

Lap Shear Strength and Thermal Stability of Diglycidyl Ether of Bisphenol A/Epoxy Novolac Adhesives with Nanoreinforcing Fillers

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ABSTRACT: Nanoreinforcing fillers have shown outstanding mechanical properties and widely used as reinforcing materials associated to polymeric matrices for high performance applications. In this study, a series of multiwalled carbon nanotubes (MWCNTs)-, nano- Al_2O_3 -, nano- SiO_2 -, and talc-reinforced epoxy resin adhesives composites were developed. The influence of different types and contents of nanofillers on adhesion, elongation at break, and thermal stability (under air and nitrogen atmospheres) of diglycidyl ether of bisphenol A (DGEBA)/epoxy novolac adhesives was investigated. A simple and effective approach to prepare adhesives with uniform and suitable dispersion of nanofillers into epoxy matrix was found to be mechanical stirring combined with ultrasonication. Transmission electron microscopic and scanning electron microscopic investigations revealed that nanofillers were homogeneously dispersed in epoxy matrix at optimized nanofiller loadings. Adhesion strength was measured by lap shear strength test as a function of nano- Al_2O_3 and MWCNTs loadings. The results indicated that the lap shear strength was significantly increased by about 50% and 70% with addition of MWCNTs and nano- Al_2O_3 up to a certain level, respectively. The highest lap shear strength was reached at 1.5 wt % of nano- Al_2O_3 loading. MWCNTs at all loadings (except 3 wt %) and nano- Al_2O_3 have enhanced onset of degradation temperature and char yield of the adhesives. By combined incorporation of 0.75 wt % nano- Al_2O_3 and 0.75 wt % MWCNTs into the epoxy novolac/DGEBA blend adhesives a synergistic effect was observed in the thermal stability of the adhesives at high temperatures (800°C). © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40017.

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INTRODUCTION

In the recent years, many research activities have been largely focused on incorporating nanofillers in polymers, because polymer-based nanocomposites exhibit much better mechanical, thermal, and multifunctional properties compared with the polymer matrices containing conventional microfillers.^{1,2} Epoxy resin and its derivatives (epoxy novolac) have a wide range of excellent physical and chemical properties which are suitable for applications in aerospace, automotive, construction, microelectronics, defense, marine, and other industries.²⁻⁸ Incorporation of various reinforcing nanosized phases into epoxy adhesive is one of the ways to enhance adhesion strength and thermal stability.^{1,5,9-13} To increase the properties of epoxy adhesives, different types of nanoparticles such as carbon nanotubes (CNTs), nanoclays, nano- SiO_2 , and nano- Al_2O_3 (alumina nanoparticles) have been utilized.^{8,9,14,15} Recently, the use of multiwalled carbon nanotubes (MWCNTs) and nano- Al_2O_3 as effective fillers in different polymer matrices, particularly epoxy adhesives, have attracted considerable interest due to their unique mechanical

and thermal properties. These nanofillers can increase lap shear strength of the adhesives.^{1,7,8,11,13,16-19} Zhai et al.⁸ investigated the effect of nano- Al_2O_3 on the adhesion strength of epoxy adhesive by pull-off adhesion tests. They demonstrated that nano- Al_2O_3 increased the pull-off adhesion. Moreover, locus of failure changed from interfacial to a mixture of interfacial and cohesive. Meguid and Sun¹⁶ added MWCNTs and aluminum nanopowders to epoxy adhesive (Hysol EA 9330) for improving tensile debonding and shear properties of the composite interfaces. The results indicated that increasing the nanofillers beyond a certain level decreases the interface strength. Yu et al.⁹ studied the effect of MWCNTs on the thermal stability and electrical conductivity of epoxy adhesive (EPIKOTE 240) through thermogravimetric analysis (TGA). Mechanical stirring and ultrasonication were used as an approach for mixing. They found that electrical conductivity and thermal stability of the epoxy adhesives improved with the addition of MWCNTs. May et al.¹⁸ investigated the effect of inorganic nanoparticles on thermal stability and butt joint strength of diglycidyl ether of bisphenol A (DGEBA) epoxy adhesive by a hybrid sol-gel method. Their

Table I. Type and Content of Fillers Incorporated into DGEBA/Epoxy Novolac Adhesives

	Sample								
	EP-0	EP-1.5AL	EP-3AL	EP-1.5NT	EP-3NT	EP-1.5Si	EP-1.5Talc	EP-0.75NT-0.75AL	EP-0.75NT-0.75Si
Weight percent	0	1.5	3	1.5	3	1.5	1.5	0.75, 0.75	0.75, 0.75
Type of filler	-	Nano-Al ₂ O ₃	Nano-Al ₂ O ₃	MWCNTs	MWCNTs	Nano-SiO ₂	Talc	MWCNTs Nano-Al ₂ O ₃	MWCNTs Nano-SiO ₂

EP, DGEBA/epoxy novolac.

results showed that with addition of inorganic nanoparticles the adhesion strength increased while cure temperature on an Al substrate was reduced. Gude et al.²⁰ investigated the effect of addition of carbon nanofibers (CNFs) and CNTs on strength and toughness of epoxy adhesive. CNFs addition resulted in an increase on the Mode I adhesive fracture energy (G_{IC} of the joint). Also CNTs increased interfacial strength between the adhesive and the composite substrate and changed the crack growth behavior as well as the macroscopic failure mode. In automotive and aerospace application, aluminum is widely used due to its light weight and therefore joining of Al plates is very important.^{6–9}

Li et al.²¹ studied synergistic effect of carbon nanotube-graphene oxide as a hybrid nanofiller on polyvinyl alcohol composites. They demonstrated that by combining of these nanofillers, tensile strength and Young's modulus were significantly improved while most of the ductility was retained. Sumfleth et al.²² reported some synergistic effects in network formation, electrical properties and charge transport in hybrid epoxy nanocomposites containing MWCNTs and carbon black (CB). They found that a considerable amount of MWCNTs can be replaced by CB without changing the electrical properties.

