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High performance epoxy nanocomposite adhesive: Effect of nanofillers on adhesive strength, curing and degradation kinetics

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Abstract

In the current study, the synergistic effect of a multi-walled carbon nanotube (MWCNT) and a nanoclay (C30B) on the mechanical, morphological and thermal behaviour of an epoxy based adhesive was investigated. The adhesive strength was investigated by conducting lap shear tests and from the test results it was observed that, Ep/1.0 C30B adhesive possessed the highest adhesive strength among all the adhesive formulations investigated and showed a 52% enhancement as compared to the pristine epoxy. Fracture analysis of different adhesive systems was investigated using scanning electron microscopy (SEM). SEM micrographs revealed that nanomaterials with different shapes and dimensions provide distinct features on the fracture surfaces due to the different energy dissipation mechanisms which they promote. The morphological variations of the epoxy based nanocomposite adhesives were investigated using transmission electron microscopy (TEM) and X-ray diffraction (XRD) techniques. The curing kinetics of the different nanofiller reinforced epoxy adhesives were examined using a non-isothermal differential scanning calorimetric (DSC) technique. The activation energy (E_a) was calculated by applying Kissinger's method and found to be increased for the Ep/1.0 CNT/1.0 C30B adhesive system as compared to the pristine epoxy. This increment can be attributed to the physical impediment impacted by the nanomaterials on the curing reaction of the epoxy resin. The degradation kinetics of the adhesive systems were also studied using thermogravimetric analysis (TGA). The corresponding activation energies (E) of the adhesive systems obtained by Kissinger's model were found to increase with addition of nanofillers, thus indicating improved thermal stability.

Keywords: MWCNTs, Clositie®30B, Epoxy, Lap-shear test, Curing kinetics, Degradation kinetics.

1. Introduction

Since the last century, adhesive bonding technology has been considered as an acceptable replacement to other joining methods owing to the substantial advantages it can bring such as homogeneous stress distribution, high corrosion resistance, aesthetics, ease of application, low weight and cost-effectiveness. Thus adhesive bonding has been frequently employed in many industries such as sports, automotive, aircraft and spacecraft structure construction[1]. Epoxy resins are critically important thermosetting materials often used as high performance adhesives for joining various substrates (such as metal to metal or metal to other materials) with outstanding properties including excellent adhesion, high strength[2], stiffness[3], low shrinkage during cure, good resistance to corrosion, excellent chemical and heat resistance[2], low volatility and dimensional stability[3]. As epoxies are pervasively used in many high performance applications, many research groups have conducted numerous investigations based on various types of reinforcements for improving their properties covering mechanical properties [4–6],adhesive strength[5,7–10], thermal properties [6,11–13], etc.

In recent decades, various organic and inorganic nanomaterials were studied as reinforcement for epoxy adhesives in order to enhance their properties[5,11,14–19]. Among these nanomaterials, carbon nanotubes (CNTs) and nanoclays have attracted the attention of researchers since results have shown that when embedded in epoxy resins, various properties can be substantially enhanced even at very low concentrations [20]. Carbon nanotubes have been intensively used as one of the most promising nanomaterial additives for next generation applications, such as in high-performance structural adhesives and multifunctional nanocomposites [21] owing to their unique atomic structure, high aspect ratio and noticeable properties including excellent mechanical, electrical [11,20] and thermal performance [11].

Various researchers have studied the adhesive strength characteristics of CNT modified epoxy adhesives and have found highly impressive increases with the addition of even low concentrations of CNTs. Yu et al[22] investigated bonding strength using the Boeing wedge test and found that strength was increased significantly with the incorporation of CNTs. Sydlik et al[17] studied the lap shear strength of a functionalized CNT reinforced epoxy adhesive and observed 36% and 27% increases in strength over pristine epoxy and unfunctionalized MWCNT incorporated epoxy respectively. May et al[10] prepared epoxy/sol-gel materials comprising MWCNTs and studied shear strength. The shear strength was enhanced by 13% with reinforcement of ~0.07 wt% MWCNTs.

Nanoclay as a natural product can be obtained very easily in huge amount at low cost, thus making it commercially acceptable for a wide range of applications [20] such as military, boat building, automotive and aerospace [23]. As a two-dimensional nanofiller nanoclay possess a large surface area, plate like morphology and excellent properties including strong adsorption and ion-exchange capacity, which are the reasons for widespread usage of nanoclay as catalyst [18,20,24]. Wang et al[2] inspected the adhesive strength of epoxy/acrylic rubber/nanoclay nanocomposites using a T-peel test and found a substantial increase of 138% with the incorporation of 3 wt% MMT as compared to a binary system without nanoclay. Nachikethas and Manoj[25] investigated the adhesive performance of nanoclay reinforced epoxy resin using lap shear and T-peel tests. With 1 wt% nanoclay loading, the lap shear strength was found to be 14% higher and peel strength 40% higher as compared to pristine epoxy. Cid et al[26] studied the adhesive properties of nanoclay modified epoxy adhesive by using two organically modified montmorillonites (Cloisite 93A (C93A) and Nanomer I.30E (I.30E)) and observed that they showed lower shear strength as compared to pristine epoxy adhesive.

Few researchers have investigated the concurrent effect of both nanomaterials as filler or as a hybrid material on various properties of epoxy resin. For instant, Ayatollahi et al[20] examined the mechanical and electrical properties of epoxy reinforced with two potential candidates i.e. multiwalled carbon nanotube and nanoclay for preparing nanocomposites using an ultrasonic technique for dispersion of the nanomaterials. The Young's modulus of epoxy/MWCNT nanocomposite was found to be superior with addition of 0.5 wt% MWCNT as compared to nanocomposite reinforced with 5 wt% of nanoclay. The simultaneous presence of MWCNT and nanoclay enhanced the Young's modulus and fracture toughness of the nanocomposites, but tensile strength was decreased for all nanocomposites except one which was incorporated with 0.5% MWCNTs (which showed an increase of 7%). Whereas electrical conductivity was enhanced with the incorporation of CNTs a reduction in electrical conductivity was observed when both nanofiller types were added. Elnaz et al [27] synthesized a chemical hybrid of CNT-Clay (CNC) and a physical hybrid of CNT-Clay (PNC) by utilizing the high-temperature decomposition of methane on the nanoclay and physical mixing of both nanomaterials, respectively. These authors investigated the synergistic effect of CNC and PNC on thermal and morphological properties of an epoxy matrix. The test results revealed that heat distortion temperature (HDT) was enhanced by 10°C at only 0.2 wt% loading of CNC compared to pristine epoxy and it was found to be higher than for the PNC. The thermal stability of the virgin epoxy was increased following the incorporation of both CNC and PNC hybrids and was more pronounced in the case of PNC.

