. "A tough polymer has superior brittle crack resistance" [17]. And according to Rao et. al. [18] it was proposed recently that toughness of semi-crystalline polymer films depends on inter-connectivity of their crystalline and amorphous phase.

The above mentioned points are some of the ways to increase environmental stress cracking resistance of the materials.

2.6 Hansen's Solubility Parameter Calculation for Prediction of ESC

Environmental Stress Cracking can be predicted by theoretical models describing how a material react to chemicals and this way, it will be faster and easier than testing all the combination to check for failure. The miscibility of polymeric materials to chemicals can be determined by Hansen's solubility parameters. According to C. M Hansen [19], polymer dissolves in chemical when there is higher degree of absorption. But, lower degree of absorption can make the materials plasticized and sometimes susceptible to ESC. With known Hansen's Solubility Parameter (HSP) of many polymers and chemicals, a correlation can be obtained between HSP and ESC to considerable accuracy. According to this theory, the closer the solubility parameter of the polymeric material is to the solubility parameter of the chemical, more are the chances of polymeric material failing in presence of the chemical. That is, in other words, increase in the value of $|\delta_p - \delta_s|$ will increase the ESCR of the polymeric material

to the chemical. Here, δ_p and δ_s are the solubility parameters of the polymer and chemical solution respectively [2]. According to C. M Hansen [19], Relative Energy Difference (RED) values can be used for correlation with ESC. Higher values of RED will correspond to lower degree of absorption since RED also tells about the difference in solubility parameters, but also including dispersive, polar and hydrogen bonding phases [19].

$$RED = \frac{R_a}{R_o} \quad (2.1)$$

where, R_o is the interaction radius that indicates maximum difference in affinity tolerable for solution. That means, the nearer the two molecules are in 3D space, more likely they are to dissolve into each other.

$$R_a^2 = 4(\delta_{D_1} - \delta_{D_2})^2 + (\delta_{P_1} - \delta_{P_2})^2 + (\delta_{H_1} - \delta_{H_2})^2 \quad (2.2)$$

where; D, P, H = dispersive, polar, hydrogen bonding phase respectively
1, 2 = polymer, chemical respectively

But, there are some limitations of this approach. When, Mai studied ESC of mixtures of miscible solvent pairs to check if rule of mixtures can be applied, it showed poor correlation of solubility parameters for mixtures to ESC, because ideally, according to theory, mixtures should be a more aggressive ESC agent than individual components [20] [2]. Another limitation to this approach is that it only tells about the compatibility of polymer with the chemical, but doesn't really tell about stress cracking when comparing same materials for testing conditions.

2.7 Different Test Methods for ESC

There are various ways in which Environmental Stress Cracking of a polymeric material can be checked with a specific fluid. But, at the same time it is difficult to have a trend which can be followed because of different properties of every polymer and the difference in how they behave when exposed to different fluids. And since there are a lot of generic polymers and tens of thousands of chemicals, it is difficult to have past experimental data on every combination. Therefore, either some testing methods are used to obtain an experimental data for a certain chemical and polymer or ESC is predicted using solubility parameters.

Hansen's solubility parameters of polymers and chemicals obtained from literature can be used to predict Environmental Stress Cracking for that particular combination, concluding the severity with which a chemical can attack that polymer. But the data obtained is not very reliable because partial solubility parameters cannot be measured for polymers at all and without accuracy for fluids, which is an important parameter for both chemical and polymer. This was proved when further testing were done and the

results were compared with the results obtained from prediction of ESC using solubility parameters [21].

Thus, it was important to obtain data for using physical experimental methods which can give more accurate results under the applied conditions. Therefore, different standard methods were developed for Environmental Stress Cracking of polymeric materials which are discussed further in this section.

2.7.1 Method I - Constant Tensile Load Method (Constant Stress Method)

Constant Tensile Load Method is a method to determine environmental stress cracking of thermoplastic polymers according to the standard ISO 22088-2:2006(E) [22]. The thermoplastic polymers according to this method are subjected to constant load in the presence of chemical agents. This standard method can be applied to those samples which are prepared by moulding and / or machining. This test is a qualitative test and cannot provide any data for design calculation.

Principle: According to this method, the test specimen is subjected to constant tensile load corresponding to the stress applied on the specimen. It is lower than the yield stress. The specimen is simultaneously kept immersed in a chemical agent against which the environmental stress cracking is to be analyzed for the material. The set-up is kept at a specific temperature. And then, the time and / or stress for specimen to break is recorded. One of these conditions - chemical agent, temperature, or the material can be varied while keeping other two constant for obtaining a data matrix to compare different materials or the same material when exposed to different conditions.

According to the ISO standard, ESC of test specimens can be determined by one of the following methods:-

1. **Method A:** Determination of the tensile stress leading to rupture at 100 hours. The stress is obtained by interpolation of graph of time to rupture versus tensile stress. Number of tests can be performed with different tensile stress and then the results can be analyzed. But the tensile stress should always be lower than the yield stress.
2. **Method B:** Determination of time to rupture when the specimen is under a specified tensile stress. This method is applied when the time to rupture exceeds 100 hours.
3. **Method C:** Determination of time to rupture for a series of applied stress. The graph of time to rupture versus applied stress is then analyzed.

The ISO standard states that if the chemical agent is a liquid at the test temperature, then the sample should be completely dipped in it but if it is highly viscous at the

temperature the material is being tested, then the specimen should be covered with a coating of the chemical of at least 2mm thick. Constant tensile load can be applied by attaching weights to one end of the material. The sample specimen should be prepared in the dumbbell shape to avoid the cracking of the material at the edges or corners and to avoid initiation of any defects from the edges too [22]

Some of the variations or modifications of this method set-up used today are as follows:-

1. **Three point bending set up:** In this variation a sample which is balanced on two points at the end of each side is bent by a constant load on the center point of the specimen. The set up is such that the specimen is immersed in the chemical and is kept at a constant temperature. Using this set up, time can be measured till the sample breaks. A series of tests can be run changing either the load, or the chemical or the material, or even the temperature to obtain a data matrix. Since the crazes occurs on the center part of the specimen, the width of the crazing zone increases with increase in the strain at that part of the material. But in constant strain testing method (discussed in section 2.6.2), the damage zone occurs on the along the specimen and thus, there is no relationship between the width of the damage zone and the strain level [21].

This three point bending set up can also be used in the constant strain method, which will be discussed later, where the specimen is subjected to a constant strain using a similar but a little modified set-up of this where the stress is not constant and is thus not measured.

2. **Single Point Notched Constant Tensile Load (NCTL) Test:** According to [15] this test is popular in the US. In this method, a single notch of depth 20% of sample thickness is made. Everything else is similar to the standard test and time is recorded for the notch to propagate and material to crack finally. According to this paper, the typical conditions used are 50°C in a 10% igepal solution with a load of 30% of the sample's yield stress is applied. But, the conditions can be varied until the sample approaches its Tg or the chemical agent is not affected by the temperature change. The stress applied can be changed too unless it is lower than the yield stress.
3. **Polyethylene Notch Tensile (PENT) Test:** The name of the method comes from the material it is generally used for. This method is also widely popular in the US. The principle is similar to the above NCTL test, the only difference being, here, there are side notches on each side of the specimen and failure is considered when the sample is split in two because of the propagation of the notch. And time for that failure is recorded [15].

4. **Full Notch Creep Test (FNCT):** This method is accepted widely in Europe for Polyethylene (PE) testing. This is preferred over PENT because of the shorter failure time in the method. In this method, the material is notched on all four sides, everything else remaining same. This method has been defined as a standard method for PE testing according to ISO 16770 [15].

2.7.2 Method II - Bent Strip Method (Constant Strain Method)

Bent strip method or constant strain method is a method for testing Environmental Stress Cracking of amorphous thermoplastics where the material specimen is subjected to a fixed flexural strain in presence of the chemical agent and kept at the testing temperature. The flexural strain is obtained by bending the specimen from the shorter edges at a fixed radius. ESC in this method is a qualitative measure of the material, where the material is analyzed according to the indicative property or time to crack after the test has been completed. This method is useful when the chemical agents are in the form of gases, liquids or solids with migrating substances in contact with the polymeric material, for example, adhesives containing plasticizers. This test similar to constant tensile load test and constant tensile deformation test is a ranking method to compare different materials [22].

Principle: According to this method, the test specimen is clamped in the set-up in such a way that the sample is bent with a constant radius to have a fixed flexural strain. The surface which is subjected to the strain is then exposed to the chemical agent and the set-up is kept at a certain temperature at which the testing needs to be done. Finally the testing is stopped when either the fixed time of the test duration is over or the material cracks, whichever happens first. Then different materials can be compared in this test or same material can be tested at different strains until the strain level is lower than the yield strain level. Also, same material can be tested at different testing environments. The tests can be repeated at different strain levels, like different stress levels in other tests to get results that can be compared for different stress and strain levels, or a combination of these factors.

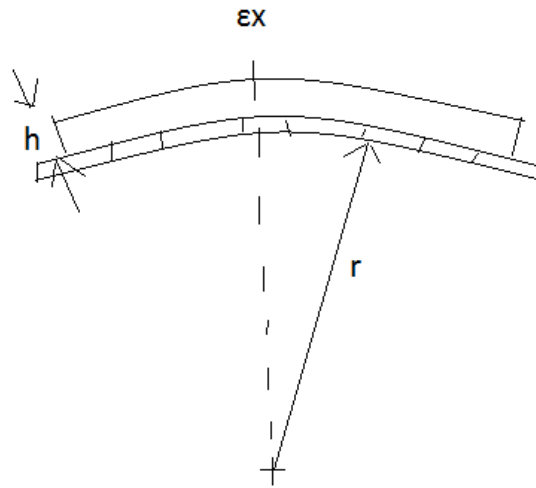
The sample in this method is not necessary supposed to be in the form of dumbbell shape. The only time when it is important for the sample to be in dumbbell shape is when it has initial notch and then the corners of the material is required to be smooth so that a crack doesn't propagate through the corners [22].

