Temperature dependence of the shear strength in adhesively bonded joints reinforced with multi-walled carbon nanotubes

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Abstract

In this paper, the temperature dependence of the strength of adhesively bonded shear lap joint reinforced with multi-walled carbon nanotubes (MWCNTs) was studied. The results showed that increasing the testing temperature diminished the improving effect of MWCNTs to the extent that beyond a critical temperature, adding nanofillers even degraded the shear strength of adhesive joints. Furthermore, using a proposed mathematical model, the optimum MWCNT weight percentages for the MWCNT-reinforced adhesives tested under different temperatures were obtained. Moreover, the scanning electron microscopy technique was used to determine the running micro-mechanisms.

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Keywords

Adhesively bonded joint

Fracture load

Elevated temperature

Multi-walled carbon nanotubes

Fractography

Nomenclature

CTE
: coefficient of thermal expansion (1/°C)

DSC
: differential scanning calorimetry

MWCNTs
: multi-walled carbon nanotubes

RSM
: response surface methodology

S
: adhesive joint strength (MPa)

SEM

scanning electron microscopy

SLJ

single lap joint

T

testing temperature (°C)

T_g

glass transition temperature (°C)

wt%

weight percentage

w

weight percentage

1. Introduction

Adhesively bonded joints have attracted considerable attentions in various industries such as automotive, marine and aeronautic industries. This is because of several merits that adhesive joints have over other conventional joints such as high strength to weight ratio, ability of joining dissimilar materials, eliminating galvanic corrosion, appropriate vibration damping and high fatigue resistance. However, there are some disadvantages that limit the applicability of adhesive joints such as requiring careful bond surface preparation, low creep strength and susceptibility to high service temperature. The behavior of adhesive joints can be considerably influenced by the service temperature. Many researchers (e.g. [1], [2], [3]) have studied the effect of temperature on mechanical behavior of adhesively bonded joints. The adhesives that are appropriate for high temperature applications are generally very brittle at low temperatures whereas, the adhesives that are designed for low service temperatures usually suffer from low strength at high temperatures. One of the techniques that researchers (e.g. [4], [5], [6]) proposed for overcoming the low resistance of adhesives to high temperature was the mixed adhesive joint technique. In this technique two adhesives were used in the joint, a stiff adhesive for the middle part of the overlap and a flexible adhesive for the overlap ends. This technique was first proposed by Hart-Smith [4], extended to low and high temperatures by da Silva and Adams [5] and then employed for aerospace applications by Marques et al. [6]. In this technique, the stiff adhesive used at the middle of the joint retained the joint strength at high temperatures, while the flexible adhesive at the overlap ends sustained the applied load at low temperatures.

Embedding nano-sized fillers in resins [7] and adhesives [8] is an efficient way of enhancing the mechanical properties of adhesive joints. There are nanoparticles of different materials and geometries such as nano-rubber [9], nano-silica [10], nano-clay [11] and carbon nanotube [12] that can be used for reinforcing adhesive joints and composite materials. MWCNTs have recently attracted considerable attentions in polymeric materials due to their exceptional mechanical, thermal and electrical properties. Several researchers (e.g. [13], [14], [15], [16], [17]) studied the effect of adding MWCNTs on mechanical behavior of adhesive joints. Londhe and Misal [13] studied the effect of MWCNTs on the shear strengthof adhesively bonded single lap joints. They showed that the MWCNT-filled adhesive resulted a maximum improvement of 17.5% in the joint strength compared with the neat adhesive joints. Gojny et al. [14] reported 10% improvement in the tensile strength of epoxy matrix composites by incorporating 0.5 wt% (wt%) of amino-functionalized double-walled carbon nanotubes into the resin. Hsiao et al. [15] studied the effect of adding MWCNTs into the adhesive layer of adhesively bonded joints and found that the strength of adhesive joint was improved by 45.6% when 5 wt% of MWCNTs was added to the epoxy adhesive. Gkikas et al. [16] showed that carbon nanotube with 0.5–1 wt% improved the shear strength of adhesive joints by 5–10%. Tabaei et al. [17] studied the effect of MWCNTs and aluminanano-powders (Al_2O_3) on the shear strength of adhesively bonded joints. The shear strength of the adhesive joints was increased by about 70% and 50% by adding alumina nano-powders and MWCNTs up to 1.5 and 3 wt%, respectively. The strength of adhesively bonded joints can be considerably dependent on the service temperature particularly when the service temperature is close to the adhesive glass transition temperature level. In this study, it was aimed to investigate whether the improving effect of MWCNTs on the adhesive strength remained the same for the elevated servicetemperatures. This was accomplished by testing the neat and reinforced adhesive joints under different controlled testing temperatures. Moreover, the fracture surfaces were assessed using the scanning electron microscopy (SEM) technique to pick up the micro-mechanisms involved in the reinforced joints. Furthermore, statistical analyses were carried out to determine the effects of elevated temperatures and added MWCNTs on the adhesive strength in more details. Then the optimum weight percentages of added MWCNTs for different testing temperatures were obtained.