In spite of published work covering the synergistic effects of combined MWCNT and nanoclay incorporation on the mechanical, electrical, thermal and morphological properties of epoxy nanocomposites, no work inspecting the lap shear strength and degradation kinetics of epoxy/CNT/nanoclay has been reported in the literature. To the best of our knowledge only a few authors have reported work on the curing kinetics of epoxy adhesive systems reinforced with CNTs and nanoclays. In the current study, the concurrent effect of two promising nanomaterials such as MWCNTs and nanoclays in relation to adhesive strength, curing and degradation kinetics and morphological properties of epoxy adhesive systems was studied. The ultrasonication technique was utilized for intensive dispersion of nanomaterials within the epoxy matrix. The adhesive strength of the nanomaterial-based epoxy adhesives was investigated by conducting lap joint testing using aluminum substrates. The fracture surfaces after lap joint testing were visualized using the SEM technique. The dispersion of CNTs and the degree of intercalation/exfoliation of the nanoclay was studied using TEM. For confirming the dispersion of CNTs, statistical analysis was carried out by using particle size distribution study and XRD was used to examine the degree of intercalation/exfoliation of nanoclay. The curing and degradation kinetics of all adhesive systems were investigated using DSC and TGA respectively and the corresponding activation energies were calculated by applying the Kissinger method.

2. Experimental

2.1. Materials

Diglycidyl ether of bisphenol A (DGEBA) (Araldite GY 250, epoxy equivalent:170-190 g/kG) was used as the base material and triethylenetetramine (TETA) (Aradur HY 951, amine value: 1443 mg KOH/gm) was used as the curing agent in this work and procured from Huntsman Int Pvt. Ltd (Mumbai, India). MWCNTs with ~70-80% purity was purchased from Excel Metal and Engg Industries (Maharashtra, India) having diameters in the range of 5-50 nm and lengths of around 1-12 µm. The organo clay, Cloisite®30B (C30B) modified by MT2EtOH i.e. methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium salt having a cation exchange capacity (CEC) of about 90 ml eq/100g was used as secondary filler. It was purchased from Southern Clay Products Inc, USA. MWCNTs and C30B were used as received for the preparation of adhesives. Aluminum plate with dimension 102x 25x 1.6 mm was used as substrate for lap shear joining. Some common chemical such as acetone used for cleaning the Al substrate prior to bonding was procured from Merck Specialities Pvt.Ltd., Mumbai, India.

2.2. Preparation of adhesives

The required parameters for the preparation of the epoxy adhesives with or without nanomaterials loading are presented in Table 1 and a schematic diagram for the development of Ep/CNT, Ep/C30B and Ep/CNT/C30B adhesives are depicted in Figure 1.

Table 1: Required parameters for adhesives preparation.

Sl No.	Samples	Conc. of CNT (wt %)	Conc. of C30B (wt %)	Mechanical Stirrer Speed (rpm)	Mechanical Stirrer Time (min)	Ultra sonication Time (min)	Vacuum Degassing Time (min)	Vacuum Degassing Temp (°C)	Curing Agent Addition Time (min)
1.	**Ep**	-	-	-	-	-	30	50	5-7
2.	**Ep/0.5 CNT**	0.5	-	2000	30	10	720	60	10
3.	**Ep/1.0 CNT**	1	-	2000	30	10	720	60	10
4.	**Ep/1.5 CNT**	1.5	-	2000	30	10	720	60	10
5.	**Ep/0.5 C30B**	-	0.5	-	60	30	720	60	10
6.	**Ep/1.0 C30B**	-	1	-	60	30	720	60	10
7.	**Ep/1.5 C30B**	-	1.5	-	60	30	720	60	10
8.	**Ep/1.0CNT/1.0 C30B**	1	1	2000	60	30	720	60	10

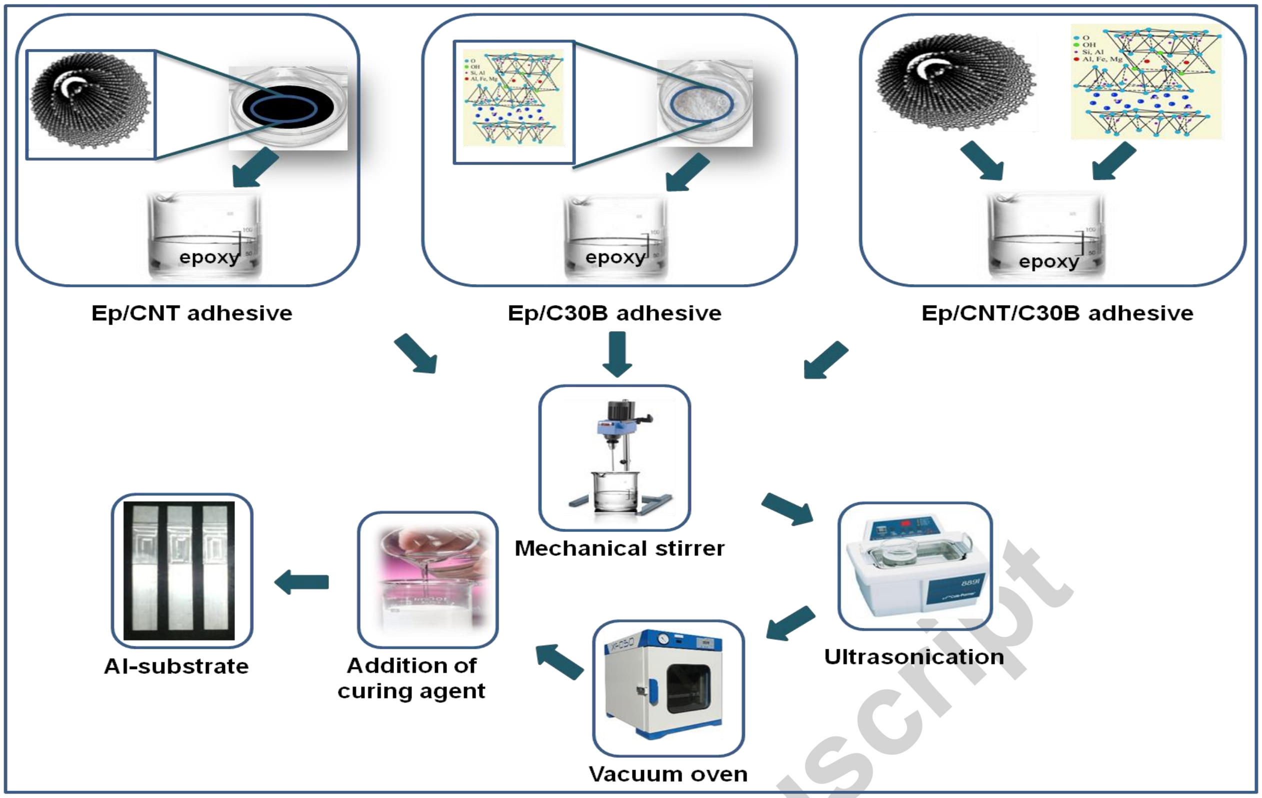

Figure 1: Schematic diagram for the development of Ep/CNT, Ep/C30B and Ep/CNT/C30B adhesives.