Following is the figure of the setup used to clamp and bend the specimen at a certain radius to obtain a fixed flexural strain.

The formula required to obtain a specific strain is described as follows:-

$$\epsilon_x = \frac{h}{2r + h} \quad (2.3)$$

where, ϵ_x = strain applied on the sample by the set up



up.png

Figure 2.10: Diagram of set-up

h = thickness of the material

r = radius of the set up

There are different variations of the set-ups apart from the standard set-up used for this method which are discussed in the following points.

2.7.2.1 Three point Bending Method

Three point bending test method is a variation of the standard test set-up in which, the test bar is clamped or supported at both ends and a rod or a indentor is placed on the centre part of the material either from beneath or from the top and is then pushed to obtain particular strain which is lower than the yield point. The specimen also simultaneously is exposed to the chemical agent at the testing temperature, such that the fluid is in contact with the strained part. The temperature as discussed in earlier section should be lower than the T_g of the material. The experiment is run for a time period or till the specimen breaks after which the materials are compared on basis of the crazes or cracks, or time to fracture based on variables like chemicals used, temperature for testing and strain levels [22].

2.7.2.2 Bell Telephone Method

According to bell telephone method, a specimen is bent almost 180° or to a specific strain level and placed in a holder. This whole holder is then placed in a test tube which is filled with the chemical agent against which the material is being tested. The whole set-up is placed at certain temperatures. Then following the same principle, after specific time, crazes or cracks are compared which can be used to compare different materials, different chemical agents or different temperatures [22].

2.7.2.3 Single or Double Cantilever Method

In single or double cantilever method, a specimen is bent using loads at one end (single cantilever) or at both ends (double cantilever), while everything else like being exposed to the chemical agent and testing temperatures remains same. The results are recorded for cracks and crazes after specific time to analyze and compare the materials.

The standard bent strip method is the most common method and set-up used for comparing the materials on basis of different things like chemicals, strain levels, temperatures, etc. because the set-up is easy to build and analyzing the materials is also easy. Another advantage of this method is that the specimen shape does not necessary needs to be dumbbell shaped. It can be a rectangular shaped specimen as well which is easier to prepare.

Furthermore, there can be other modifications of this test like a single notch bent strip test, and other varieties of these.

2.7.3 Method III - Constant Tensile Deformation Method

Constant tensile deformation Method [ISO 22088-5:2006(E)] is a standard method described according to ISO standards which is similar to constant strain method. In both the methods, the specimens are held at a specific strain in the presence of the test environment. The difference between the methods are that in constant strain method, the set-ups are different than the set-ups in this method. In this method, tensile stress is applied to stretch the two opposite ends of the long side of the specimen and then the specimen is held at constant tensile deformation or constant strain on the sample. Whereas, in constant strain method, the samples obtain a constant strain by bending the samples from the opposite long edges of the specimen. In constant strain method, the samples are at fixed flexural strain during the testing. These two methods are described as separate or different methods according to the ISO 22088 standard [22].

Principle: The principle of this method remains the same as that of constant strain method (ISO 22088-3) where, the specimens are held at specific tensile deformation / strain while being immersed in the testing chemical agent at a specific testing temperature. But the condition for all the methods is that the stress applied should

be lower than the yield point, or breaking point if the material does not exhibit yield point.

The molecular structure of the polymeric material gets weakened by continuous ESC in presence of chemicals compared to in presence of air only and absence of any chemical [22].

In this method, the materials are prepared in the dumbbell shaped specimens. The shorter ends of the samples are held in the tensile testing instrument and stress lower than yield stress is applied such that the specimen is at constant tensile deformation. The set-up is immersed in the chemical agent used for testing. And the whole set-up is kept at a constant temperature. The test is started when the specimen is held at the constant tensile deformation and is stopped when the material cracks recording the time to failure of the material [22].

2.7.4 Method IV - Micro-hardness Measurement Method

Micro-hardness measurement method for Environmental Stress Cracking and polymer degradation detection is a method which has been becoming popular in recent times. A lot of interest has been shown in using this because of the simple principle it has with a simple set up and also because of the shallow nominal depth of penetration which can be as low as few micrometers [1].

The principle of this method is that a pyramid diamond indenter with the sharp edge facing toward the material is impressed on the surface of the material, which is kept at the known load. The diamond is impressed for a specific time and the material is either dipped in the chemical for which it is being tested or the chemical is applied on the material if the fluid is highly viscous. The area of impression is then calculated using a microscope. Eventually, micro-hardness number is calculated according to the following formula:

$$MH = \frac{1.854 * F}{d^2} \quad (2.4)$$

where, F = indenter load (kgf)
d = mean diagonal length (mm)

In this method, indenter load is very important and the lower it is the more sensitive the method is to detect surface defects. Therefore, it's good to choose indenter load as low as possible.

The method has increased usage in recent history and has the potential of getting good results with respect to compatibility between the material and chemical at specific conditions. But this method is still not a standard method according to ISO standards [1].

2.7.5 Method V - Monotonic Creep Method

Monotonic Creep method is a method similar to slow strain rate testing technique which is used to test stress corrosion cracking for metals.

Principle: This method was developed for thermoplastics and in this method, the sample is subjected to constant stress for which, its strain rate is observed and recorded. Different chemicals can be compared by plotting a stress vs. strain curve for the same material [1]

2.8 Analysis Techniques of ESC

After the experiments, Environmental Stress Cracking can be analyzed using various techniques. The simplest way to analyze ESC of materials is by simply observing the materials through an optical microscope to look for crazes and cracks in the materials and eventually comparing them on the basis of amounts of crazes and cracks after a specific test time, or to compare them on the basis of which material got fractures the fastest. Another method for observing the materials can be using Scanning Electron Microscope (SEM) or Transmission Electron Microscope (TEM) if it is difficult to differentiate between materials in an optical microscope. These methods are qualitative analysis and cannot provide quantitative data for comparison. Microscopy analysis to look for cracks and crazes is also known as fractography. These tests are basically morphology analysis.

While using SEM, the samples are cleaned ultrasonically using a mixture of isopropanol and de-ionized water and before inspection in SEM the surfaces of the samples are gold sputter coated for better images [23].

Another method of analysis of ESC could be using tensile testing after the experiments have been conducted. This analysis technique is possible only if, after the experiments, the samples only show crazes and don't crack. Then, in those samples tensile testing can be done to see the amount of stress it needs to actually fracture. This test, although it provides numbers and quantitative data, is not a direct analysis technique. Also, this test can only be used when comparing different chemical agents exposed to the same material or different temperature used during testing for the same material. This test will not be valid when ESC is being tested for different materials because they can have different yield points and fracture point from the starting, even before the test was started. In this, the elongation of the specimen at the time of cracking can also be compared.

Another simple technique is to measure time to failure, in which an experiment runs until the material breaks after which the time for failure is recorded. And finally, after all the experiments are over, time to failure of all the materials can be compared and on this basis, the materials can be judged to be superior or inferior to one another for ESC

for the parameters tested.

Yet another method of analysis is to measure flexural stress and finally plotting it against duration of the test to compare different chemical agents or temperatures. This method can be applied when employing constant strain method [23].

The ESC of materials within the presence of chemicals can be predicted by Hansen's solubility parameters. According to this method for prediction, the closer to zero the equation: $(\delta_p - \delta_l)^2$ is, the more compatible are the polymer (p) and the chemical agent (l) and the more severe ESC is.

Furthermore, techniques like Fourier Transformation Infra-red (FTIR) spectroscopy, Differential Scanning Calorimetry (DSC), Dynamic Mechanical Thermal Analysis (DMTA), etc. can be used to analyze the samples for whether the polymeric material has been degraded by the chemical agent or not, and if the molecular structure has been changed or not. For example, spectra can be obtained from FTIR showing any difference between molecular groups present before and after the tests. Similarly, DSC can provide data regarding glass transition temperature (T_g) of the material. DMTA can also provide information about T_g and polymer composition. Therefore, these analysis techniques can be applied to check if there is any polymer degradation taking place.

As it can be seen from above mentioned techniques for analysis of ESC, it is mostly a qualitative test because in most cases it is not possible to obtain facts or figures for direct ESC measurements.

2.9 Limitations or Drawbacks of ESC study

One of the major limitation or drawback of ESC studies is that results from experiments done in the past can be rarely used in the current or future studies. The reason being that there are tens of thousands of chemicals, a lot of many general polymers and that's why there can a lot of possible combinations of the parameters which can be tested. Having said this, every combination can behave differently and thus a trend cannot be created from the past data as well. The only way to know the results for a specific combination is to use them in the tests using the methods mentioned above in this chapter.

Chapter 3

Experimental Methodology & Analysis Techniques

3.1 ESC Test Method chosen

There are various testing methods for ESC. These methods are discussed in the section 2.7. From the main five methods for ESC evaluation, the method selected was **Bent Strip Method (Constant Strain Method)** described in section 2.7.2. The basic principle of this method includes bending of samples to a certain radius when fixed to the set-up, so that a constant strain is applied on the sample.