2. Materials and experimental procedure

In order to study the effect of MWCNTs on degrading influence of elevated temperature on the shear strength of adhesive joints, unreinforced and reinforced single lap joints (SLJs) with different weight percentages of MWCNTs were manufactured and tested under quasi-static loading.

2.1. Materials

The adhesive joints were fabricated by bonding substrates made of Aluminum 6061-T6 with a bi-component epoxy adhesive named Araldite 2011 [18]. The Young's modulus, the ultimate shear and tensile strengths of the substrates were 69 GPa, 200 MPa and 300 MPa, respectively [19]. The substrates were cut from a 4 mm thick aluminum sheet with the dimensions of 100 × 25 mm^2. Moreover, MWCNTs used for reinforcing the epoxy adhesive had a purity of 95%, the length of 30 μm and the outer diameter of 20–30 nm. The nanofillerswere supplied by Neutrino Co. located in Iran. In order to choose the testing temperaturelevels, the differential scanning calorimetry (DSC) test was conducted to measure the adhesive glass transition temperature (T_g) according to ASTM D3418-15 standard [20]. The DSC test was carried out using a Mettler Toledo DSC calorimeter (Switzerland). For this purpose, an adhesive sample with a known mass was prepared. The adhesive sample was placed in a 40 μL aluminum crucible and heated under a nitrogen gas flow of 50 mL/min. The adhesive sample was heated, cooled and reheated from −10 to 90 °C at a heating rate of 20 °C/min. Fig. 1 shows the DSC heating curves of the adhesive. The second heating curve was used to measure T_g.

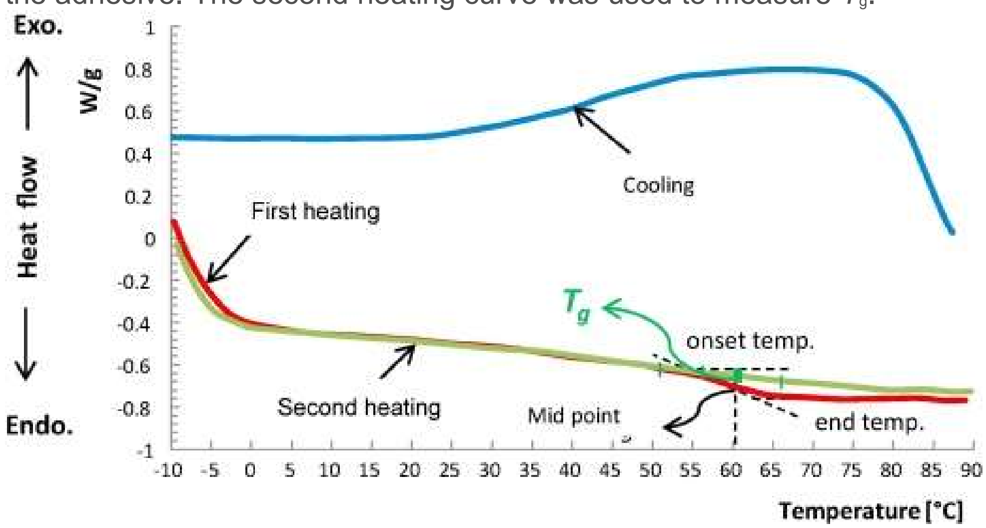

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Fig. 1. The DSC test result of adhesive.

Three temperatures including onset, mid-point and end temperatures can be seen in Fig. 1. For most applications, the mid-point temperature is designated as the glass transition temperature according to ASTM D3418 standard. Therefore, the glass transition temperature of the adhesive was obtained as 60.2 °C.

2.2. Specimen manufacturing

The unreinforced and reinforced SLJs with MWCNTs were manufactured. The adhesive was reinforced with MWCNTs with two different weight percentages of 0.1 and 0.3. To disperse the nanofillers into the adhesive layer, first MWCNTs were added to the binder part of the adhesive and the mixture was mechanically mixed for 10 min at 180 rpm. Then the mixture was ultra-sonicated for 1 h at a power of 70 W and a work cycle of 1 s on/off. In order to prevent the mixture temperature from rising too much, the mixture was placed in a container of ice and water during the sonication process to reduce the mixture temperature. After completing the sonication process, the hardener was added to the mixture with a weight ratio of 100–80 for the binder to hardener and the mixture was mechanically stirred for 10 min at 180 rpm. The mixing procedure was performed slowly to reduce producing air bubbles into the adhesive in the course of stirring, as the entrapped air bubbles can degrade the adhesive joint strength. It should be mentioned that implementing vacuum degassing could more efficiently minimize the air bubbles. However, it was attempted to follow exactly the same procedure for manufacturing all samples including the neat and reinforced adhesive joints in this study.