In this work, we investigate the effect of different types of nanofillers such as MWCNTs, nano-Al₂O₃, nano-SiO₂ and their combinations, as hybrid nanofillers, on the lap shear strength, thermal stability and elongation at break of DGEBA/epoxy novolac adhesives. The effect of new mixing strategy for incorporating the hybrid nanofillers into a hybrid resin (i.e., DGEBA/epoxy novolac blends) as novel and efficient adhesives on the mechanical and thermal properties of the adhesive will be discussed in this paper for the first time. Also, the synergistic effect resulting from combination of MWCNTs and nano-Al₂O₃ on the thermal stability of the developed adhesives will be explored here.

EXPERIMENTAL

Materials

DGEBA/epoxy novolac (Sana Corporation, China) blend was used as an epoxy resin matrix. The epoxy resin blend was prepared by mixing 34 wt % DGEBA, 34 wt % epoxy novolac, and 15 wt % of triethylenetetramine (TETA; Sana Corporation, China) as an aliphatic hardener. The rest of material was 14–16.25 wt % solvent. The epoxy equivalent weight of the DGEBA at 25°C was 170. 1-Propanol (Merck, Germany, Mw = 60 g/mol)

was used as solvent. TETA is a room temperature curing agent for both the used resins. Several types of reinforcing fillers were used. MWCNTs with an outer diameter of about 10–30 nm; a length of about 10–15 μm (SSA = 1000 m²/g) obtained from Chengdu Corporation (China). Al₂O₃ nanoparticles with average size of about 80 nm (SSA = 10 m²/g) were purchased from Sigma Aldrich. Nano-SiO₂ with average size of about 7 nm (SSA = 390 ± 40 m²/g) was obtained from Sigma Aldrich and talc powder was supplied by Sana Corporation, China. Before using, all the fillers were dried at 110°C for 24 h in vacuum to eliminate the agglomeration caused by hydroscopic absorption. The filler content and type of the used epoxy resin are shown in Table I. The sheets used as an adherent for lap shear strength tests were made from aluminum–copper alloy (AL2024-T3).

Preparation of Nanofilled Epoxy Adhesive Composite

Epoxy adhesive used in this work was a room temperature curing two-component type. All ingredients except hardener (resins, nanofillers, and solvent) were mixed in a vessel. The ingredients should be mixed well to achieve a good level of dispersion. Since epoxy novolac is solid at room temperature, prior to mixing epoxy novolac was heated to 90°C to decrease its viscosity. The mixing should be done quickly to avoid temperature reduction otherwise the material will stick to mixer. For the epoxy resin samples containing two fillers, at first the fillers have been mixed mechanically together and then added to the other ingredients. In order to disperse nanofillers in the epoxy resin, initially the mixture was sonicated for 20 min at 80°C by an ultrasonic bath 35 kHz (Bandelin, Germany) thereafter it was mechanically stirred at 2000 rpm for 40 min at room temperature. For having a better distribution, the mixture was again sonicated about 20 min at 80°C. After ultrasonication, the mixture was placed in a vacuum chamber ($P = -700$ mbar) for about 2 h at 80°C to remove bubbles trapped in the mixture during the stirring and sonicating steps. Finally, hardening agent was added to the mixture with hand stirring to ensure homogeneity. For post curing, the mixture was maintained at room temperature for at least 24 h before testing.

Surface Treatment

In order to attain maximum joint performance, the surface of aluminum plates was abraded with a sand paper (150#). This roughening operation should be done half an hour before utilizing the aluminum substrate to prevent oxidation. Then, the

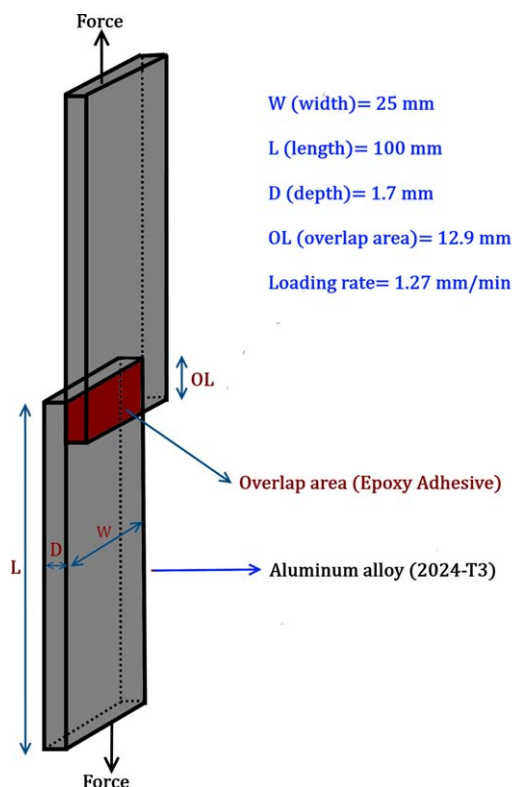


Figure 1. Geometry and dimensions of samples used for lap shear strength test. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

substrates were degreased with acetone to remove any moisture, oxidation and dust.