Bent Strip Method has different variations depending on the type, shape and structure of fixtures or the set-ups which are also explained in section 2.7.2. The variation used in the testing and analysis of ESC of ABS and PC/ABS in this thesis was the **Double cantilever - Bent strip method** in which the samples were bent and fixed with both of the shorter edges of the samples held at their positions by tightening the set-ups with screwed rods.

The reasons behind selecting this method type and variation are that firstly it is an ISO standard method used for ESC experimentation. This method is also basic and easy to prepare which reduces the time for building the set-ups. The method is a faster method of testing compared to other standard methods. Bent strip method is the most commonly used test method for ESC testing and analysis. Another reason to use this method is that, a dumbbell shaped specimen or sample is not required in this case and a simple rectangular cut sample can be used for testing which makes the preparation of the samples easy and faster. Comparing this method to other methods, for example in the constant tensile load method as described in section 2.7.1, a dumbbell shaped specimen is required for testing since it requires application of load or stress by holding and stretching the grips from the shorter edges. Another issue with other test methods is that they require proper instruments and equipment to conduct the testing, like a tensile

machine in constant tensile load method. This would lead to spending more time on preparation of samples for the required shape and size and conducting the tests will require more time too because then, either multiple tensile testing instruments would have been required, or test one sample at a time, which is not feasible.

3.2 Preparation of Set-up

The set-ups were prepared by the Finmekanik workshop at Volvo Car Corporation. They used aluminium blocks to shape them into the fixtures with a certain radius, length and width by grinding and cutting the samples using CAD and programming tools to achieve the dimensions.

The radius of set-ups differed according to the thickness of the samples, so that a constant strain of 2% was applied on the middle section of the samples when they were attached to the fixtures.



Figure 3.1: Set-up

The radii of the fixtures were calculated using the equation 2.3. And the calculations are as follows:-

$$\epsilon_x = 2\% = 0.02$$

$$r = \frac{h}{2} \frac{1 - \epsilon_x}{\epsilon_x} \quad (3.1)$$

So, for materials with varying thickness of 2mm, 2.5mm, 3mm and 3.5 mm, the radii calculated for the respective thickness are:

- thickness of the sample(h) = 2.0mm, r = 49.00mm
- thickness of the sample(h) = 2.5mm, r = 61.25mm
- thickness of the sample(h) = 3.0mm, r = 73.50mm
- thickness of the sample(h) = 3.5mm, r = 85.75mm

3.3 Preparation of samples

Rough samples were prepared by the Finmekanik workshop at Volvo Cars Corporation. The samples were cut in the dimensions of 102 mm x 22 mm x h, where h is the thickness of the samples with which they were already supplied with. These samples were cut from bigger injection moulded ABS or PC/ABS plaques manufactured and supplied by respective material suppliers.

In the next step these samples were water grinded from the edges to remove as many defects as possible, so that ideally the samples do not contain any initiation defects that would lead to acceleration of the cracking process.

Finally samples were annealed before testing them for a certain period of time (usually for 4 hours for most materials) at an elevated temperature of 80°C according to the manufacturer or supplier of each material. The annealing was done to relax the molecules in the materials in case the material had any stresses due to the preparation processes.

Yield point (%) of the respective materials were found using the material data sheets provided by the respective material suppliers. This data was useful to select a strain level which was lower than this yield point in order to follow the theory of ESC. These values are shown in Table 3.1.

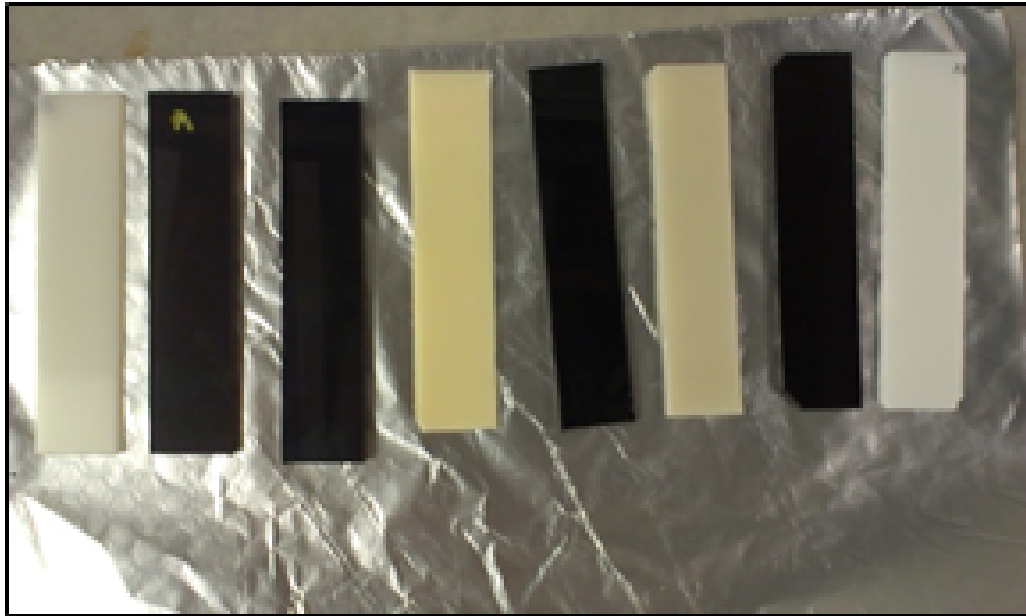


Figure 3.2: Samples

Table 3.1: Yield Points of the materials

Sample no.	Yield Point (%)
1	2.2
2	3.3
3	3.2
4	3.3
5	4.4
6	2.6
7	2.6
8	4.1

3.4 Experimental Scope

Study of ESC includes various parameters, which makes it a broad study and difficult to obtain a trend. That's why the experimental scope of this thesis had to be kept in such a way that there could be some meaningful results from the experiments performed including the important factors that can have influence on the tests.

The experimental scope of this thesis work included various kinds of ABS and

PC/ABS plaques materials, supplied by different suppliers, which are used in the interiors of the car. These plaques, after cutting, were used for the testing at constant strain of 2%, which is less than the yield point of the materials as can be seen from the table above. For this ESC testing two chemicals - PEG of molecular weight 400 and an assembly aid used in the Volvo cars industry containing PEG and PPG as major components were used. The ESC study of these materials at 2% constant strain level in combination of the above chemicals were tested at three different temperatures - room temperature (23°C), 50°C and 75°C.

Thus, there were combinations of the temperature level, chemical agent applied and material chosen. All these different combinations were tested for ESC analysis. For example, each material was tested for PEG 400 at each temperature level, and with the assembly aid applied again at each temperature level. And after the testing a data matrix of the results of all combinations were obtained which were inferred eventually for the results.

3.5 Experimental Methodology

The following is the experimental procedure which was followed to conduct the ESC testing of the above mentioned materials.

Two samples of each ABS and PC/ABS materials were placed in the set-up according to their respective thicknesses, as calculated above in the section 3.2, such that the strain at mid point of the samples was constant at 2%. Then the samples were fixed by tightening the screws around the edges of the samples. The set-ups firstly were then inverted and placed on a cup made out of aluminum foil. The chemical agents PEG 400 was poured in these aluminum foil cases. The set-ups were placed inverted on the foils with chemical agent in such a way that the samples were dipped in the chemical solution but the samples didn't touch the tray bottom or else there will be extra stresses from the tray on the samples. Three sets of each tray were prepared and then one was kept at room temperature, one in a oven at 50°C and the third one in oven at 75°C.

Similarly, the above procedure was repeated for the tests replacing one of the factors, namely - the materials, the temperature levels, or the chemical from PEG 400 to the assembly aid (containing PEG and PPG) or to no chemical. This would mean every material was tested with PEG 400 at room temperature, 50°C and 75°C; then with the assembly aid at these three temperature levels and finally without any chemicals again at these three temperatures.

The ESC testing of these materials were concluded and stopped when the materials cracked when exposed to chemical agents or after certain period of time in case of testing without chemicals. The materials were checked regularly for crazes and cracks.

The materials were then analyzed using various analysis techniques like visual analysis, optical microscopy and FTIR which will be discussed in the next chapter.

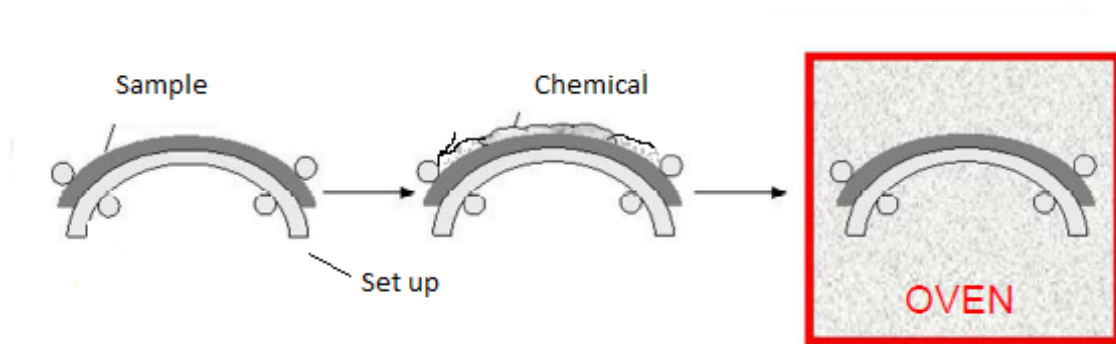


Figure 3.3: Steps for experimental procedure



Figure 3.4: Test conducted when material exposed to chemical at Room Temperature

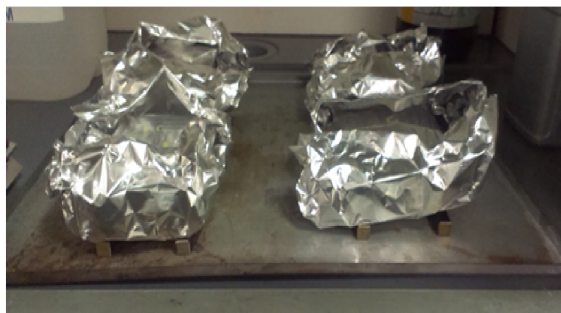


Figure 3.5: Set-up in oven - Test conducted at elevated temperature when exposed to chemical