Prior to bonding, the aluminum substrates were treated in a sulfuric acid etching solution followed by anodizing according to ASTM D2651 standard [21] to provide better adhesion between the substrates and the adhesive. For manufacturing the joints, the adhesive was applied on the substrates. Then, the substrates were placed in a manufacturing fixture. The geometrical dimensions of the adhesive joints are presented in Fig. 2.

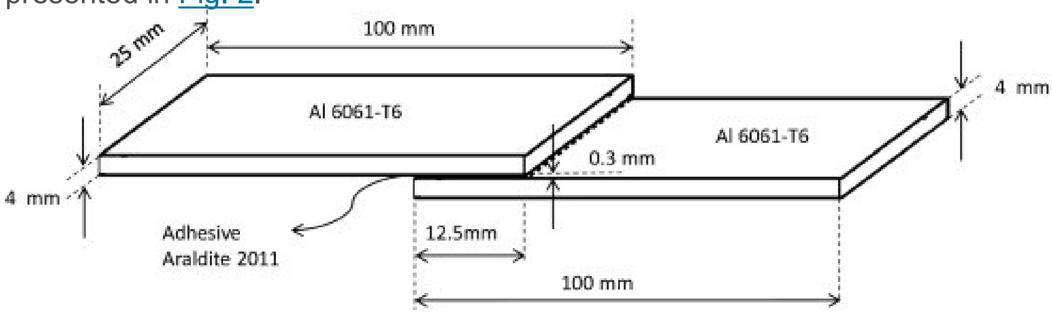

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Fig. 2. The geometrical dimensions of SLJs (not to scale).

As shown in Fig. 2, the adhesive thickness and the overlap length and width of the joints were 0.3, 12.5 and 25 mm, respectively. In order to apply a controlled pressure on the joints and maintain the adhesive thickness fixed and uniform and keep the substrates aligned, a manufacturing fixture, shown in Fig. 3, was utilized. Using the manufacturing fixture, several SLJs can be fabricated at the same time. The adhesive thickness of the joints was controlled by using two 4.3 ± 0.01 mm thick shims on the top and bottom of the joints group as shown in Fig. 3. Moreover, identical blocks were placed between the joints in order to separate the joints during manufacturing. Furthermore, in order to apply controlled pressure during the curing process, a spring-loaded mechanism was used as shown in Fig. 3.

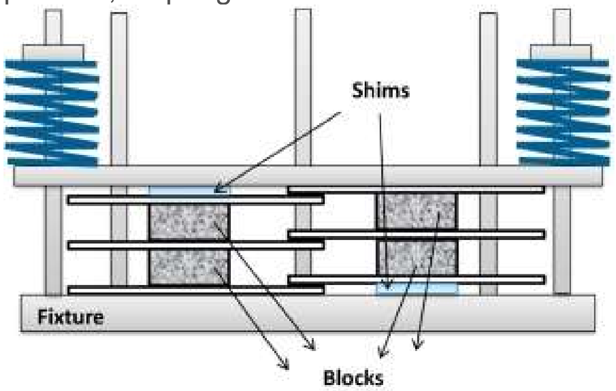

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Fig. 3. The manufacturing fixture of SLJs.

The single lap adhesive joints were cured in an oven at a temperature of 40 °C for 16 h according to the Araldite 2011 data sheet.

2.3. Mechanical testing

To evaluate the effect of MWCNTs on degrading influence of elevated temperature, the manufactured unreinforced and reinforced SLJs were tested under quasi-static loading using the SANTAM universal testing machine. The device was equipped with an oven in order to supply controlled elevated temperatures. The quasi-static tests were carried out under four temperature levels of 23 °C (room temperature), 40 °C, 50 °C and 60 °C. The tensile testswere conducted under displacement control with a constant rate of 0.5 mm/min. Each test was repeated at least four times to ensure the repeatability of the results.

3. Experimental results and discussion

3.1. The joint strength

The strengths of the unreinforced and reinforced SLJs with different weight percentages of MWCNTs under four different temperature levels were obtained and compared to evaluate the degrading influence of elevated testing temperature on the effect of MWCNTs on the strength of adhesive single lap joints. Fig. 4 shows variations of the adhesive joint strengths against the testing temperature level for different weight percentages of MWCNTs. The joint strengths were calculated as the failure loads of SLJs divided by the bond area.