The epoxy nanoadhesives were prepared by considering the ratio of epoxy resin: hardener as 100:19 (w/w) which was optimized according to maximum adhesive strength of the prepared epoxy adhesive. The optimized ratio can be compared to the stoichiometric ratio of epoxy: hardener i.e. 100:13 (w/w) as mentioned by the manufacturer (Huntsman Int Pvt Ltd). The DGEBA resin was degassed in a vacuum oven to eliminate trapped air bubbles. The base resin was mixed with hardener and applied to the respective substrates and cured for 24 hr at room temperature followed by post-curing at 100°C for 2 h to ensure complete curing of the system. The development procedures of epoxy nanocomposite adhesives (such as Ep/CNT, Ep/C30B, Ep/CNT/C30B) were almost similar with minor contrast in each formulation. Initially the base resin was heated at 100°C for 1 h to reduce its viscosity and for avoiding the formation of air bubbles. Nanomaterials formulations with different compositions (0.5, 1, 1.5 wt %) were mixed with epoxy resin using a mechanical stirrer. The nanoclay (C30B) was kept at 105°C for 1 h to remove moisture prior to mixing with the base resin. After mixing, the mixture was sonicated using a high intensity ultrasonic processor (6.5L capacity, M/s Darsh Technologies, India) at 500W and 40 kHz followed by degassing in a vacuum oven to remove trapped air. The mixture was cooled to room temperature prior to mixing with the curing agent. Then, it was applied to the Al substrate and subjected to curing under the conditions described above. The Ep/CNT/C30B adhesive was fabricated by considering the optimum concentration of CNT and C30B using the procedure described above.

2.3. Characterization

2.3.1. Lap shear test

As described above, to investigate the adhesive strength of the epoxy based adhesives, lap shear tests were conducted using aluminum substrates. The lap shear specimens were created using two 102× 25×1.6 mm dimensions acid etched aluminum substrates with a 12.7mm overlap. At the overlap portion adhesives were applied and uniformly compressed and then cured prior to testing. The shear tests of each system were carried out as per ASTM D-1002 with cross head speed of 1.27mm/minute using a Universal Testing Machine (UTM), LR-100NK (3382 Instron Instruments Ltd, U.K.).

2.3.2. Scanning electron microscopy (SEM)

Fractographic analysis of failed adhesive joints was conducted using a scanning electron microscope (SEM) (EVO MA 15, Carl Zeiss SMT, Germany) with 5 KeV accelerating voltage at 10 µm resolution. Fracture surfaces were coated with gold prior to the SEM analysis to minimize surface charging effects. A comparative study of fracture surfaces of different nanomaterial based epoxy adhesives was done based on the results from SEM.

2.3.3. Transmission electron microscopy (TEM)

The ultrasonic technique was used to disperse the nanomaterials in the base resin. To investigate the extent of dispersion of CNT and degree of intercalation/exfoliation of nanoclay, transmission electron microscopy (TEM) (JEM 1400, JEOL, Japan) with 120 KeV accelerating voltage at different resolutions was used. Specimen thicknesses of 70-90 nm were prepared using a microtome.

A particle size distribution study was conducted to examine the dispersion of CNTs within the epoxy matrix.

2.3.4. X-ray diffraction (XRD)

X-ray diffraction analysis of cloisite 30B (C30B) and epoxy nanocomposite adhesives reinforced with C30B were carried out to examine their degree of intercalation/exfoliation using a XRD system (Shimadzu, XRD-7000L, Japan) with CuKα radiation ($\lambda = 1.54$ Å). The XRD patterns were recorded at angle 2θ (2° to 10°) with a scanning rate of 1°/min.

2.3.5. Differential scanning calorimetry (DSC)

To examine the curing behavior of the pristine epoxy adhesive and the nanomaterial-based adhesives, differential scanning calorimetry (DSC) (Q 20, TA Instruments, USA) was used. The uncured systems of 2-10mg weight were heated from 30°C to 200°C at dynamic heating rates of 5, 10 and 15°C/min.

2.3.5.1 Curing kinetics study

To analyze the curing kinetics of DGEBA/TETA system with or without various nanomaterials, the study of activation energy (E_a) for curing is contributory. In the DSC technique, usually the degree of conversion (α) is assumed to be directly proportional to the area under the heat flow curve and can be expressed by Eq. (1):

$$\boldsymbol{\alpha(t) = \frac{H_p(t)}{\Delta H_{Total}}} \qquad (1)$$

where $H_p(t)$ is the partial heat of cure reaction at time t, ΔH_{Total} is the total heat of cure reaction. The rate of conversion ($\frac{d\alpha}{dt}$) at a given temperature (T) is generally denoted by Eq. (2):

$$\boldsymbol{\frac{d\alpha}{dt} = K(T)f(\alpha)} \qquad (2)$$

where T is the temperature; $K(T)$ is the temperature dependent reaction rate constant; $f(\alpha)$ is a kinetic model function dependent on α. The reaction rate constant $K(T)$ normally follows Arrhenius form and can be indicated by Eq (3):

$$\boldsymbol{K(T) = A.\exp(-x)} \qquad (3)$$

where A is the pre-exponential factor, x is equal to $\frac{E_a}{RT}$ in which E_a is the activation energy of the reaction (for curing study); R is the universal gas constant (8.314 J/K mol). The activation energy (E_a) can be calculated using different models; in the current study, Kissinger's method was adopted and expressed by Eq. (4):

$$\boldsymbol{ln\left(\frac{\beta}{T_m^2}\right) = C - \frac{E_a}{RT_m}} \qquad (4)$$

where β is the heating rate; T_m is the maximum temperature of the exothermic peak and C is a constant. By plotting the linear relationship of $ln\left(\frac{\beta}{T_m^2}\right)$ vs $\frac{1}{T_m}$, the value of E_a can be calculated from the slope of the graph.

2.3.6. Thermogravimetric analysis (TGA)

The thermal stability and degradation kinetics studies of the adhesives were examined using thermogravimetric analysis (TGA) (Q 50, TA Instruments, USA). Samples of about ≤10mg were taken and scanned from 30°C to 800°C at heating rates of 5, 10, 15°C/min in a nitrogen atmosphere.

2.3.6.1 Degradation kinetics study

The degradation kinetics studies allow us to examine in which temperature range the systems decompose with reference to the virgin material. The calculations of activation energy for degradation (E) of the adhesive systems were obligatory for exhaustive analysis of degradation kinetics.

Kissinger's method was utilized to determine activation energy of degradation (E) as expressed by Eq. (5):

$$\ln\left(\frac{\beta}{T_{md}^{2}}\right) = C - \frac{E}{RT_{md}} \qquad (5)$$

where β is the heating rate; T_{md} is the maximum temperature of the derivative weight loss curve; C is a constant; R is the universal gas constant (8.314 J/K mol). E can be calculated from the slope of the plot $\ln\left(\frac{\beta}{T_{md}^{2}}\right)$ vs $\frac{1}{T_{md}}$ curve.

3. Results and discussion

3.1 Mechanical properties

3.1.1. Lap shear strength test

The shear strengths of Ep, Ep/CNT, Ep/C30B and Ep/CNT/C30B adhesives with different compositions of Ep/CNT and Ep/C30B are labeled and represented in Table 2. Similarly shear stress vs. traverse displacement curves are depicted in Figure 2.