Figure 3.6: No chemical test

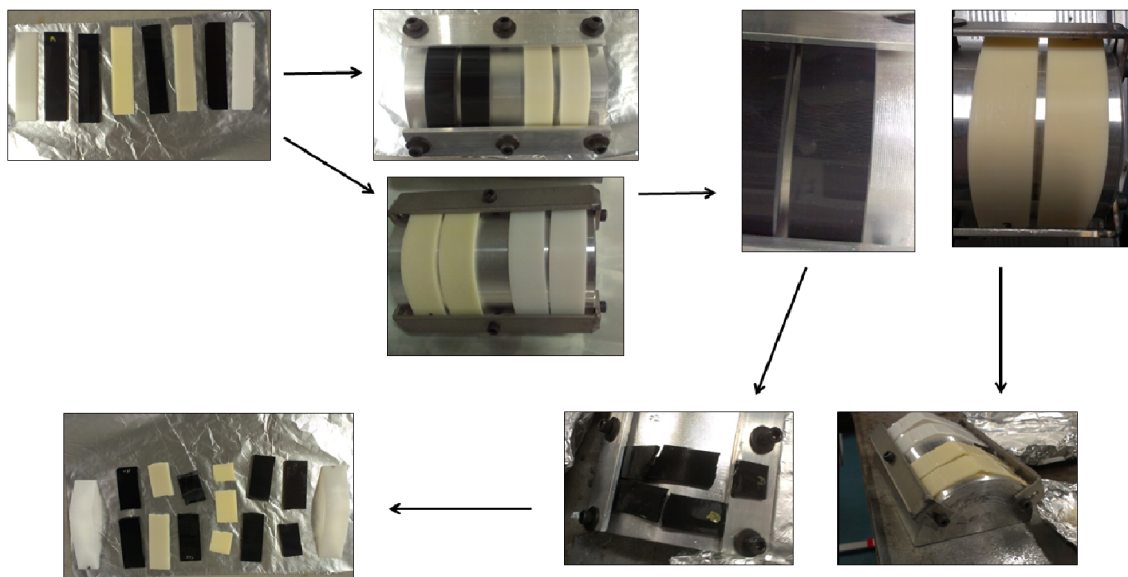


Figure 3.7: Steps of ESC testing

3.6 Analysis Techniques

3.6.1 DSC

In this method, a Pyris 1 Differential Scanning Calorimeter (DSC) by PerkinElmer Instruments was used, where a small piece of the sample was cut and weighed to be around 7.5 mg to 8 mg. This cup was then placed in a very small aluminum cup and then covered with a top plate. The cup was then placed in the DSC equipment and then the relevant details were entered on the program on the computer running the DSC analysis. The initial state for starting the tests chosen were 50°C temperature and 20°C/min rate of increase in temperature. The analysis was recorded for the sample to be heated from 50°C to 175°C with two heating and two cooling steps.

Further, after the testing, heat flow curves were selected and zoomed to the part where there were disturbances in the curve. Tangential lines then helped the program to obtain ΔC_p values and eventually calculate the T_g or 2 T_g values (in case of polymer blend) of the material. An example of sample 5 is shown below in the Fig 4.2.



Figure 3.8: DSC Instrument

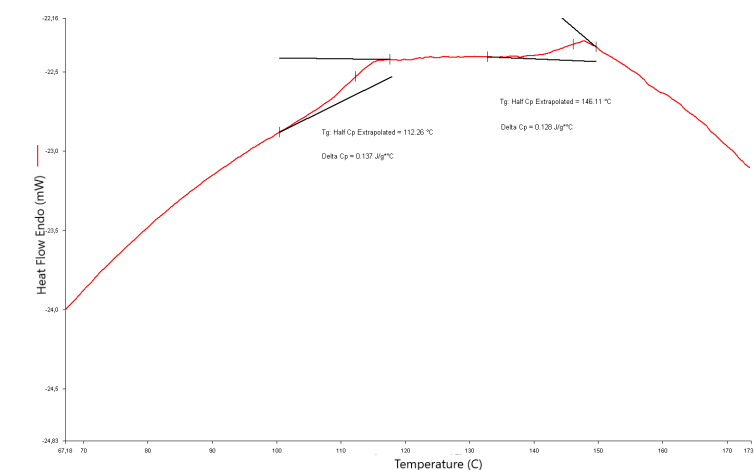


Figure 3.9: Example of calculation of Tg

3.6.2 FTIR

In this method, a Thermo Fischer Nicolet iS50 FT-IR instrument was used. Tested samples were taken and cleaned by a soft tissue to remove the fluids from the surface of the material. These samples were then placed on the FTIR instrument and FTIR spectra were obtained on the computer connected to the instrument. This procedure was repeated for all the tested samples and then for the untested samples for the reference to check for the deviation or degradation in the material after the testing if any compared to the untested parts.



Figure 3.10: FTIR Instrument

Chapter 4

Results & Analysis

4.1 Analysis Techniques Used

Analysis techniques which were used for analyzing ESC tests were visual analysis which included visually checking the materials for crazes and cracks and further analyzing the materials with the help of optical microscope. FTIR analysis technique was also employed to check whether there was any chemical reaction between the chemical agent and the material, which could cause a chemical change and most probably degradation in the material. According to ESC theory, there should not be any chemical change in the molecular structure of the material due to the chemical attack.

Also, there was a preliminary analysis used to verify the material properties by DSC. This analysis provided us with the information about the materials and whether the material analyzed is a pure polymer or blend of two or more polymers and with what kind of polymers does the material consist of.

4.2 DSC

DSC was used to analyze the samples before testing them for ESC. It was employed to obtain the material characteristics of the samples delivered by different suppliers. DSC helped in identifying the material by referring the T_g values to the literature values of the polymers and polymer blends. The T_g values which were referred to the literature were obtained from the DSC analysis.

Table 4.1: Tg values of samples analyzed by DSC

Sample no.	Tg1 (°C)	Tg2 (°C)
1	113	-
2	114	-
3	115	145
4	114	-
5	112	146
6	114	-
7	112	-
8	115	145

The above table which have the Tg values obtained from DSC for the samples shows that Sample no 3, 5 and 8 are polymer blends as they have two Tg values present and when these values were referred to the literature handbook - "*plaster Materialval och Materialdata*" [24], it showed that these materials are the polymer blends of PC/ABS. Whereas, other samples are pure polymeric materials because of their only single Tg value and when these were referred to literature, they corresponded to ABS polymeric materials. Thus sample 3, 5 and 8 are PC/ABS materials and the rest are pure ABS materials.

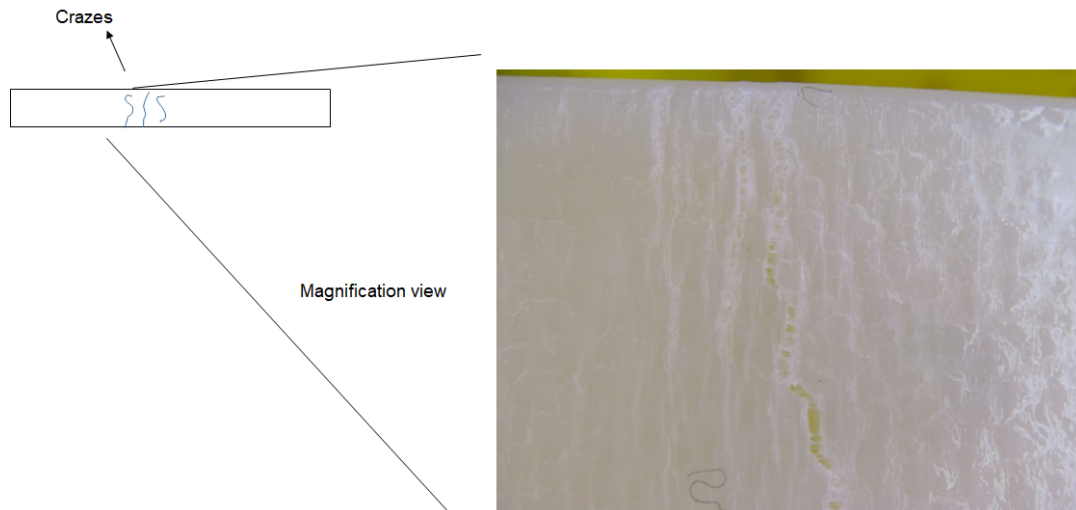
4.3 Visual Analysis and Optical Microscope

After the ESC testing was completed, the materials were analyzed visually to check for crazes and cracks in the samples and if possible compare the samples with each other and rank them accordingly. Another parameter to compare the materials was the time taken for the materials to craze or crack. These crazes or cracks were first checked and analyzed visually and then by optical microscope to see how far the crazing has gone from the area of crack and also how does it look magnifying the area where it cracked or crazed.

The ESC tests were stopped when the materials cracked and then the duration of the experiment was recorded. Then the materials were compared on the basis of time taken for the material to crack.