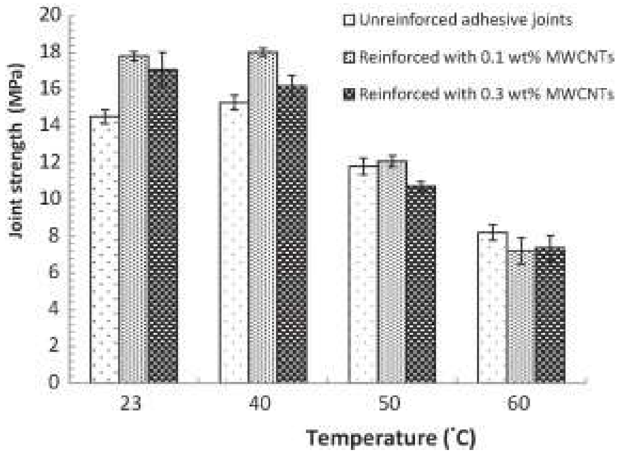

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Fig. 4. Effects of MWCNT weight percentage and testing temperature on the strengths of adhesive joints.

According to Fig. 4, variations of strength versus the testing temperature revealed that the optimum strength occurred at the testing temperature of 40 °C (i.e. the adhesive curing temperature). Moreover, by raising the testing temperature above 40 °C, the joint strengths of the unreinforced and reinforced adhesives were declined. This shows the degrading influence of high temperatures on the mechanical strength of adhesives. However, the decreasing slopes of the strength versus testing temperature curves corresponding to the reinforced adhesives with MWCNTs were steeper compared to that of unreinforced adhesive. This signifies that although adding MWCNTs into the adhesive layer can improve the joint strength at lower temperatures, it can have negative effect of the joint strength at higher temperatures. Table 1 lists the percentage differences between the strengths of unreinforced and reinforced SLJs with different weight percentages tested at four different testing temperatures.

Table 1. Percentage difference between the strengths of reinforced and unreinforced SLJs at different testing temperatures.

Temperature (°C)	% difference in strength compared with the unreinforced SLJ	
	0.1 wt% MWCNTs	0.3 wt% MWCNTs
23	22.7%	22.2%
40	17.9%	5.7%
50	2.5%	−9.2%
60	−12.2%	−10.2%

As presented in Table 1, at testing temperature levels of 23 °C, 40 °C and 50 °C, by adding 0.1 wt% of MWCNTs into the adhesive layer, the joint strengths were increased by 22.7%, 17.9% and 2.5%, respectively, compared to the unreinforced adhesive joints. Also, by adding 0.3 wt% of MWCNTs to the adhesive layer, the adhesive joint strength improved by 22.2% and 5.7%, when tested under testing temperatures of 23 and 40 °C, respectively. However, the strength of the reinforced adhesive joint with 0.1 wt% MWCNTs was lower than the strength of unreinforced adhesive joints when tested at 60 °C. For the reinforced adhesive with 0.3 wt% MWCNTs, adding nanofillers imposed negative effect on the joint strength when the testing temperature reached 50 °C. This shows that the improving effect of MWCNTs on the load bearing capacity of the adhesive joint can considerably be dependent on the testing temperature and this dependency is intensified by increasing the nanofiller weight percentage.

3.2. The fractography

The fracture surfaces of the adhesive joints were investigated visually and using the SEM technique. The visual observation of the fracture surfaces revealed that the failure mode in all samples were interfacial and near interfacial within the adhesive. Moreover, the fracture surfaces were more deeply assessed using SEM images. As seen in Fig. 5, the samples were cut and placed on a sample holder and sputter-coated with a thin layer of gold to increase the conductivity of electrons on the surfaces and to prevent the build-up of electric charge. A 15–25 kV accelerating voltage was applied to accomplish the desired magnification.

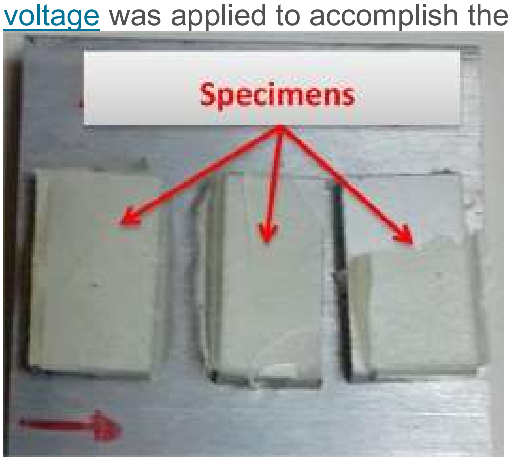

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Fig. 5. The prepared specimens for SEM fractography.

Fig. 6, Fig. 7, Fig. 8 show micrographs of the fracture surfaces corresponding to the unreinforced and reinforced adhesive joints with 0.1 and 0.3 wt% MWCNTs, respectively, tested under different temperatures. At higher temperatures, adhesive materials tend to become more ductile due to the increased mobility of polymer chains that allows the material to deform more easily. Moreover, as seen in Fig. 6, numerous voids can be observed on the fracture surfaces of the unreinforced adhesive joints tested under elevate temperatures.