From Table 2 and Figure 2(a), it can be interpret that as the loading of CNT increased up to 1 wt%, the shear strength of the epoxy adhesive improved by 24.7% (for 0.5 wt%) and 48.2% (for 1.0 wt%) which can be attributed to the higher interaction of CNTs with epoxy resin owing to their high aspect ratio [28]. However, 1.5 wt% addition of CNTs reduced the shear strength of the adhesive by 18% as compared to the Ep/1.0 CNT system. This decrement was due to the agglomeration of fillers which restricts load transfer from the matrix to the CNTs, causing crack initiation and easy propagation [29]. In the case of the Ep/C30B adhesives, the addition of nanoclay with 0.5 and 1 wt% imparts higher shear strength to the virgin epoxy by ~ 43% and 52% respectively. However, at concentrations greater than 1 wt%, strength tended to decrease by up to 21% in comparison to the Ep/1.0 C30B system. The increment can be attributed to the development of exfoliation of nanoclays within the epoxy matrix which can be confirmed from the XRD results. Additionally the shear strength increased possibly due to the higher contact surface area of nanoclay platelets owing to their high aspect ratio. Furthermore, when the loading of nanoclay increases beyond the optimized value, the nanomaterial undergoes agglomeration resulting in a low contact area and eventually a reduced shear strength [30].

Table 2: Lap shear test of Ep, Ep/CNT, Ep/C30B, Ep/CNT/C30B adhesives systems.

Sl No.	Sample	Shear Strength (MPa)
1.	**Ep**	**5.54±0.82**
2.	Ep/0.5 CNT	6.91±0.91
3.	**Ep/1.0 CNT**	**8.21±0.63**
4.	Ep/1.5 CNT	6.68±0.72
5.	Ep/0.5 C30B	7.97±0.78
6.	**Ep/1.0 C30B**	**8.46±0.96**
7.	Ep/1.5 C30B	6.67±0.84
8.	**Ep/1.0 CNT/1.0 C30B**	**5.80±0.61**

From the test results, it is evident that the incorporation of different nanomaterials in the epoxy resin increases the shear strength of the neat epoxy. The neat epoxy showed a shear strength of 5.54 MPa. When 1 wt% of CNT was incorporated into the epoxy, the shear strength increased by 48% which can be attributed to an increase in fracture energy. Due to their high aspect ratio, CNTs provide bridging between epoxy matrixes and thus result in better adhesion between them. When a crack propagates in a CNT loaded nanocomposites, crack tips cannot break the strong CNTs due to a bridging effect thus providing a higher strength for the nanofilled adhesive in comparison to that of the epoxy resin [3]. Similar trends have been observed by other researchers. Jojibabu et al [31] detected a 53% increment in lap shear strength of the epoxy resin with 1 wt% MWCNTs loading, whereas Singh et al [29] observed ~104% enhancement with the addition of 0.5 wt% MWCNTs. In the case of nanoclay incorporation, strength increases by 52% with respect to the epoxy resin possibly due to the exfoliation/intercalation of nanoplatelets within the epoxy system and the formation of nanocomposites. This behavior may also be due to an increase in the interactions between the carboxylic ester groups of the polymer, and the -OH groups of the C30B clay which provides good adhesion between the nanoclay and matrix [32]. Therefore, increased adhesion between nanoclay and epoxy results in enhanced adhesion between the adhesive and the Al substrate, which is often stated as being one of the main reasons for the increase in the adhesive strength observed. A similar tendency has been reported by other research groups. For example, Ilyin et al [33] and lakshmi et al [34] found 40-65% increments in the shear strength of a cured epoxy resin with the addition of nanoclays. In this work, when both nanomaterials were incorporated into the base resin, an increase in strength of only 4.69 % can be attributed to the agglomeration of both the nanomaterials. Both nanomaterials form a hybrid network based on the interaction between the particles, on their shape (aspect ratio) and on their inter-particle distance. The applied stress can be transferred to the hybrid filler based on this particle-bridging mechanism. But there might be the possibility of regions where only CNTs or C30B are present. Therefore, the applied stress can’t be properly transferred to the hybrid filler as the border between these regions could be weak place, where the adhesive fails and is detached from the adherent. This results in poor shear strength of the epoxy adhesive system reinforced by both nanomaterials [35]. This consideration is confirmed by the TEM micrograph for the Ep/1.0 CNT/1.0 C30B system as shown in Figure 4c.

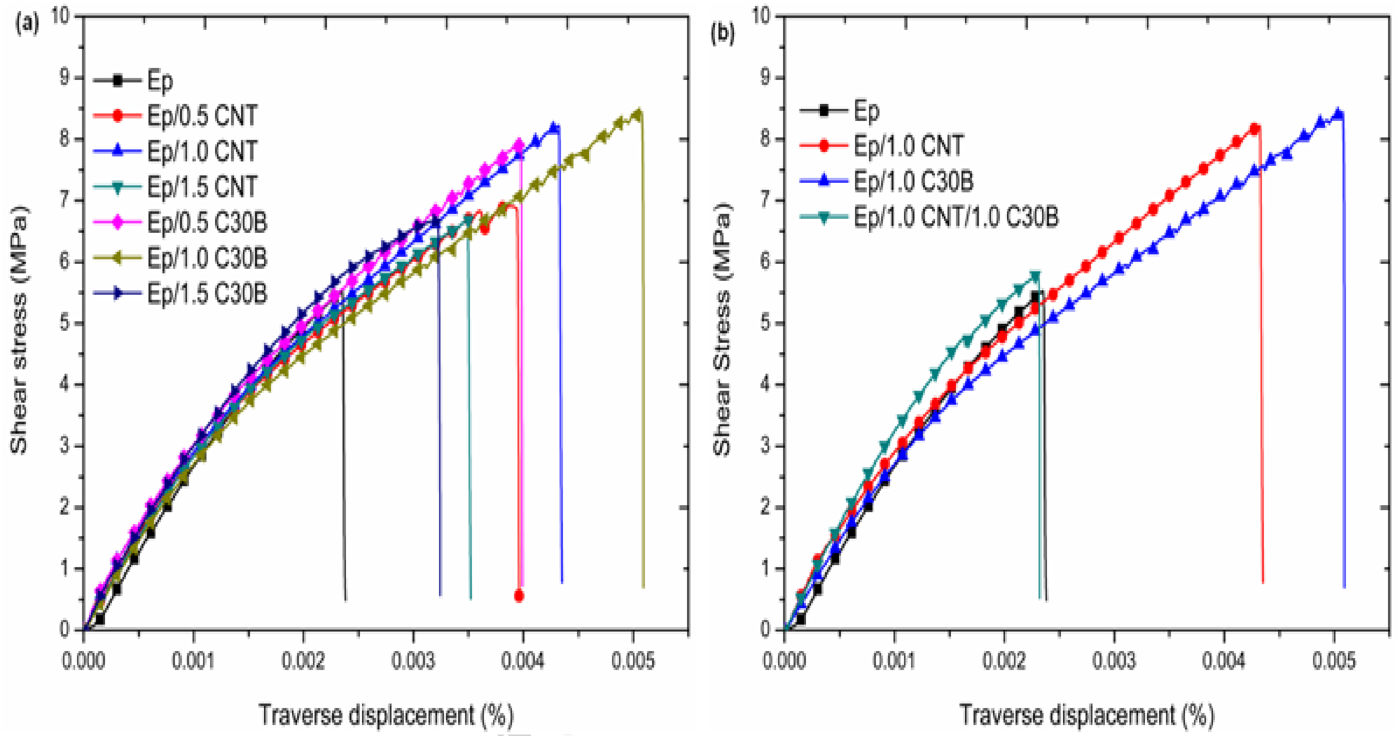

Figure 2: Shear stress vs. traverse displacement curves of all compositions of Ep/CNT and Ep/C30B (a), comparison of all adhesive formulations (b)

3.2 Morphological properties

3.2.1. Fractography

The surface morphology of fractured surfaces reflects the reason why mechanical properties of adhesives prepared from nanomaterials with different surface properties are different. SEM analysis of fractured surfaces of the adhesives are presented in Figure 3.