Characterization and Analysis

Lap Shear Strength Test. The tensile lap shear tests were performed with a crosshead speed of 1.27 mm/min using a Universal Testing Machine (Gotech, Taiwan). Five samples for this test were prepared according to ASTM D1002. The geometry and dimensions of the joints used for the lap shear strength test are shown in Figure 1.

To attain the lap joints and control adhesive bond line thickness, a simple clamping force was used so that the bonded area was subjected to an applied pressure of 3 MPa during the curing stage.²³ This procedure produced lap joint specimens with average adhesive thickness layer of $25 \mu\text{m} \pm 2$ measured by a micrometer gauge.

The elongation at break was measured by Universal Testing Machine according to ASTM D5083-10 standard. The dumbbell-shaped specimens were compression molded into the required shape using an appropriate mold.

Thermal Stability Analysis. Thermal stability and degradation of samples were determined by TGA using TGA Q 5000TA Instruments. One sample from each group was heated from ambient temperature to 800°C under air and nitrogen atmospheres with heating rate of $10^\circ\text{C}/\text{min}$ to study the degradation behavior of the developed adhesives under oxidative and thermo-oxidative conditions, respectively. The sample weight

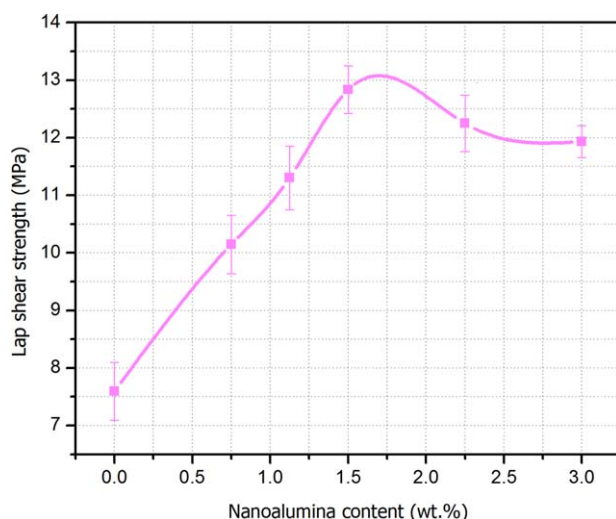


Figure 2. Effect of nano- Al_2O_3 content (wt %) on the lap shear strength. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

was about 10 mg. The residual char at 800°C , onset of degradation temperature (T_{IDT}) and maximum rate of weight loss (T_{max}) were determined for evaluating the thermal stability.

Surface Characterization

Scanning Electron Microscopic. Morphological analysis was carried out using a scanning electron microscopy (SEM), Ultra Plus Zeiss NTS. Specimens were cut with a microtome at room temperature. The specimens containing nano- SiO_2 and nano- Al_2O_3 were sputter coated with Pt to make the sample surface conductive. For these specimens, voltage of 3 kV was used. Other samples were not sputter coated and investigated with voltage of 20 kV. Aperture size for all samples was $30 \mu\text{m}$.

Transmission Electron Microscopic. The dispersion state of the MWCNTs in the epoxy adhesive blend was determined using a transmission electron microscopy (TEM), JEOL JEM-2100. The samples were cleaned ultrasonically for about 1 h and dried in an oven at 40°C for 12 h. Then 20–40 nm thick sections were ultramicrotomed on a Sorvall MT microtome using a diamond knife. The thin nanometer thick sections were carefully collected on a TEM grid with a support layer.

RESULTS AND DISCUSSION

Effect of Different Types of Nanoreinforcing Fillers on the Lap Shear Strength of DGEBA/Epoxy Novolac Adhesives

Nano- Al_2O_3 Loading. Figure 2 shows the lap shear strength of the epoxy adhesive as a function of different weight percents of nano- Al_2O_3 . Initially the lap shear strength of epoxy adhesive shows increasing trend up to 1.5 wt % of nano- Al_2O_3 loadings. This particular loading (1.5 wt %) can be considered as percolation threshold for the system. Then after the lap shear strength reduces by about 1 MPa with increasing of nano- Al_2O_3 loadings in the range of 1.5–3 wt % possibly due to agglomeration of the nanoparticles. It is also seen that the epoxy adhesive containing 1.5 wt % nano- Al_2O_3 shows about 70% improvement in the lap shear strength as compared to the neat adhesive. Figure 3 shows a typical scanning electron photomicrographs of

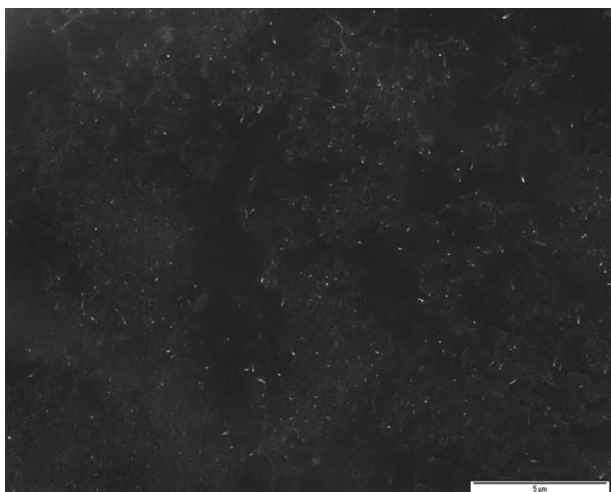


Figure 3. Scanning electron micrograph of epoxy adhesive filled with 1.5 wt % of nano- Al_2O_3 .