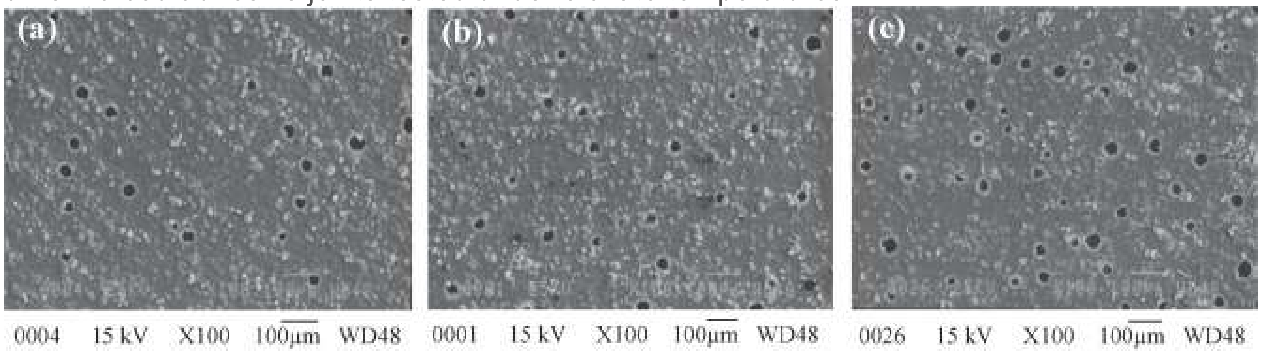

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Fig. 6. Fracture surfaces of the unreinforced adhesive joints tested under different temperatures of (a) 40 °C, (b) 50 °C and (c) 60 °C.

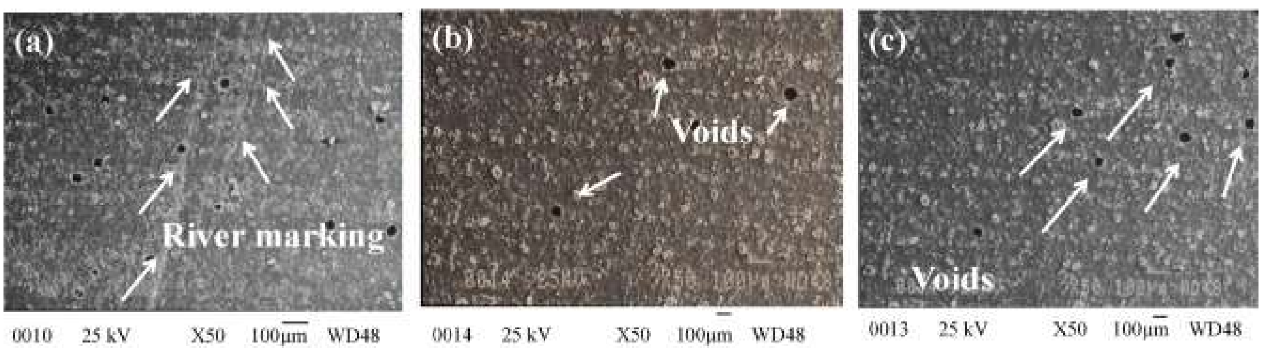

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Fig. 7. Fracture surfaces of SLJs reinforced with 0.1 wt% MWCNTs tested under different testing temperatures of (a) 40 °C, (b) 50 °C and (c) 60 °C.

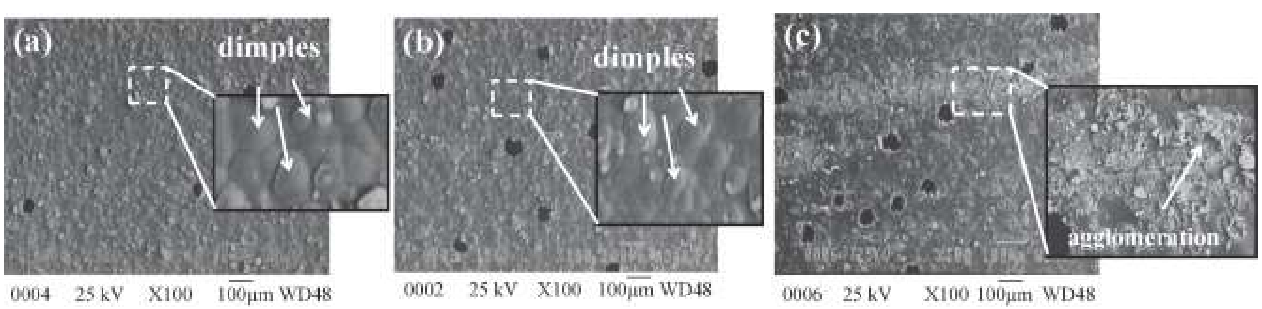

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Fig. 8. Fracture surfaces of SLJs reinforced with 0.3 wt% MWCNTs tested under three testing temperatures of (a) 40 °C, (b) 50 °C and (c) 60 °C.