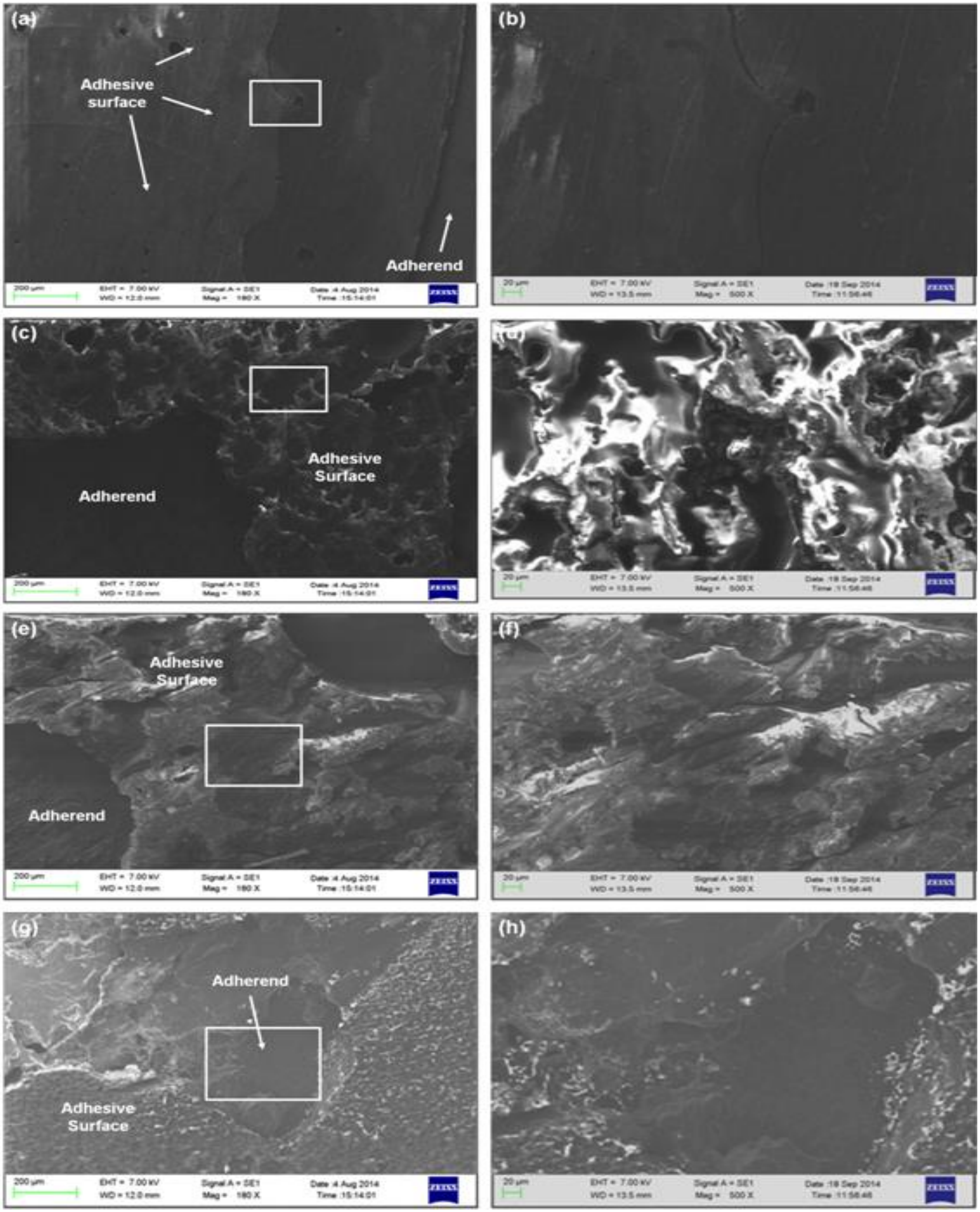

Figure 3: SEM micrographs of Ep (a), Ep/1.0 CNT (c), Ep/1.0 C30B (e), Ep/1.0 CNT/1.0 C30B (g); Magnified image of adhesive of Ep (b), Ep/1.0 CNT (d), Ep/1.0 C30B (f), Ep/1.0 CNT/1.0 C30B (h)

The fracture surface of the neat epoxy depicted in Figure 3(a-b) seems to be smooth which is a typical feature of brittle fracture behavior. In this case, the fracture would seem macroscopically adhesive; but some portions of substrate have trapped adhesives which indicate a microscopic mixed fracture. The adhesive fracture means that the breakage is interfacial failure which occurs in the adhesive–adherend interface. Therefore the main cause of failure resides on weak bonding forces or weak-boundary layer adhesion. The opposite situation is a cohesive fracture, where the rupture occurs in the layer of adhesive remaining on both adherend surfaces, which is normally caused by the lack of mechanical resistance of the adhesive. Similar types of fracture behavior have also been observed with epoxy adhesive by other researchers [1].

As the fillers were incorporated in the polymer the surface roughness increases, suggesting that the crack propagation in the nanocomposite adhesives of Ep/1.0 CNT, Ep/1.0 C30B, and Ep/1.0 CNT/1.0 C30B is restricted by rigid and stiff fillers as presented in Figure 3 (c)-3(h). In other words, the segments of primary crack front require more energy to propagate between the fillers, indicating that local deviations of the crack are necessary to fracture the nanocomposites completely which leads to higher fracture toughness values. The adhesives modified with MWCNTs with the long cylindrical shapes depicted in Figure 3 (c-d) possess high aspect ratios (means very small diameters compared with their lengths) so that the main energy dissipating mechanism will be crack bridging with crack deviation being only a secondary mechanism. Because of crack bridging CNTs provide better adhesion and higher strength than pristine epoxy which can be confirmed by the lap shear strength results. However, in the case of epoxy reinforced with nanoclay as shown in Figure 3 (e-f), crack deviations would be the main energy dissipation mechanism. As nanoclay is a two-dimensional nanofiller with a large surface area, when a crack reaches a nanoclay particle, the crack will have to travel a longer path along the surface area of nanoclay layers before it continues its overall trajectory. This will result in a higher strength than for the neat epoxy adhesive. The adhesive incorporated with both nanomaterials i.e. nanoclay and MWNTs (depicted in Figure 3 (g-h)) did not show the expected improvements in adhesive strength. As mentioned earlier, the two main enhancement mechanisms are crack bridging for MWNTs and crack deviation for nanoclay. The nanoclay can easily overshadow the crack bridging effect of the MWCNTs owing to their large aspect ratio and thus restricting the ability of MWCNT in terminating the crack deviation mechanism. Similar fractography results have also been found by Ayatollahi et al [20].