epoxy adhesive sample loaded with 1.5 wt % nano- Al_2O_3 (EP-1.5AL) which indicates that 1.5 wt % nano- Al_2O_3 is well dispersed in the epoxy adhesive by the applied series of mechanical stirring and ultrasonication steps. When nano- Al_2O_3 particles are added into an epoxy resin, cure kinetics of the resin might be affected due to the catalytic effect of hydroxyl groups on the particles.²⁴ As a result, cross-links are reinforced which increase interaction between alumina nanoparticles and functional groups of epoxy resin.¹⁸ On the other hand, existence of Al in the substrate and the nano- Al_2O_3 filled epoxy adhesive may increase the interaction between these components.¹³

The rough surface increases adhesion strength via enlarging the interaction area.²³ Nano- Al_2O_3 perhaps enlarges the interaction area and/or enhances the lap shear strength per interaction area.⁸ As reported by many researchers, lap shear strength increases, when the surface is abraded by sand paper.^{8–13} As shown in Figure 2, when 1.5 wt % of nano- Al_2O_3 is added to unmodified epoxy resin, the lap shear strength increases from 7.6 to 12.9 MPa. This is the highest lap shear strength achieved (about 70% improvement). By addition of higher amounts of nano- Al_2O_3 (from 1.5 to 3 wt %), the surface wetting ability of the adhesive reduces and therefore the lap shear strength decreases as compared to EP-1.5AL.^{7,8}

MWCNTs Loading. Figure 4 shows variation of the lap shear strength of epoxy adhesive against different levels of MWCNTs. In the presence of MWCNTs, the lap shear strength of adhesive increases in the entire studied range of MWCNTs loadings. It seems CNTs as reinforcing fillers has some positive effects on enhancement of degree of cross-linking of epoxy resin and hence the lap shear strength of the nanofilled adhesive increases up to certain level of CNTs loading.²⁵ Also due to the interaction of MWCNTs with epoxy chains, it is possible that some MWCNTs are trapped between cross-linked and uncross-linked regions. In fact, MWCNTs act as reinforcement or bridge between these domains.²⁵ The dispersion state of MWCNTs in the epoxy resin was studied by SEM and TEM techniques. As shown in Figure 4, addition of MWCNTs from 0 to 1.125 wt %,

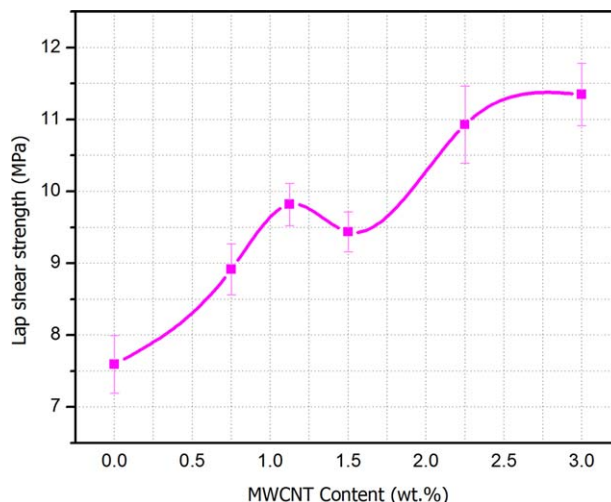


Figure 4. Effect of MWCNTs content (wt %) on the lap shear strength. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

increases the lap shear strength of epoxy adhesive because of enhanced contact surface between polymer chain and MWCNTs.²⁵ On the other hand, gaps and nanovoids within the adhesive matrix are decreased as compared to epoxy resin.¹⁸ Figure 5 represents a typical TEM image of epoxy adhesive loaded with 1.125 wt % of MWCNTs. Good dispersion and distribution of MWCNTs within epoxy matrix are evident in this transmission electron micrograph. The lap shear strength value is ~ 9.8 MPa at 1.125 wt % of MWCNTs loading. At 1.125–1.5 wt % of MWCNTs content, the lap shear strength decreases to 8.9 MPa. This might be attributed to formation of agglomerates at high loading of MWCNTs (1.5 wt %). Hence, penetration of polymer chain into agglomerates reduces due to development of stress concentration leading to the decreased lap shear strength. The size of MWCNTs agglomerates in samples loaded with 2.25 and 3 wt % of MWCNTs is more than that of sample filled with 1.5 wt % MWCNTs. Hence, the frictional effects are developed among MWCNTs. This increases temperature which in

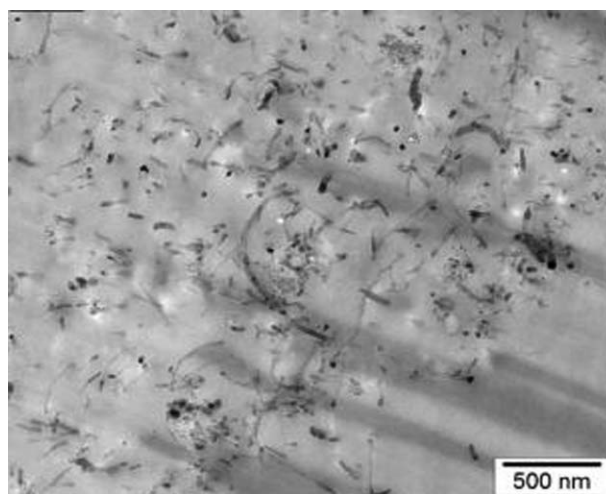


Figure 5. TEM image of epoxy adhesive filled with 1.125 wt % of MWCNTs.