The pictures below in Fig 4.2, 4.3 and 4.4 are the samples which were tested with PEG 400 or an assembly fluid at one of the three temperature levels. These pictures are zoomed microscopy images of the tested samples and shows the crazes or the cracked edge taken from an optical microscope. Fig 4.2 shows that a sample with crazes was taken and magnified to the area where crazes were present to take the picture. Similarly samples in Fig 4.3 and 4.4 are the magnified images of the area of the samples where

the material cracked and crazes were present.



img 1.png

Figure 4.1: Crack and crazes in the sample no. 4 (ABS) as seen from an optical microscope

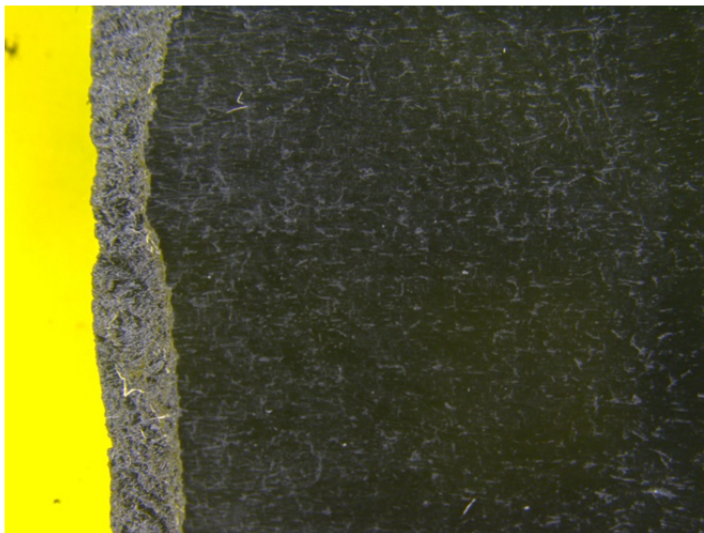


Figure 4.2: Crack and crazes in a sample no. 5 (PC/ABS) as seen from an optical microscope

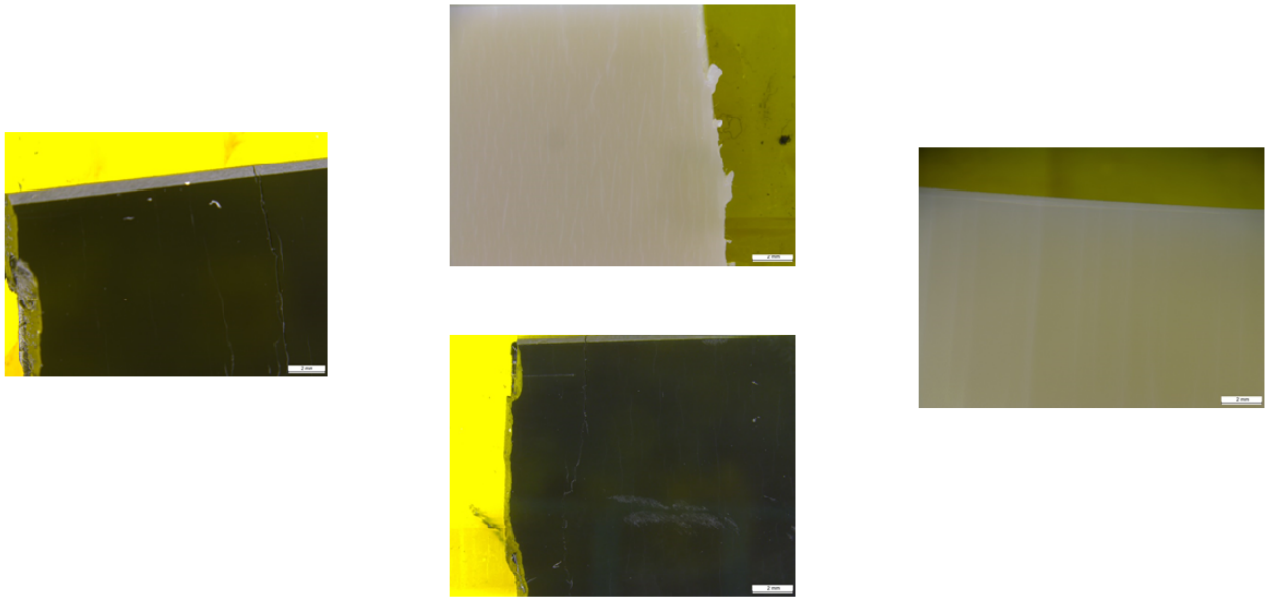


Figure 4.3: Microscopy images for other samples - Sample no. 2 (ABS - white), Sample no. 7 (ABS - black)

The picture in Fig 4.5 are the zoomed microscopy images of neat samples which were tested without chemicals and thus shows only crazes and no cracks on the material.

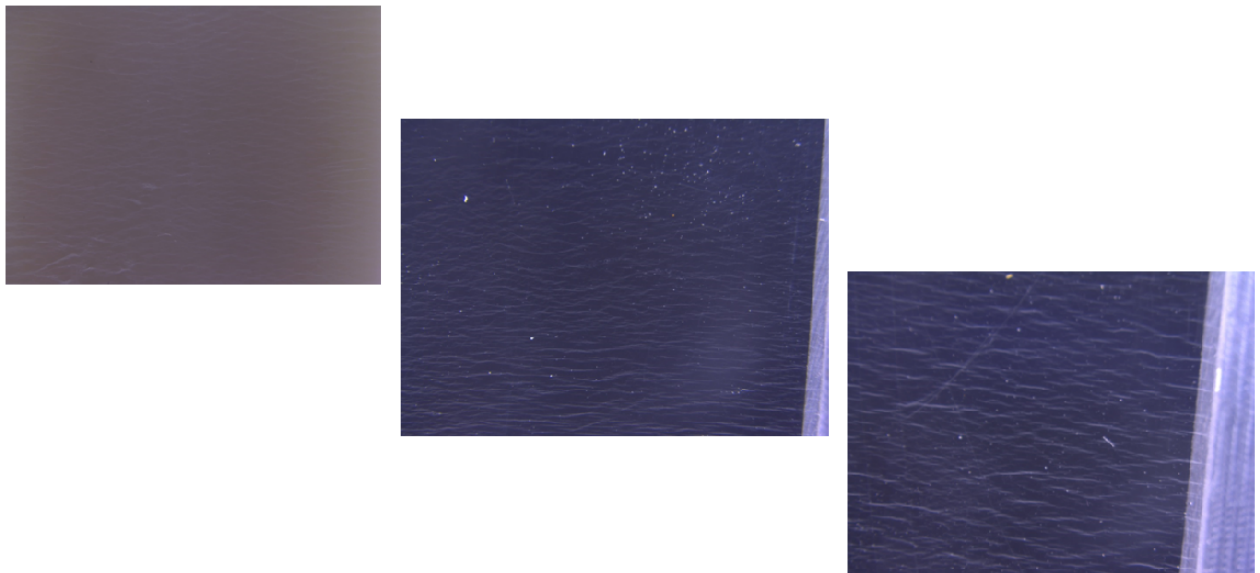


Figure 4.4: Microscopy images for neat samples tested without chemical - Sample no 1 (ABS), 3 (PC/ABS) and 8 (PC/ABS)

4.4 Results

The results obtained from the ESC experiments done with chemicals are shown below in Tables 4.2, 4.3 and 4.4.

Table 4.2: Results for tests conducted with chemicals at 75°C

Sample no.	Time to crack with PEG 400 (h)	Time to crack with assembly fluid (h)
1	<24 h	<24 h
2	<24 h (only crazed)	<24 h (only crazed)
3	<24 h	<24 h
4	<24 h	<24 h
5	<24 h	<24 h
6	<24 h	<24 h
7	<24 h	<24 h
8	<24 h	<24 h

Table 4.3: Results for tests conducted with chemicals at 50°C

Sample no.	Time to crack with PEG 400 (h)	Time to crack with assembly fluid (h)
1	<24 h	<24 h
2	<24 h (only crazed)	<24 h (only crazed)
3	<24 h	<24 h
4	<24 h	<24 h
5	<24 h	<24 h
6	<24 h	<24 h
7	<24 h	<24 h
8	<24 h	<24 h

Table 4.4: Results for tests conducted with chemicals at Room Temperature

Sample no.	Time to crack with PEG 400 (h)	Time to crack with assembly fluid (h)
1	<24 h	<24 h
2	<24 h (only crazed)	<24 h (only crazed)
3	<24 h	<24 h
4	<24 h	<24 h
5	<24 h	<24 h
6	<24 h	<24 h
7	<24 h	<24 h
8	<24 h	<24 h

The Tables 4.2 - 4.4 show that, when different ABS or PC/ABS materials were tested with different chemical agents at 2% strain and at different temperature levels (Room temperature, 50°C and 75°C), all the materials cracked within 24 hours. The time recorded for all materials when exposed to chemicals and strain level was the same, that is, within 24 hours because it was difficult to record precise time for cracking for every sample kept for ESC testing. The samples were checked regularly for cracking, but still it was not possible to have accurate time recordings for every sample. Experiments recorded in few of the published papers, for example, written by J. P. Robert, et. al. [10], L. F. AL-Saidi, et. al. [21], B. Borisova, et. al. [25], it was taking couple of weeks to 6 weeks for fracture the samples. Compared to those, it was much faster in our case. This could be due to various reasons, one of them being the strain level chosen for the samples though under the yield point and in the elastic region, but still was high and close to the yield point. Another reason that could effect the cracking is that the chemicals which were used were very aggressive and could have caused the acceleration in cracking of the samples. Presence of initial defects at the edges of the samples after their preparation can also be a potential reason behind the faster cracking process. These individual reasons can also have an accumulative affect to decrease the time for fracture of the materials.