3.2.2. Dispersion assessment

Dispersion of multiwalled carbon nanotubes (MWCNT) and the degree of intercalation and/or exfoliation of nanoclay in the DGEBA-TETA system was evaluated. Figure 4 (a-c) depicts TEM micrographs of Ep/1.0 CNT, Ep/1.0 C30B and Ep/1.0 CNT/1.0 C30B respectively. A statistical study of the Ep/1.0 CNT adhesive system was conducted using particle size distribution method as shown in Figure 4 (d-e). Figure 4 (f) indicates XRD graphs of the pristine C30B and Ep/1.0 C30B adhesive systems.

It is observable from Figure 4(a) that a few CNTs are individually dispersed within the epoxy matrix (as indicated by black arrows) and the dark portion of the micrographs can be considered as agglomerated portion of CNTs. As individual CNTs are present in the micrograph we can conclude that the ultrasonic technique was successful in breaking up the initial CNT agglomerates. However, the ultrasonication process can’t break the bundles of carbon nanotubes into single tubes indicating that the duration and intensity of the ultrasonication process were insufficient to fully break-up and disperse all the CNTs. From the statistical data indicated in Figure 4 (d-e) it is clearly evident that CNTs maintained their dimensions (as mentioned by the manufacturer) even after inclusion within the base resin. Therefore, it can be concluded that individual CNTs do indeed exist in the adhesive system along with a reduced number of CNT agglomerates.

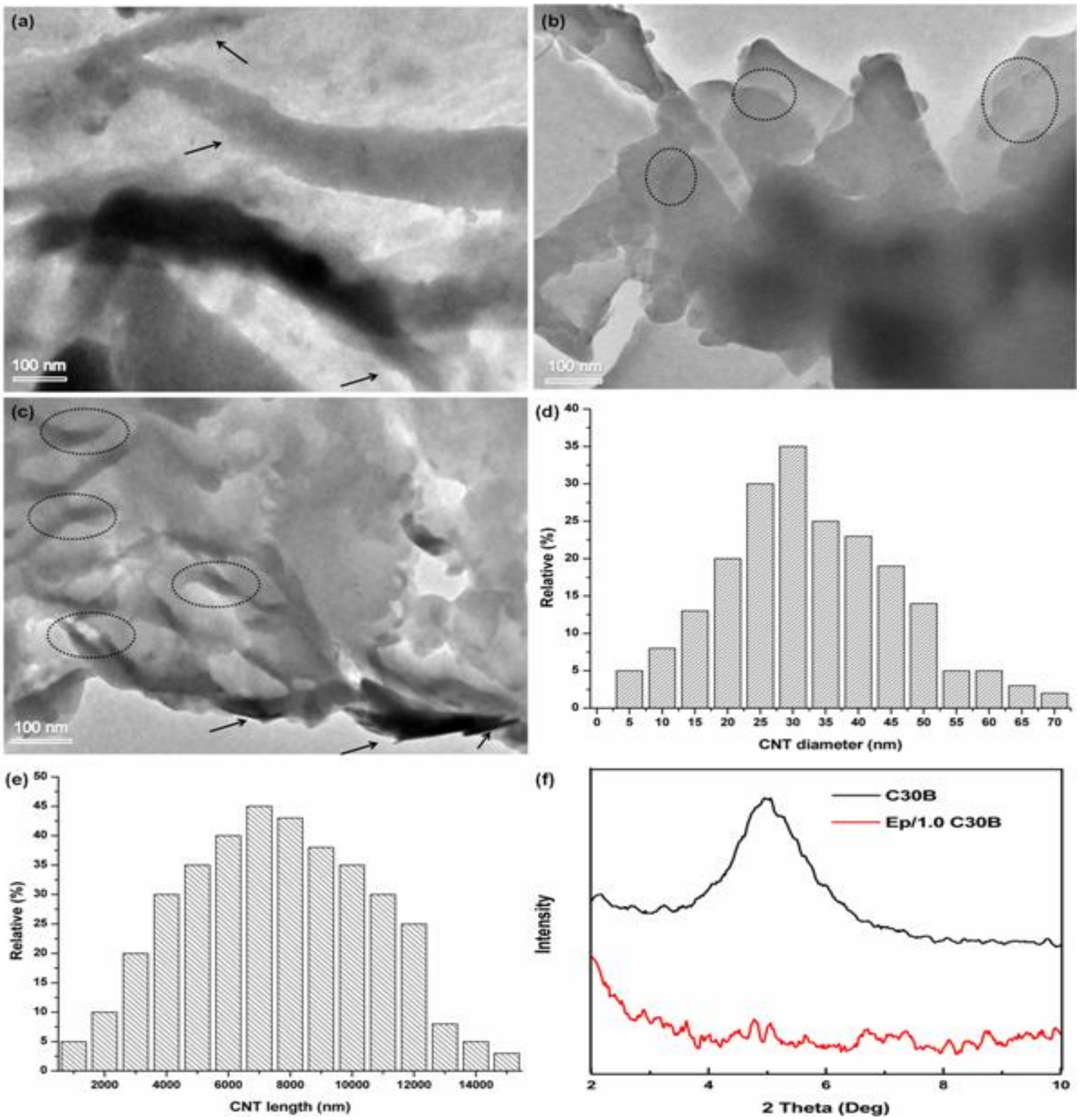

Figure 4: TEM micrograph of Ep/1.0 CNT (a), Ep/1.0 C30B (b), Ep/1.0 CNT/1.0 C30B (c); Statistical analysis of CNT size distribution (d), (e); XRD spectra of C30B and Ep/1.0 C30B (f).

Figure 4(b) shows TEM images of the 1.0 wt% nanoclay (C30B) loaded epoxy resin. The nanoclay platelets are indicated by black circles but intercalation/ exfoliation of C30B can be confirmed from the image. Therefore, XRD was performed to confirm the degree of intercalated or exfoliated structure of C30B within the Ep/1.0 C30B cured adhesive system. The results are shown in Figure 4(f). The diffraction peak of C30B nanoclay appeared at $2\theta=5.15°$ with basal spacing of nanoclay galleries of 1.71 nm. However, the XRD patterns of the nanofilled adhesive systems didn't reveal any diffraction peaks thus confirming the exfoliated nanoclay structure throughout the matrix [36]. This results in a higher shear strength of the nanoclay reinforced epoxy adhesive in comparison with other adhesives. As can be seen from Figure 4(c), the CNTs are indicated by black arrows and nanoclay platelets are specified by black circles. It can be concluded that there might be the possibility of the presence of regions where only CNTs or C30B are present and the border between these regions could be mechanically weak, where the adhesive fails and is detached from the adherent. This could be the reason for the lower shear strength of the adhesive systems reinforced with both nanofillers.

3.3. Thermal properties

3.3.1. Curing kinetics study

Figure 5(a-d) depicts the DSC thermograms of the Ep, Ep/1.0 CNT, Ep/1.0 C30B, Ep/1.0 CNT/1.0 C30B adhesive systems at heating rates of 5, 10 and 15°C/min. Figure 6(a) shows the heat flow versus temperature curves of all epoxy formulations at 10°C/min for comparison. The parameters obtained from the DSC curves such as the initial curing temperature (T_i), maximum curing temperature (T_m), final curing temperature (T_f) and total heat of cure (ΔH_{Total}) at different heating rates (β) are summarized in Table 3.