The voids observed in the SEM micrographs of adhesive joint fracture surfaces were most probably the entrapped micro-sized air bubbles enlarged under elevated temperatures in the course of loading. Consequently, this caused the joint strength of the adhesive joints to decrease. Previous studies [22], [23] have shown that voids have detrimental effect on the mechanical properties of polymers such as strength.

Fig. 7 shows the fracture surfaces of the reinforced adhesive joints with 0.1 wt% MWCNTs tested under different temperatures. As can be seen in Fig. 7, the number and size of the voids were considerably decreased in the adhesive joints reinforced with 0.1 wt% MWCNTs compared with the unreinforced adhesive joints. This was because the added nanofillers could retain the polymeric chains and suppressed growth of small micro-voids. Moreover, river-like marks were easily observed on the fracture surfaces of the joints reinforced with 0.1 wt% MWCNTs, particularly at lower testing temperatures (see Fig. 7(a)).

The river-like marks usually are produced when a couple of newly formed crack planes join together in the course of loading [24]. The river-like marks indicate brittle failure and resistance of material against the plastic deformation. The presence of nanofillers in the adhesive can facilitate deviating the crack growth and forming multiple crack growth patterns, thus the formation of river-like marks can be intensified. However, by increasing the testing temperature, the river-like marks were rather suppressed denoting more ductile material behavior (see Fig. 7). Actually, there were two contrary factors affecting micro-voids, one was the elevated temperature coupled with applied load that promoted void growth and the other one was MWCNTs that retained the polymeric chains and suppressed growth of small micro-voids. Depending which factor dominated the other, changing temperature and weight percentage of MWCNT resulted in either increase or decrease in the strength of adhesive joints.

Fig. 8 demonstrates the fracture surfaces corresponding to the reinforced adhesive joints with 0.3 wt% MWCNTs. As shown in Fig. 8(a) and (b), dimples can be observed on the fracture surfaces of the adhesive joints reinforced with 0.3 wt% MWCNTs tested under 40 °C and 50 °C testing temperatures. This was also reported in other studies (e.g. [24], [25]). As shown in Fig. 8, adding higher wt% of MWCNTs into the adhesive layer gave rise to nanofiller agglomeration. This is typical in nano-adhesives and nanocomposites that there is often an optimum wt% of nanofillers at which the maximum improvement in mechanical properties is obtained and adding higher content of nanofillers diminishes the beneficial effects of nanofillers. This has been reported by many researchers (e.g. [13], [17], [26], [27]).

There are several factors that can influence the optimum weight percentage of nanofiller such as the nanofiller type, characteristics of the matrix and dispersion method. The aggregated nanofillers led to local stress concentration and caused the joint strength of the adhesive joints to decrease. Dimples are usually formed from the coalescent of particles after debonding. Moreover, in this study, dimples were observed on the fracture surfaces corresponding to the adhesive joints reinforced with 0.3 wt% MWCNTs. Therefore, when higher weight percentage of MWCNTs (i.e. 0.3 wt%, in this study) were added to the adhesive layer, MWCNT agglomerations were easily formed. This was previously reported by many researchers. On the other hand, since the coefficient of thermal expansion (CTE) of the adhesive Araldite 2011 was more than four times higher compared to the CTE of MWCNTs at elevated testing temperatures, the adhesive tended to expand more compared to the nanofillers. This mismatch in thermal expansions provided loci from which voids could be formed and coalesced in case of MWCNT agglomerations. However, investigating this required more extensive and dedicated experimental tests and can be considered as future research.

4. The mathematical model

Statistical Analysis was used to analyze the experimental data and determine the interaction between the factors (including the testing temperature and the weight percentage of added MWCNTs). For the statistical analysis, the response surface methodology (RSM) using the miscellaneous design model was employed. A two-factor three level factorial design was utilized. The low and high levels for the factor of temperature were 23 °C and 60 °C and for the factor of MWCNT weight percentages were 0 and 0.3 wt%. Each test was repeated at least three times.

To achieve a better understanding on the effects of testing temperature and weight percentage of MWCNTs and also the influence of the testing temperature on the effect of added MWCNTs on the adhesive joint strength, a mathematical model was derived using RSM. The response surface methodology suggested a quadratic mathematical model (Eq. (1)).

$$S=(0.9444)T+(38.2779)w-(0.0136)T^2-(64.7969)w^2-(0.3666)Tw+0.1655 \quad (1)$$

in which *S* is the adhesive joint strength, *T* is the testing temperature and *w* is the weight percentage of added MWCNTs.

Table 2 demonstrates the analysis of variance for the response surface quadratic model obtained by RSM. As seen in Table 2, the model had a p-value of <0.05 indicating the significance of the model. As seen in Table 2, the effect of *w* on the shear strength is negligible. It means that the detrimental influence of elevated temperature subdued the effect of MWCNT nanofillers at elevated temperatures. As seen in Table 2, the model had an F-value of 19.11 and a p-value of 0.0006 indicating that there was only a 0.06% chance that the F-value of 19.11 occurred due to noise, consequently, the model was significant.