Results of the reference experiments done without chemicals are shown below in the Table 4.5, 4.6 and 4.7.

Table 4.5: Results for tests conducted for the neat samples at 75°C

Sample no.	Yield point	Material	Result
1	2.2	ABS	Crazing from day 3
2	3.3	ABS	Crazing from day 3
3	3.2	PC/ABS	No Crazing
4	3.3	ABS	Crazing from day 3
5	4.4	PC/ABS	No Crazing
6	2.6	ABS	Crazing from day 2
7	2.6	ABS	Crazing from day 2
8	4.1	PC/ABS	No Crazing

Table 4.6: Results for tests conducted for the neat samples at 50°C

Sample no.	Yield point	Material	Result
1	2.2	ABS	Crazing from day 3
2	3.3	ABS	Crazing from day 3
3	3.2	PC/ABS	No Crazing
4	3.3	ABS	Crazing from day 3
5	4.4	PC/ABS	No Crazing
6	2.6	ABS	Crazing from day 2
7	2.6	ABS	Crazing from day 2
8	4.1	PC/ABS	No Crazing

Table 4.7: Results for tests conducted for the neat samples at Room temperature

Sample no.	Yield point	Material	Result
1	2.2	ABS	Crazing from day 6
2	3.3	ABS	Crazing from day 6
3	3.2	PC/ABS	No Crazing
4	3.3	ABS	Crazing from day 7
5	4.4	PC/ABS	No Crazing
6	2.6	ABS	Crazing from day 2
7	2.6	ABS	Crazing from day 2
8	4.1	PC/ABS	No Crazing

The results shown in the tables 4.5 - 4.7 are for the experiments done when 2% strain was applied on the materials and the materials were kept at different temperature

levels. But these materials were not exposed to any chemical. There were differences seen within the materials when these tests were finished. Some materials took longer to obtain crazes as compared to some other materials where crazes occurred faster. As it can be seen from the the tables, when the test was conducted for 35 days; sample 3, 5 and 8 which didn't craze at all which have the higher yield points and are also PC/ABS materials. This suggests that almost all the materials have a proportional co-relation of time taken for crazing and the yield point of the materials. Thus the above tables may also show that the materials with higher yield points took more time to craze when exposed to same strain level compared to materials with lower yield point. The results can also indicate that the polymeric blends have better resistance to ESC. These tests also helped in comparing the materials and to show which samples are better compared to others and rank them. This could not be done with the results obtained from tests conducted with chemicals due to various reasons discussed above.

Another point which can be observed is that the results obtained at room temperature and at 50 °C are different but results at 50°C and 75°C are identical, which means that increasing the temperature increased the rate of cracking but till 50°C only, beyond that the rate has been constant. This means that temperature has an affect on the rate of the cracking but till a certain point.

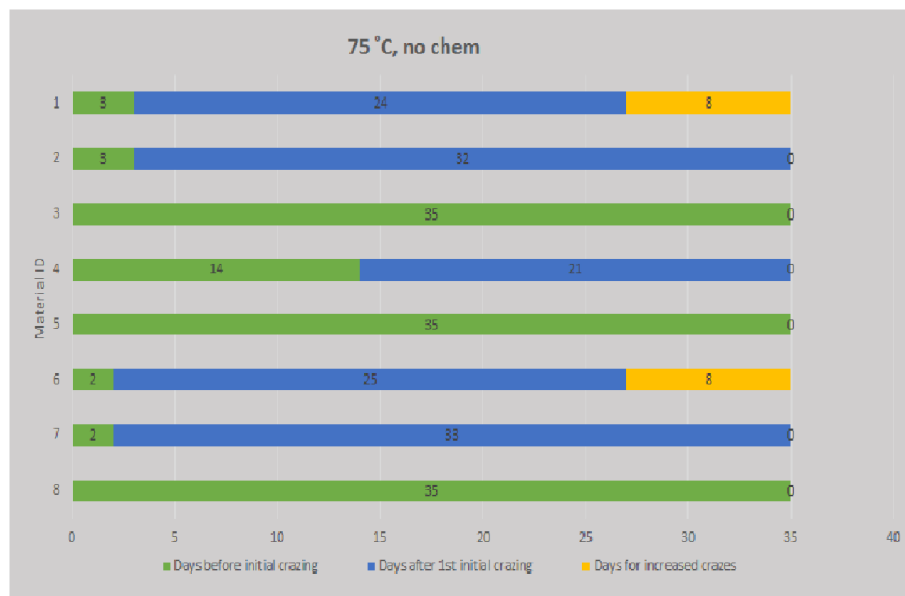


Figure 4.5: Graph showing days for no crazes and then increase in crazing (in days) for no chemical tests at 75°C

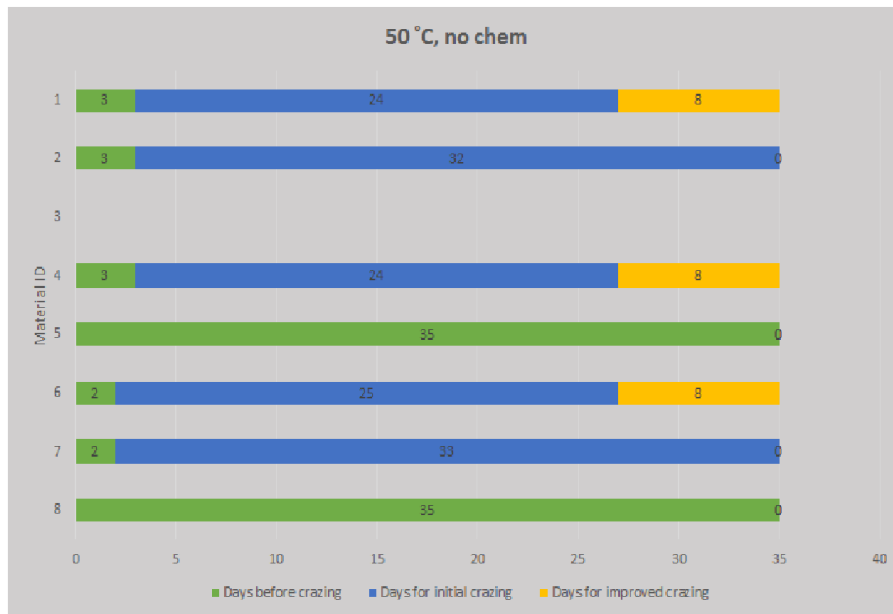


Figure 4.6: Graph showing days for no crazes and then increase in crazing (in days) for no chemical tests at 50°C

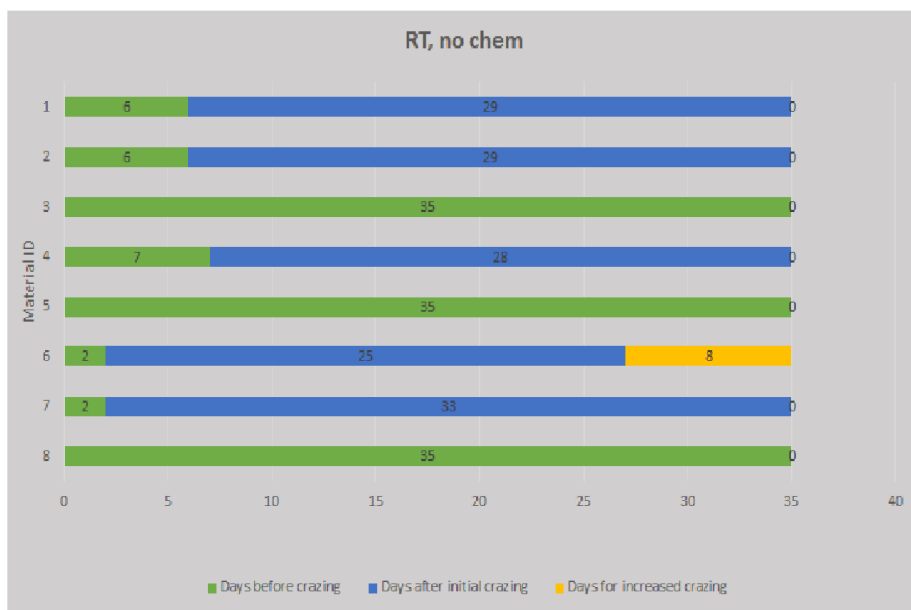


Figure 4.7: Graph showing days for no crazes and then increase in crazing (in days) for no chemical tests at Room Temperature

The above figures - Fig 4.7 - 4.9 are the graphs showing the increase in crazing in days for no chemical tests for 75°C, 50°C and room temperature respectively. These graphs corresponds to the above mentioned tables that shows the number of days it took for the material for crazing to start on them and then. Thus, it can be observed in these graphs also that there is no crazing in sample 3, 5 and 8 which are PC/ABS.

4.5 FTIR

FTIR Analysis technique was employed on the tested samples with untested samples being the reference to check whether there was a degradation or a change in chemical structure in the sample due to exposure of the chemical agent on the material.

According to the ESC phenomenon, there should not be any degradation or change in the chemical structure in the material due to the attack of the chemical agent. In ESC, when a chemical attacks the material, it only fills the void spaces and swells the material, eventually breaking the secondary bonds because of which cracking occurs, but there is no degradation in the material.