All the adhesive systems reveal a single exothermic peak, which is a typical characteristic of an epoxy resin curing process. As the curing performance of an epoxy resin is a function of temperature as well as time, an increase in the heating rate leads to a shift in exothermic peak towards a higher temperature range which is attributed to the lesser time obtained by the epoxy resin for transitioning at a given temperature.

The influence of different nanomaterials on the epoxy resin can be verified from the values of T_i, T_m and ΔH_{Total} as listed in Table 3. The values of initial T_i and maximum T_m temperatures are different at different heating rates for all adhesive formulations. This behavior can be attributed to the increase of kinetic energy of the system per molecule with higher heating rates. The initial T_i values shifted to lower temperatures (as shown in Table 3) with the existence of nanomaterials (1.0 CNT, 1.0 C30B, 1.0 CNT/1.0 C30B) as the nanofillers were capable of reaching the exothermic peak at a faster rate as compared to pristine epoxy [37]. The inclusion of the nanomaterials within the epoxy resin reveals similar trends for ΔH_{Total} values. In the case of the Ep/1.0 CNT adhesive, the ΔH_{Total} value significantly decreased as compared to the virgin epoxy system. This decrement can be attributed to the steric hindrance promoted by the CNTs owing to their high surface area which has also been observed by other researchers [38]. As MWCNTs act as a physical barrier and thus restrict polymer chain mobility, this is usually stated as another reason for the ΔH_{Total} decrement. Similar findings have been detected by others [29,39]. On the other hand, the total heat of cure of the epoxy was also reduced with the incorporation of cloisite 30B (C30B) which can be ascribed to the catalytic effect of nanoclay, which results in an increment of reaction rate with rapid curing at lower temperatures as observed by Paluvai et al [18]. Compared with Ep/1.0 CNT and Ep/1.0 C30B, the ΔH_{Total} of Ep/1.0 CNT/1.0 C30B is higher which can be attributed to the concurrent effect of the nanofillers that forms a hybrid network reaching the exothermic peak rapidly owing to the combined effect of high thermal conductivity of the CNT and catalytic effect of the C30B respectively [37].

Table 3: Parameters obtained from DSC non-isothermal experiment and activation energy (E_a) calculated using Kissinger method.

Sl No.	**Samples**	**Heating rate (β) (°C/min)**	**Temperatures**			**ΔH_{Total} (J/g)**	**Activation energy (E_a) (kJ/mol)**
			T_i (°C)	**T_m (°C)**	**T_f (°C)**		
		5	51.5	87	158.6	580	
1.	**Ep**	10	62.9	98.01	178.8	586	57.2
		15	73.7	107.6	169.6	607	
		5	36.3	87.5	128.9	439	
2.	**Ep/1.0 CNT**	10	41.3	98.6	137.6	492	46
		15	47.0	111.7	154.5	478	
		5	36.2	86.6	124.3	421	
3.	**Ep/1.0 C30B**	10	40.8	98.6	138.7	481	45
		15	45.7	111.3	152.6	452	
		5	36.9	90	122.8	491	
4.	**Ep/1.0 CNT/1.0 C30B**	10	38.4	98.8	139.3	576	93.1
		15	46.9	102.2	148.1	443	

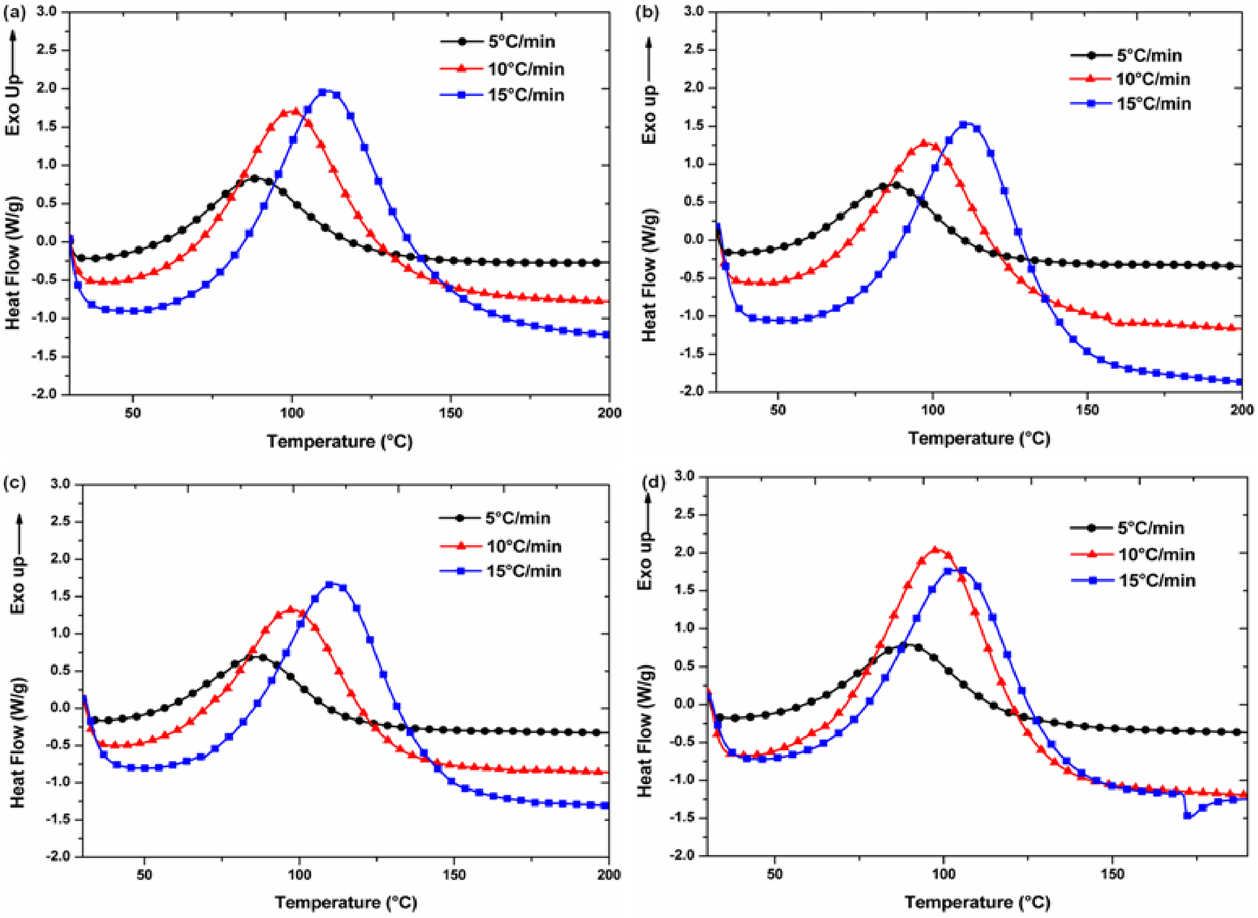

Figure 5: Heat flow vs. temperature graphs of Ep (a), Ep/1.0 CNT (b), Ep/1.0 C30B (c) and Ep/1.0 CNT/1.0 C30B (d).