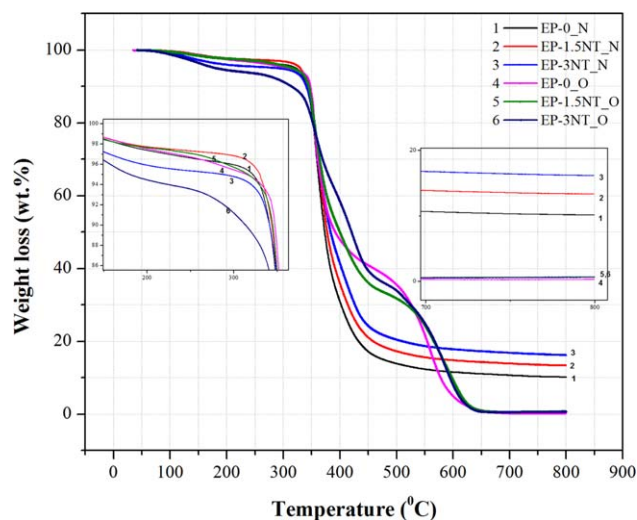


Figure 6. TGA thermograms of epoxy adhesive filled with different contents of MWCNTs (_N denotes samples tested under N₂ atmosphere and _O denotes samples tested under O₂ atmosphere). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

turn can increase cross-linking density.²⁵ Afterward, more bulk of epoxy adhesive will be cured which further reinforces the structure, leading to the enhanced lap shear strength values. In fact, increasing of lap shear strength at high level of MWCNTs may be attributed to viscosity enhancement.

The elongation at break of epoxy adhesive containing MWCNTs and nano-Al₂O₃ was also measured and result showed a slight change in elongation from 0.88 to 1.22 ± 0.4% by the nanofillers incorporation. Because of this minor variations the elongation at break data are not discussed any further.

Effect of Different Types of Nanoreinforcing Fillers on the Thermal Stability of Epoxy Adhesives

Degradation Behavior of DGEBA/Epoxy Novolac Adhesive Filled by MWCNTs. The thermal degradation and stability of epoxy/MWCNTs adhesive were studied by TGA. Cyclic structure increases thermal stability of polymers and in this regard polymers degrade at higher temperatures. The blend of DGEBA with epoxy should have higher thermal stability as compared to neat DGEBA due to existence of cyclic structures in epoxy novolac.²⁶ Figure 6 shows the TGA thermograms of unfilled cured epoxy resin and epoxy/MWCNTs adhesives with different contents of MWCNTs under air and nitrogen atmospheres. As it can be seen from Figure 6, all the systems decompose mainly in three-stage and two-stage processes in air and nitrogen atmospheres, respectively. Figure 6 also indicates that the first stages of weight loss (initiation of degradation) under air and nitrogen atmospheres are almost identical but the char yield of samples degraded under nitrogen atmosphere is more than that of samples degraded under the air. In the first stage of degradation process in nitrogen atmosphere, $T_{IDT,1}$ of EP-0, EP-1.5NT, and EP-3NT samples are 140.5, 148.3, and 110.3°C, respectively. In this step, weight loss takes place at temperatures lower than 200°C. This is possibly due to decomposition of low molecular weight compounds (such as 1-propanol). In the second stage of degradation process, $T_{IDT,2}$ of EP-0, EP-1.5NT, and EP-3NT

samples are 321.8, 330.2, and 308.6°C, respectively. The highest weight loss occurs in the second step of degradation for all the specimens.⁹ When 1.5 wt % of MWCNTs is added to unfilled epoxy adhesive, $T_{IDT,2}$ increases by 8.4°C due to reduction of polymer chain mobility and slippage in matrix under influence of MWCNTs.²⁷

Degradation of EP-3NT sample containing 3 wt % MWCNTs begins at a lower temperature than that of EP-1.5NT. Also its $T_{IDT,2}$ is about 13.2°C lower than that of EP-1.5NT possibly due to MWCNTs aggregates formation in polymer matrix which decreases contact surface area of epoxy chain with MWCNTs, and hence increases chains slippage in matrix.²⁸ On the other hand, due to poor affinity between epoxy chains and MWCNTs, more voids are present in the nanocomposite that would lead to increase in slippage of polymer chains and consequent reduction in thermal stability.^{27,29}

It is also seen that in all specimens, the maximum of weight loss rate and T_{max} occur in the second stage of degradation process which indicates that epoxy resin mainly degrades at this stage.⁹ The T_{max} values for EP-0, EP-1.5NT, and EP-3NT are 358, 362, and 363°C, respectively. This shows that by increasing MWCNTs content, the weight loss of epoxy adhesive occurs at slightly higher temperatures.