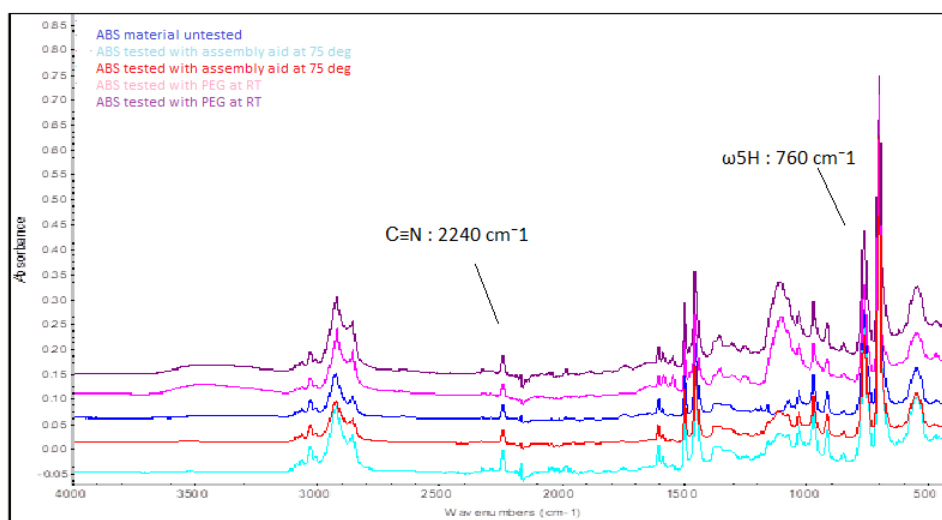


Figure 4.8: FTIR Spectra of ABS material - untested, tested with assembly aid and PEG 400

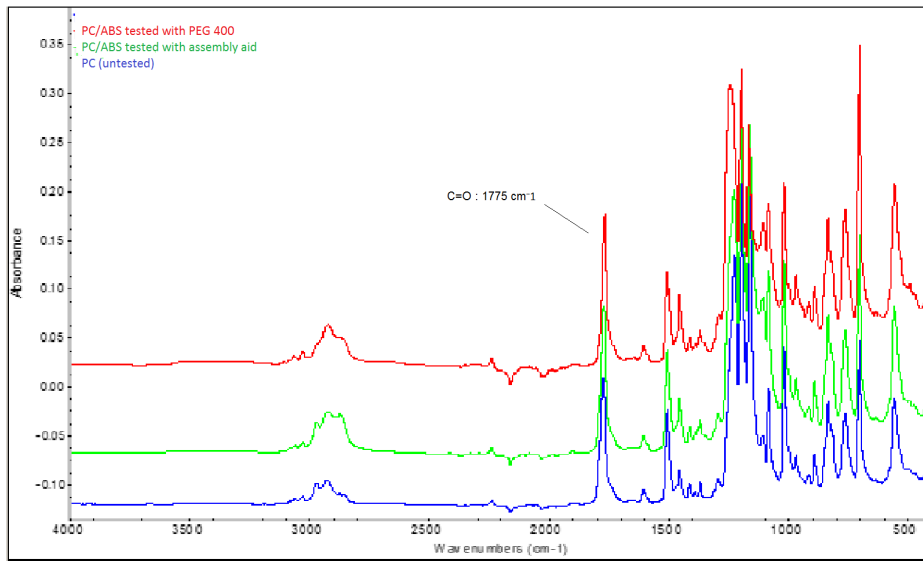


Figure 4.9: FTIR Spectra of PC/ABS material - untested, tested with assembly aid and PEG 400