Table 2. Analysis of variance for the response surface quadratic model.

Source	Sum of squares	df	Mean square	F-value	p-value Prob > F
Model	204.78	5	40.96	19.11	0.0006
T-Temperature	124.49	1	124.49	58.08	0.0001
w-Weight percentage	1.77	1	1.77	0.83	0.3936
T*w*	4.14	1	4.14	1.93	0.2071
T^2	50.83	1	50.83	23.72	0.0018
w^2	3.13	1	3.13	1.46	0.2659
Residual	15.00	7	2.14		
Lack of fit	2.42	3	0.81	0.26	0.8535

Moreover, the high p-value (>0.05) for the lack of fit implies that the model error (residuals excluding replicate variation) was not significantly greater than the replicate error. Therefore, the model had no lack of fit and was of sufficient complexity to describe the results adequately. Furthermore, a high R-squared value of 0.9317 (close to unity) and a high Adequate precision value of 11.205 (>4) were obtained for the model implying statistically acceptable model.

A diagnostic test was carried out to graphically analyze the model and assess the model validity. Fig. 9 shows the normal probability plot of residuals for the adhesive joint strength. This plot assures that the results were normally distributed.

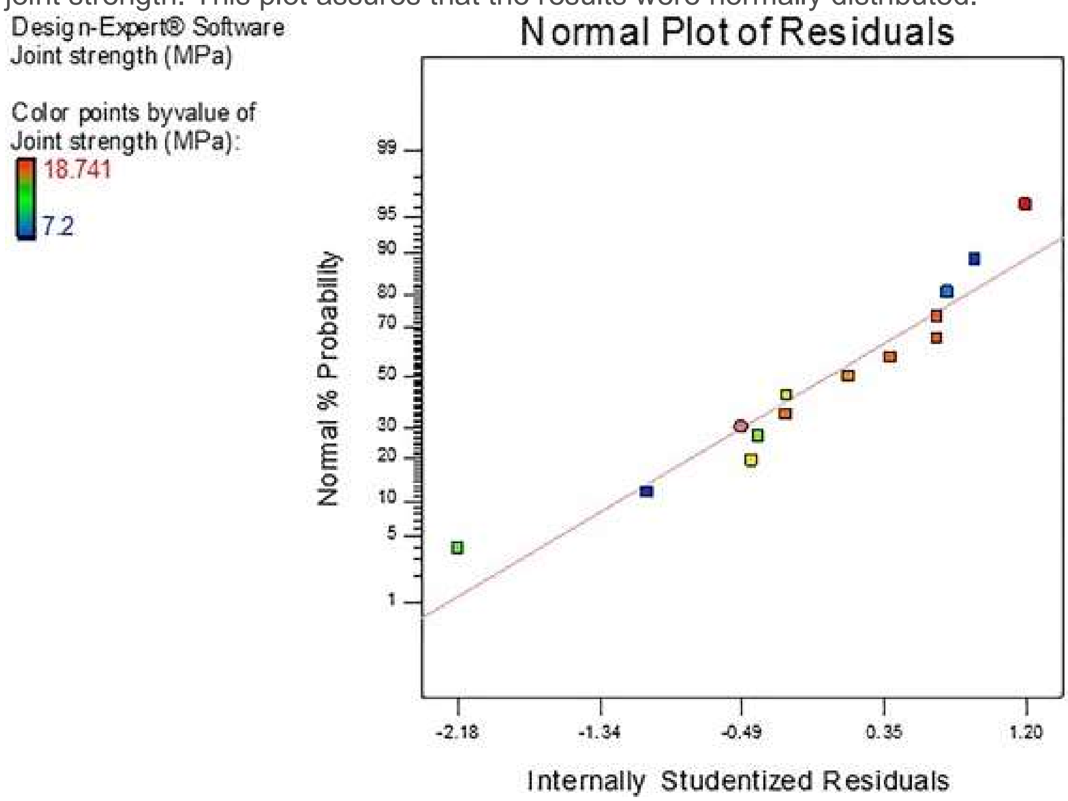

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Fig. 9. Normal probability plot of residuals for the joint strength.

The points narrowly scattered around a straight line indicate that the residuals followed a normal distribution and the derived joint strength model would not be improved by change in the transformation.

Fig. 10 shows the 3D contour plot of the adhesive joint strength versus the two factors including the testing temperature and wt% of MWCNTs. It can be concluded from Fig. 10that the optimum wt% of MWCNTs depended on the testing temperature and it decreased when the testing temperature increased.