Under nitrogen atmosphere, the char yield for EP-0 and EP-1.5NT samples are 10.1 and 11.9 wt %, respectively implying that MWCNTs can increase thermal stability and char yield of the epoxy adhesive. The char yield for EP-3NT sample is 13.2 wt % which indicates that the MWCNTs can somewhat prevent decomposition process of secondary degradation products occurring before 800°C. Under nitrogen atmosphere, MWCNTs do not decompose till 800°C, whereas in air atmosphere it mainly degrades. Therefore under nitrogen atmosphere, the char yield of epoxy matrix was calculated without considering the amount of nanofillers. Under air atmosphere, the char yield of EP-0, EP-1.5NT, and EP-3NT samples are 0.25, 0.7, and 0.7 wt % respectively. After 800°C in air atmosphere, due to air accelerated oxidation process epoxy/MWCNTs samples decompose with a very high weight loss (99.3 wt %).

Degradation Behavior of DGEBA/Epoxy Novolac Adhesive Filled by Nano-Al₂O₃. Figure 7 displays TGA traces under air and nitrogen atmospheres for unfilled cured epoxy resin and nano-Al₂O₃-filled (with different weight fractions) epoxy resin. As it is evident from Figure 7, under nitrogen atmosphere, decomposition of epoxy/nano-Al₂O₃ (according to the thermogravimetric data) involves two stages degradation process in the range of 110–254 and 310–450°C. In the first stage of weight loss process of epoxy matrix, the $T_{IDT,1}$ values of EP-0, EP-1.5AL, and EP-3AL are 140.5, 172.6, and 170.2°C, respectively. 1-propanol (bp = 105°C) degrades at this stage. Addition of nano-Al₂O₃ increases thermal stability at the first stage (degradation initiation) due to lower mobility of epoxy chain whereby slippage of chains decreases.¹⁰ In the second stage process, the $T_{IDT,2}$ values of EP-0, EP-1.5AL, and EP-3AL samples are 321.8, 332.8, and 327.2.6°C, respectively. By addition of 1.5 wt % nano-Al₂O₃ to neat epoxy resin adhesive, $T_{IDT,2}$ raises by 11°C which indicates the effective role of nano-Al₂O₃ in the initiation

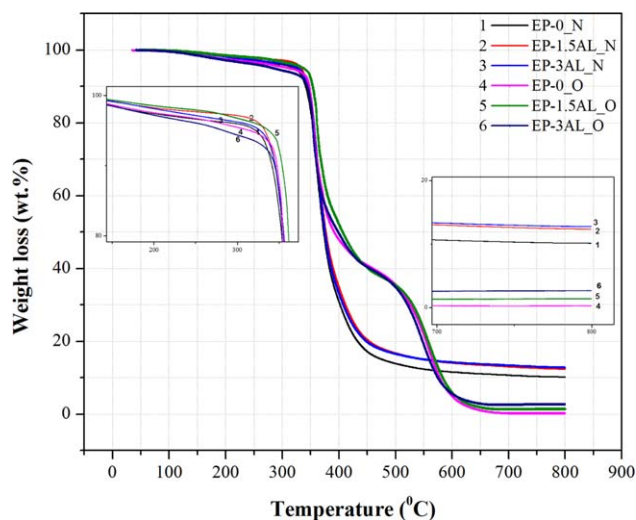


Figure 7. TGA thermograms of epoxy adhesive filled with different contents of nano- Al_2O_3 (_N denotes samples tested under N_2 atmosphere and _O denotes samples tested under O_2 atmosphere). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

stage of decomposition process. The T_{max} values for EP-0, EP-1.5AL, and EP-3AL samples are 358, 360, and 359°C, respectively. Alteration of T_{max} is negligible at this stage of degradation.

Under nitrogen atmosphere, nano- Al_2O_3 does not degrade¹ up to 800°C and by incorporation of nano- Al_2O_3 in epoxy resin char yield increases as compared to neat epoxy resin. The char yields of EP-1.5AL and EP-3AL samples are 10.9 and 9.8 wt %, respectively. For EP-3AL, this is an unexpected char yield because when nano- Al_2O_3 content increases up to a certain value, it might increase filler–filler interaction rather than filler–polymer.³⁰ Therefore, nano- Al_2O_3 cannot prevent the slippage of epoxy¹⁰ leading to the reduction of char yield as compared to EP-0 and EP-1.5AL samples.

Under air atmosphere, the char yields of EP-0, EP-1.5AL, and EP-3AL samples are 0.25, 0, and 0.1 wt %, respectively which indicates that the char yield value of samples degraded under air atmosphere is less than that of samples degraded in nitrogen atmosphere. Because of acceleration effect of air, final weight loss of epoxy adhesive matrix degraded under air atmosphere increases as compared to the one degraded in nitrogen atmosphere. It can be seen that under air atmosphere nano- Al_2O_3 does not prevent decomposition of epoxy matrix and degradation products.

While epoxy matrix degrades under nitrogen atmosphere, nano- Al_2O_3 and MWCNTs increase thermal degradation at low and high temperatures, respectively. Nano- Al_2O_3 particles increase onset of degradation temperature, whereas MWCNTs enhance the char yield. At air atmosphere, both nanofillers could not remarkably change the char yield and onset of degradation temperature.