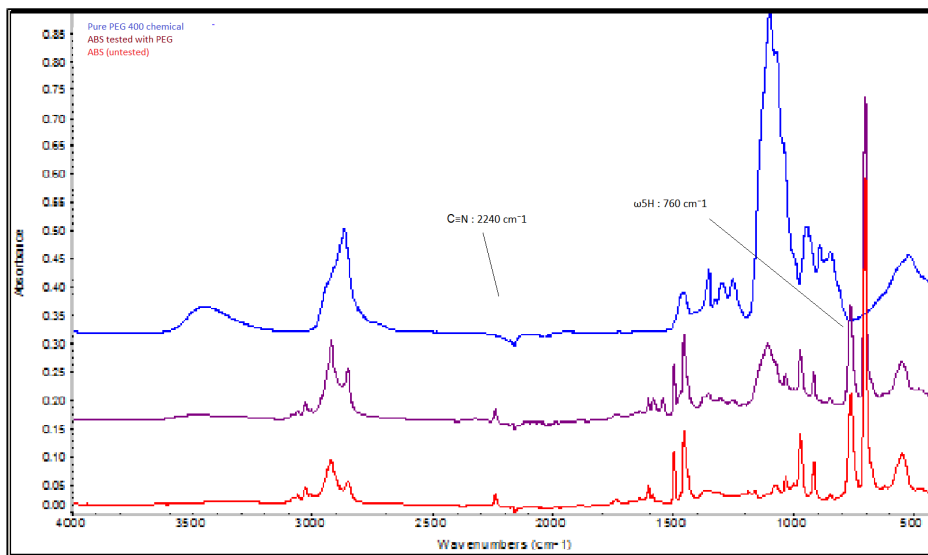


Figure 4.10: FTIR Spectra of ABS material with comparison to PEG 400 chemical

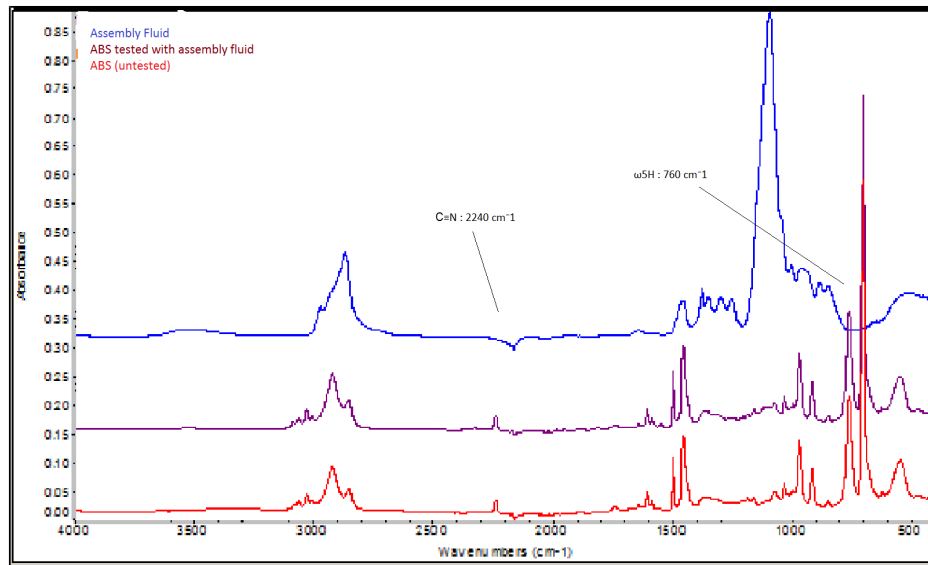


Figure 4.11: FTIR Spectra of ABS material with comparison to Assembly Aid

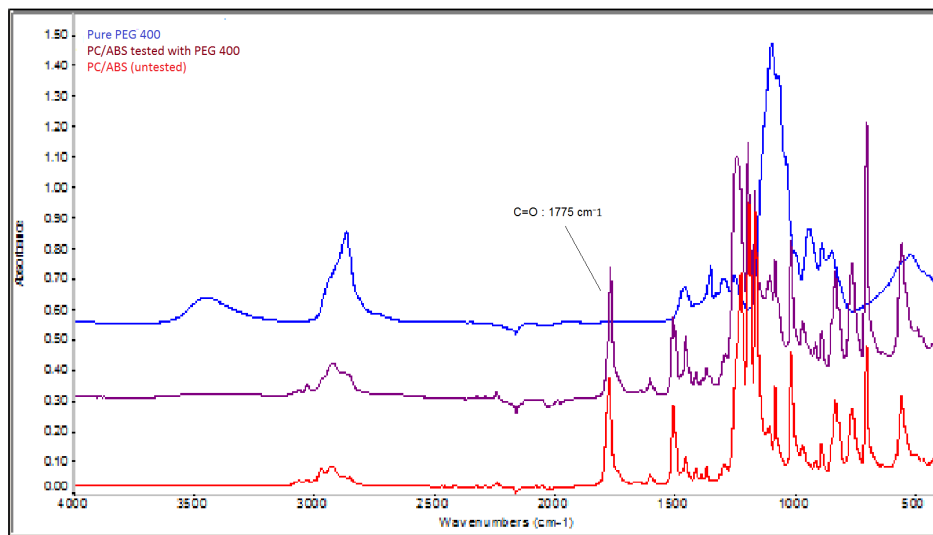


Figure 4.12: FTIR Spectra of PC/ABS material with comparison to PEG 400 chemical

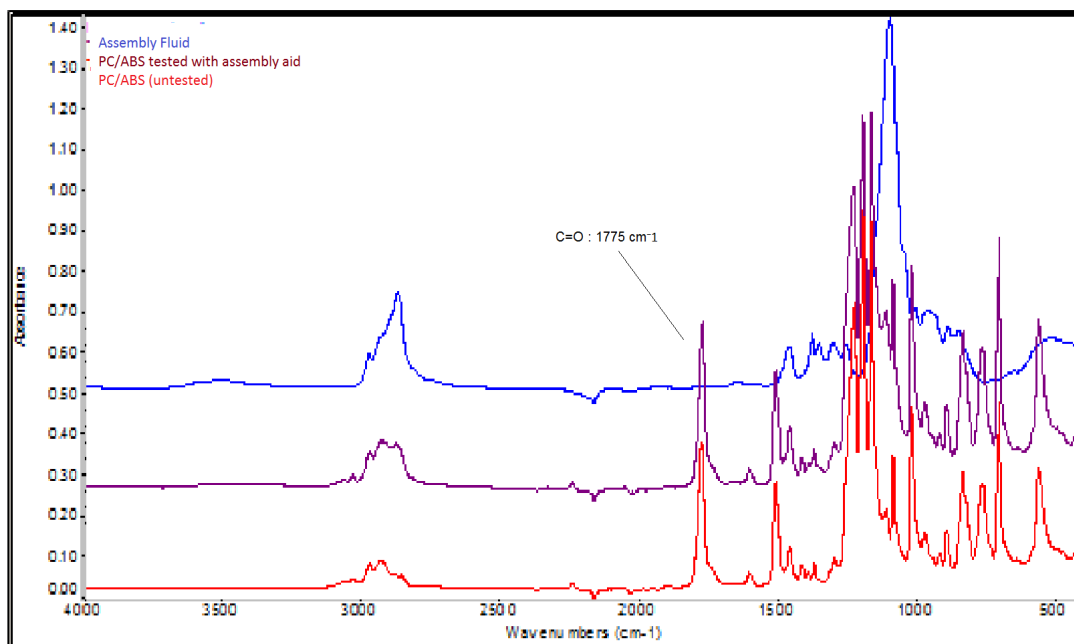


Figure 4.13: FTIR Spectra of PC/ABS material with comparison to Assembly Fluid

Figure 4.10 and 4.11 show the FTIR spectra of ABS and PC/ABS samples respectively. Both the figures contain FTIR spectras of the samples untested and also tested with PEG 400 and assembly fluid. Figures 4.8 - 4.13 with FTIR spectra are marked with certain peaks which characterize the materials and are different for PC/ABS from ABS. The peak assigned for PC/ABS samples is - C=O at 1775 cm^{-1} . The peaks marked for ABS samples are CN at 2240 cm^{-1} and $\omega 5\text{H}$ at 760 cm^{-1} .

Figure 4.12 includes FTIR spectra of ABS sample untested, tested with PEG 400 and pure PEG 400 chemical. Similarly, Fig. 4.13 has FTIR spectras of ABS sample untested, tested with assembly aid and pure assembly aid. Fig. 4.14 and 4.15 contains FTIR spectra of PC/ABS samples untested, tested with PEG 400 and assembly aid respectively and pure PEG 400 and assembly fluid respectively. All the above figures show that the chemicals do not change the chemical structure of the material, since the FTIR spectra of samples tested remains same as of the FTIR spectra of samples untested. Except in some FTIR spectra where there is a change in one peak of tested material from the untested sample in the right end region where it is crowded with a lot of peaks. This could be because of some chemical left on the sample even after cleaning the sample and the overlapping chemical on the surface of the material affected the FTIR spectra. FTIR technique was employed to check whether the materials degraded after testing in

the presence of chemicals, that is, did chemicals change the structure of materials and not just break the secondary bonds of these materials. This was done comparing the tested parts with untested parts to check whether there are any changes in the peaks, new peaks introduced or did the existing peaks shifted. So, overall this suggests that the tests conducted occurred according to the criterion of ESC.

4.6 Discussions

To summarize the experiments performed and the results obtained, it is observed that all the materials when exposed to the chemicals at 2% constant strain and different temperature levels cracked under twenty four hours and thus the materials could not be differentiated on the basis of time in this case. Although there was inaccuracy in measuring exact time of fracture which affected the results. But also there are high chances that this situation occurred because of two main reasons - one of which is the high aggressiveness of the chemicals and second one, which might be the more important reason is the high strain value applied on the materials. Ideally, the strain should have been somewhere in the middle or lower part of the elastic region, 0.5% or 1%. 2% strain value, which was on the upper part of elastic region and close to yield point was chosen to accelerate the experiments to make up for the time lost during preparation of the set-ups and the samples. To compare the materials with different yield point, same percentage of strain level compared to the material's respective yield points can be chosen for the testing.

During the second part of the experiments, when the materials were tested without chemicals, there is evident difference between the time for crazes to occur on the surface of the materials. This set of experiments though was stress cracking in air instead of materials being exposed to chemicals, but still it helped in differentiating and comparing the materials on the basis of time taken by the samples to get crazes. These experiments showed that the materials showed difference when tested in different temperatures as well. It was observed that increasing the temperature from room temperature to 50°C the crazing accelerated meaning, the crazes occurred faster when temperature was increased, but till a certain temperature, after which the speed of crazing was similar. This was seen when the results of 50°C were compared to the results of 75°C and it was found that time for crazing was similar in most cases.

Another important result which was observed from the experiments conducted without chemical was that the samples which were the polymeric blend of PC/ABS were more resistant to cracking than pure ABS materials. This was expected according to the theory of ESC which says that polymer blends are better materials to resist ESC than pure polymers due to the fact that polymer blends have more entanglements in the secondary bonds which makes the materials tougher and also they have less void spaces due to which chemicals cannot sweep in easily to attack the materials.

4.7 Sources of Error

While performing the experiments there were some sources of error which were difficult to avoid and these could have impacted the results to some extent. Sources of error which could have effected the results were inaccuracy of time, presence of initial defect, difference in sample dimensions.

First source of error was that there could be defects present from the starting at the edges. When the samples where cut from bigger sized plaques, they were water grinded to remove or reduce the edge and corner defects or notches to minimum number and size so that these notches or defects do not help in accelerating the crazing and eventually cracking of the materials. Still, it would be difficult to make the materials totally smooth and 100% defect free and there could be some defects in the materials present still which could impact the time taken for crazing and cracking process. This error could be avoided by testing a lot of samples.

Secondly, the materials had different thickness, some were 2mm thick while some were 2.5mm thick, whereas some were 3mm thick and some 3.5mm thick. Also, though every material was supposed to be cut 102mm long and 22mm wide, but there was inaccuracy in that as well. And though, all samples irrespective of their thickness were subjected to 2% strain, different samples required different set-ups. This could have led to some minor differences in the radii of set-ups or the area on the material which had 2% strain. Also, difference in dimensions could have probably influenced the rate of cracking. For example, wider material would take longer to crack completely than narrower material.

Not a source of error, but there was inaccuracy in measurement of time as it was difficult to measure exact time of cracking in every sample and thus the difference in the time of the cracking process could not be measured between the materials.

Chapter 5

Conclusions

5.1 Conclusion

With a swiftly changing automobile industry, it is also important for the materials area in the industry to keep up the pace, so that the materials used in the interiors and exteriors of the automobiles should be good enough to have the style and comfort wanted by the customers with the safety features required for them. The materials used in automobiles play an important role for the safety of the passengers. The automobiles are safer when right materials are chosen with right conditions so that they do not fail easily.

This thesis study helped setting up the most suitable ESC test method at Volvo Car Corporation (VCC) for future testing of ESC of materials used in the cars. The learning outcomes from this study might prove to be useful for the industry.

After studying all the results of this thesis work, the ESC tests with chemicals showed that either the chemicals were very aggressive for the materials or / and the strain level chosen being too high. While comparing the chemical and without chemical tests, where without chemical tests are the reference tests for the chemical ESC tests may conclude PC/ABS polymeric blend materials might be much better than pure ABS materials for ESCR. There can also be a conclusion that shows that almost all the material had one to one correlation with respect to their yield point, i.e., higher the yield point of the material, more resistant were they to crazing when tested for same strain level. Another thing which may be concluded when comparing both the ESC and the reference (without chemical) tests was to avoid using the assembly aid or pure PEG with these materials for assembling or even during other times, because this can increase the risk of cracking of these materials. On the other hand, no significant conclusion could be drawn from the chemical tests alone since all the samples failed quite fast and the material's comparison was not possible. Though, two other points to be concluded are that the lower the stress or strain applied on the materials, the better and these materials with combination of other factors when exposed to elevated temperatures might cause the

materials to break.

5.2 Future work

There are several possibilities for further work in this topic. From a theoretical study point of view, Hansen solubility parameter model can be used to check the compatibility between the polymers and the chemicals. This model is not fully accurate because this model does not work accurately for mixtures and shows poor correlation to these mixtures of miscible solvent pairs. The reason for this non - correlation is that according to the theory, mixtures should be more aggressive ESC agents than individual components as discussed in section 2.6.

The method and the apparatus used during the experimentation can be used in future to evaluate ESC of new materials and / or different chemicals and at different conditions which includes temperature levels and strain applied on the materials. For ESC testing in future, there can be a lot of permutations and combinations of materials selected to be tested, chemical agents to be used on the samples, temperature levels and strain level applied on the samples.

A good starting point would be using the materials selected according to the area of interest and the chemicals which are generally used in any application areas where these materials are involved and choosing the three temperature levels as chosen for this project, but reducing the strain level from 2% and apply 0.5% or 1% strain level.

5.3 Reflections

This thesis project is important in many ways for the automobile industry because ESC is a major concern for the polymers, as it is one of main reasons for the amorphous polymers to fracture. By studying the main types of polymers - ABS and PC/ABS used in the cars when exposed to different chemicals either during assembling or by consumers at certain other conditions which include temperature and stress or strain levels applied on the materials, it can be seen which materials are better when exposed to a certain chemical or vice versa, that is, which chemical should be used when a certain type of polymeric material is being used. Apart from the right material and chemical selection or combination of both, this study also helps in choosing the optimum temperature and stress or strain level that should be applied on the material.

This study with relevant future work can help in right material selection and right conditions according to the material to increase the service lifetime of the component in the car and thus reduce the cost of maintenance.

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