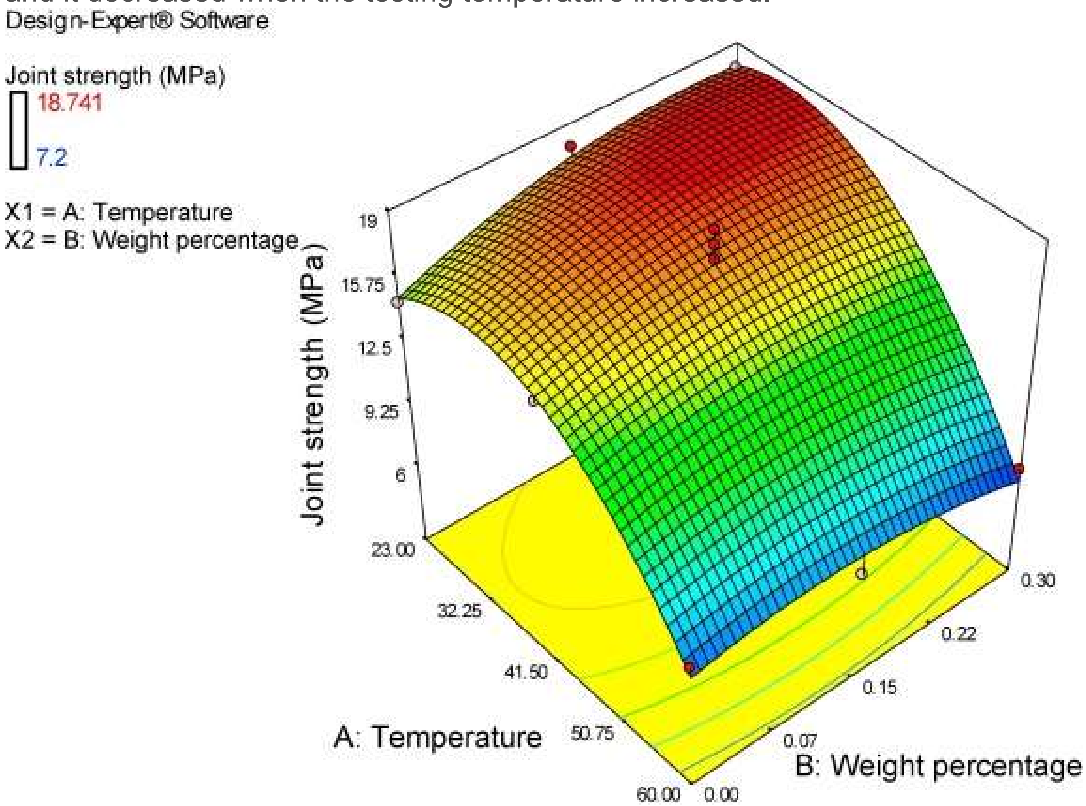

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Fig. 10. The 3D contour plot illustrating the effect of temperature and weight percentage on the strength of adhesive joint.

More specifically, this can be found by differentiating Eq. (1) with respect to the parameter *w*(wt% of MWCNTs) and equating the result to zero. It can be determined based on Eq. (1)that the optimum wt% of MWCNTs for the adhesive joints tested under the temperature levels of 23, 40 and 60 °C are about 0.23, 0.18 and 0.06 wt%, respectively. It should be noted that the mathematical model presented in Eq. (1) is material dependent and needs to be redefined if the adhesive is changed.

5. Conclusions

Adding MWCNTs into the adhesive layer of adhesive joints has the capability of improving adhesive joint strength. In this study, it was aimed to study whether this improving effect was depended on the testing temperature. For this purpose, an epoxy adhesive was reinforced with different weight percentages of MWCNTs including 0.1 and 0.3 wt%. Single lap adhesive joints were fabricated using the unreinforced and reinforced adhesives and tested under quasi-static loading and different testing temperatures of 23, 40, 50 and 60 °C. The results indicated that the maximum strength values of the reinforced and unreinforced adhesive joints were obtained at the curing temperature of adhesive. Moreover, when the testing temperature was increased, the improving effect of adding MWCNTs decreased accordingly. Also, by further increasing the testing temperature, adding MWCNTs degraded the adhesive joint strength. The fracture surfaces of the neat and reinforced adhesive joints tested under different temperatures were assessed using SEM fractography. It was found out that the entrapped micro-sized air bubbles were influenced by two contrary factors of elevated temperature and added MWCNTs. The elevated temperature coupled with applied load promoted void growth. Whereas, when 0.1 wt% MWCNTs were added to the adhesive, river-like marks appeared on the fracture surfaces and relatively less voids were observed compared with the unreinforced samples signifying that growth of the small micro-voids was relatively suppressed by retaining the polymeric chains. However, further increasing the weight percentage of MWCNTs gave rise to nanofiller agglomeration and imposed negative effect of the adhesive joint strength. Statistical analyses were carried out on the experimental results and a mathematical model was derived. The variance analyses were conducted and it was approved that the mathematical model was statistically significant.