Degradation Behavior Comparison of Different Nanoreinforcing Fillers. Figure 8 shows effect of nanoreinforcing fillers on the thermal stability of DGEBA/epoxy novolac resin under air and

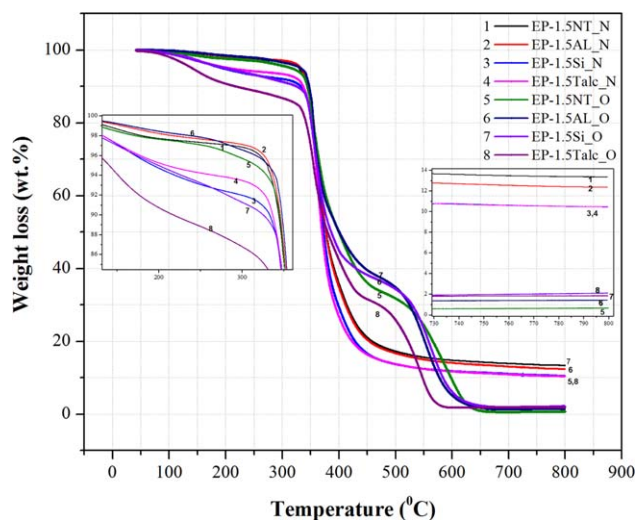


Figure 8. Comparison of TGA thermograms of epoxy adhesives filled with 1.5 wt % of different types of nanofillers (_N denotes samples tested under N_2 atmosphere and _O denotes samples tested under O_2 atmosphere). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

nitrogen atmospheres. Samples with 1.5 wt % loading of the MWCNTs, nano- Al_2O_3 , nano- SiO_2 , and talc are compared here. It is seen that under nitrogen atmosphere, incorporating of 1.5 wt % of nano- SiO_2 or talc leads to reduction in T_{IDT} of epoxy adhesive. Even EP-1.5Talc sample degrades at a temperature lower than that of neat epoxy resin. Talc diameter is large; hence, it has low contact surface area with polymer chain,²⁶ and this enhances slippage of epoxy chains. As it is shown in the previous sections, EP-1.5AL and EP-1.5NT samples under nitrogen atmosphere had higher thermal stability as compared to the unfilled resin, whereas char yield values for EP-1.5Si and EP-1.5Talc samples are about 9 wt % which indicates that talc and nano- SiO_2 reduce char yield of neat epoxy matrix (Figure 8).

Under air atmosphere, char yields of EP-1.5NT, EP-1.5AL, EP-1.5Talc, and EP-1.5Si samples are about 0.7, 1.5, 1.8, and 2 wt %, respectively. The char yield values in air atmosphere are less than those in nitrogen atmosphere because of the air accelerated oxidation process of epoxy matrix.

Synergistic Effect on the Thermal Stability of Epoxy Adhesive

Figure 9 shows TGA thermograms of epoxy adhesive containing nano- Al_2O_3 and MWCNTs under nitrogen atmosphere. Char yield values of EP-1.5NT, EP-1.5AL, and EP-0.75NT-0.75AL samples are 11.9, 10.9, and 12.5 wt %, respectively. Considering a simple mixing rule the char yield value of EP-0.75NT-0.75AL sample should fall between 11.9 and 10.9 wt %, whereas the thermal stability of EP-0.75NT-0.75AL is considerably higher than the samples loaded with 1.5 wt % of any of the individual nanoparticles. This hints toward this fact that by combining nano- Al_2O_3 and MWCNTs a synergistic effect is achieved on the thermal stability at high temperatures (800°C), which can be attributed to several factors. Firstly, the aspect ratio of nano- Al_2O_3 is less than that of MWCNTs and hence it can be positioned in between MWCNTs. The nano- Al_2O_3 particles can be

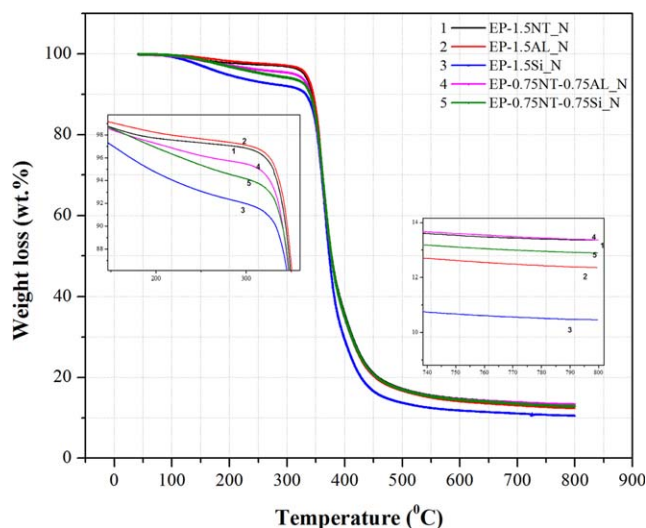


Figure 9. TGA thermograms of epoxy adhesives containing two types of nanofillers (_N denotes samples tested under N₂ atmosphere and _O denotes samples tested under O₂ atmosphere). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

randomly dispersed in the areas where MWCNTs are touching each other or are accessible to each other. A schematic model as shown in Figure 10 can demonstrate this synergism in a better way. As a result an interconnected (cocontinuous) and compact network of nanofillers is formed within epoxy matrix, as evidenced by the TEM image presented in Figure 11, leading to the improved performance. Secondly, due to its large surface area and hence the good contact with MWCNTs the nano-Al₂O₃ can act as support for MWCNTs which helps in maintaining the high aspect ratio of MWCNTs.³¹ Third, the synergism originates from the bridging (pathway) of nano-Al₂O₃ by MWCNTs which lead to forming a denser structure of hybrid system than the single system.^{22,32} According to these factors, chain slipping of epoxy matrix among the hybrid nanofillers network due to the extended surface area of MWCNTs–nano-Al₂O₃ junctions may decrease leading to the decreased

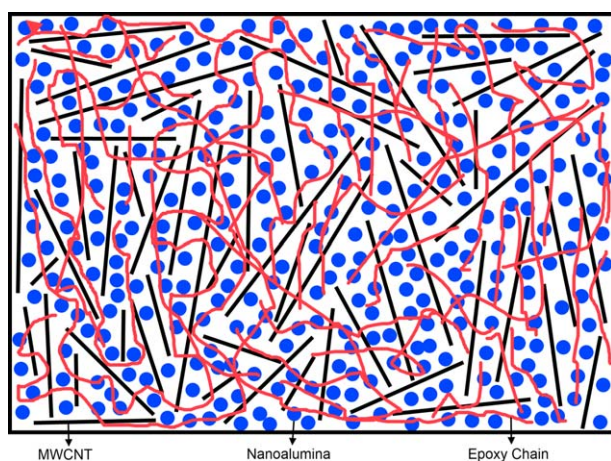


Figure 10. Schematic representing epoxy bulk containing both MWCNTs and nano-Al₂O₃. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

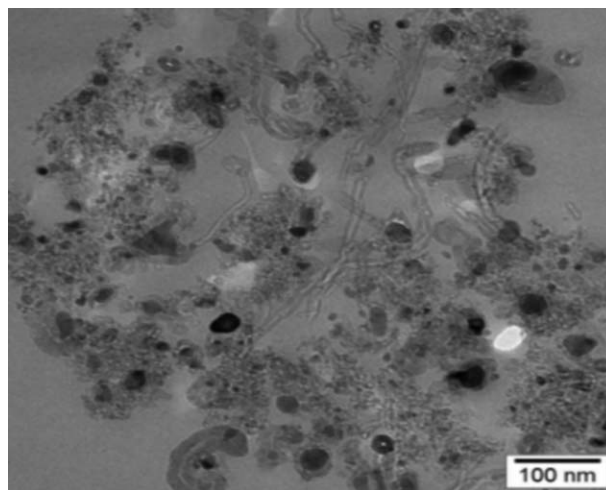


Figure 11. TEM image of epoxy adhesive filled with 0.75 wt % MWCNTs and 0.75 wt % nano-Al₂O₃ (EP-0.75NT-0.75AL).

char yield of epoxy adhesive.^{31,32} In principle, if a MWCNT is substituted by several spherical nanoparticles, the thermal stability increases at high temperature (800°C). No such synergistic effect on thermal properties was detected when nano-SiO₂ was used in combination with MWCNTs.

CONCLUSIONS

In this work, a series of novel adhesives based on DGEBA/epoxy novolac system with different nanofillers were developed. The lap shear strength and thermal stability of the epoxy adhesives filled with various types of nanofillers such as MWCNTs, nano-Al₂O₃, nano-SiO₂, and talc were investigated. It was demonstrated that incorporating epoxy adhesive with nanofillers can clearly increase the lap shear strength of DGEBA/epoxy novolac adhesive. Two percolation thresholds were found on the lap shear for CNTs (first: 1.125 wt % and second: up to 3 wt %). For nano-Al₂O₃, only one percolation threshold at 1.5 wt % was obtained. The enhancement of lap shear strength was higher by nano-Al₂O₃ incorporation than MWCNTs. MWCNTs at all the studied loadings (except 3 wt %) and nano-Al₂O₃ have enhanced thermal degradation parameters such as $T_{IDT,1}$, $T_{IDT,2}$ and char yield of DGEBA/epoxy novolac adhesive (under nitrogen atmosphere). While epoxy matrix degraded under nitrogen atmosphere, MWCNTs and nano-Al₂O₃ increased its thermal stability at high and low temperatures, respectively. The efficiency of nano-Al₂O₃ in increasing onset of degradation temperature was more than that of MWCNTs while the MWCNTs loaded samples had a higher char yield than that of samples loaded with nano-Al₂O₃. Hence, thermal stability of epoxy adhesives containing MWCNTs at high temperatures was better than nano-Al₂O₃-filled epoxy adhesives, but at air atmosphere both nanofillers did not remarkably change the char yield and onset of degradation temperature. Thermal stability of epoxy adhesive was decreased by nano-SiO₂ and talc incorporation. In all samples heated under air atmosphere; char yield was very low because of air accelerated oxidation process of epoxy/MWCNTs degradation. The thermal stability of sample loaded with a hybrid filler, i.e., EP-0.75NT-0.75AL was much higher

than the samples loaded with any of those individual nanoparticles. This hinted toward this fact that by combining nano- Al_2O_3 with MWCNTs a synergistic effect was seen on the thermal stability at high temperatures (800°C). Nanofillers (nano- Al_2O_3 and MWCNTs)-reinforced epoxy adhesives were successfully developed by using mechanical stirring followed by ultrasonication. Microscopic results confirmed well distribution of nanofillers in epoxy adhesive. Elongation at break of the developed adhesives did not change remarkably by changing the nanofillers content.

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