For an additional explanation, the degree of conversion (α) versus temperature curves of all epoxy formulations were plotted and are depicted in Figure 6(b). For all epoxy systems, the complete degree of conversion associated with a higher temperature indicated that a higher percentage of cure occurs at a relatively higher temperature. The degree of conversion (α) of the pristine epoxy adhesive is higher as compared to its nanocomposite adhesives and when the temperature increases, the α of each adhesive systems gradually approaches to each other. In addition, the thermograms of degree of conversion (α) as a function of temperature resemble S or sigmoid-shaped curves as expected in the case of a non-isothermal curing process. Similar findings have been obtained by others [29,37]. The rates of conversion ($\frac{d\alpha}{dt}$) as a function of degree of conversion (α) were plotted and are depicted in Figure 6(c). As evident from the graphs, the rate of conversion ($\frac{d\alpha}{dt}$) = 0 occurs at the initial and terminal stages of the curing process which indicates that the curing reactions of all the epoxy systems studied are autocatalytic. Similar results have been obtained by Singh et al [40] and Sahoo et al [41].

The activation energies (E_a) of the Ep, Ep/1.0 CNT, Ep/1.0 C30B and Ep/1.0 CNT/1.0 C30B adhesive formulations were calculated considering T_m values at each heating rate by using the Kissinger equation (Eq. 4) and the acquired values are presented in Table 3. The E_a of a curing process is representative of the potential barrier of that reaction. As shown in Figure 6(d), the E_a values for Ep, Ep/1.0 CNT, Ep/1.0 C30B and Ep/1.0 CNT/1.0 C30B were calculated to be 57.2, 46, 45 and 93.1 kJ/mol respectively. As MWCNT was incorporated in the epoxy, the E_a was significantly reduced as compared to the pristine resin, since a CNT can act as a catalyst owing to its high thermal conductivity. Similar results have been obtained by Nusrat et al [39] and Susin et al [42]. In the case of Ep/1.0 C30B, the addition of C30B into an epoxy adhesive facilitates strong bonding between epoxy matrix and nanofiller indicating higher reactivity of the system as compared to virgin epoxy. Thus, the inclusion of nanoclay considerably lowers the activation energy of the epoxy system. Similar trends has been observed by other researchers [43]. However, in the case of the Ep/1.0 CNT/1.0 C30B system, the E_a value escalates significantly as compared to the unmodified epoxy system. This behaviour can be attributed to the physical impediment that impacts on curing reaction by the nanomaterials. The presence of nanomaterials restricts polymer chain mobility, which is usually stated as one of the main reasons for increments in E_a. Similar findings have been found by Elnaz et al [37].

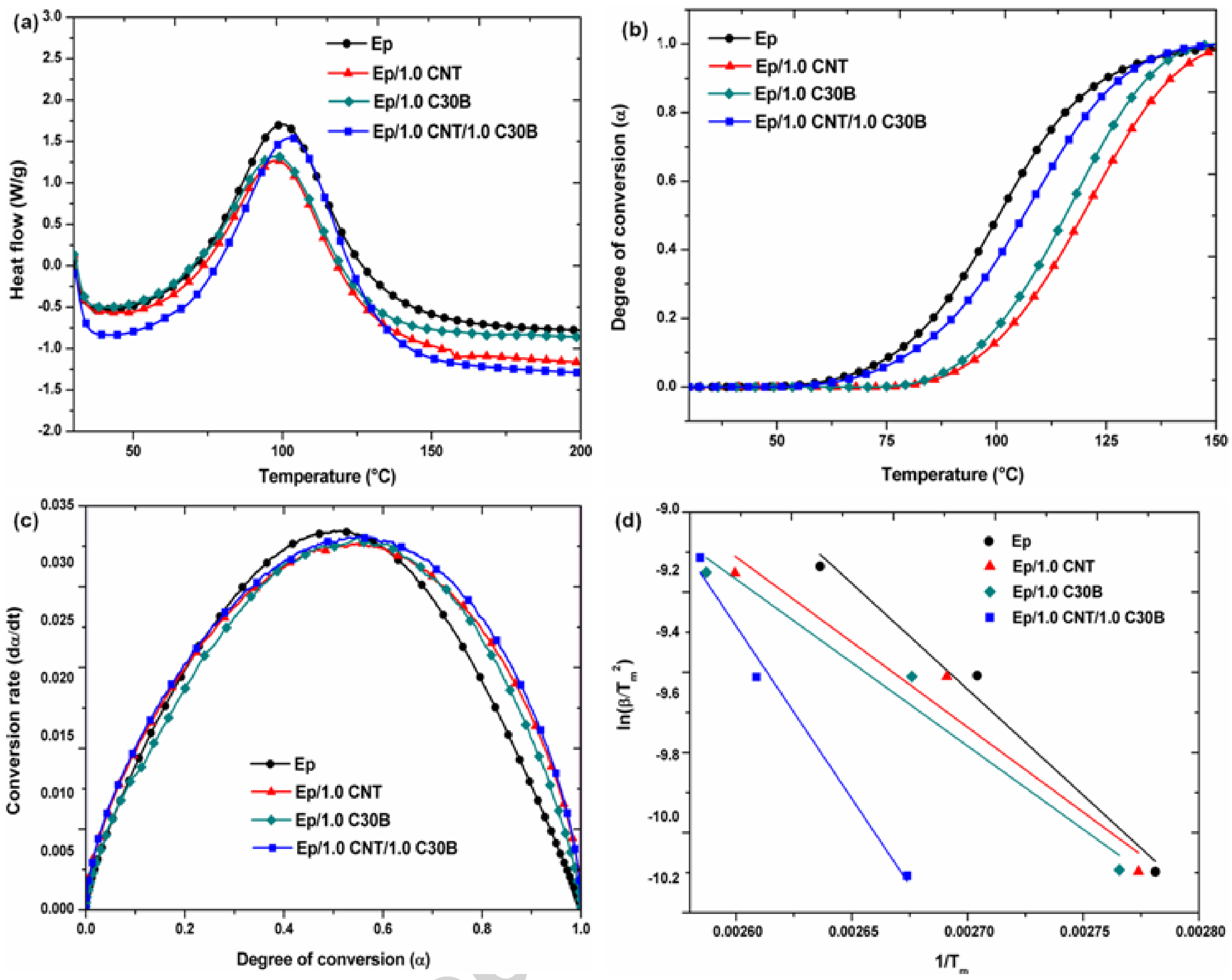

Figure 6: Comparison of all epoxy formulations at heating rate of 10°C/min (a) Heat flow vs. temperature curves, (b) Degree of conversion (α) vs. temperature graphs, (c) Conversion rate ($^{d\alpha}/_{dt}$) vs. degree of conversion (α) graphs; (d) Kissinger's plot for E_a of all adhesive systems.

3.3.2. Degradation kinetics study

The thermal stability of the Ep, Ep/1.0 CNT, Ep/1.0 C30B and Ep/1.0 CNT/1.0 C30B adhesive formulations as a function of temperature from 30 to 800°C at 10°C/min were investigated using TGA with the results obtained depicted in Figure 7. Table 4 summarizes the obtained parameters (such as maximum temperature (T_{md}) and final temperature (T_{fd}) of the derivative weight loss curve) from TGA for all adhesive formulations at heating rates (β) 5, 10 and 15°C/min (in case of Ep only at 10°C/min).

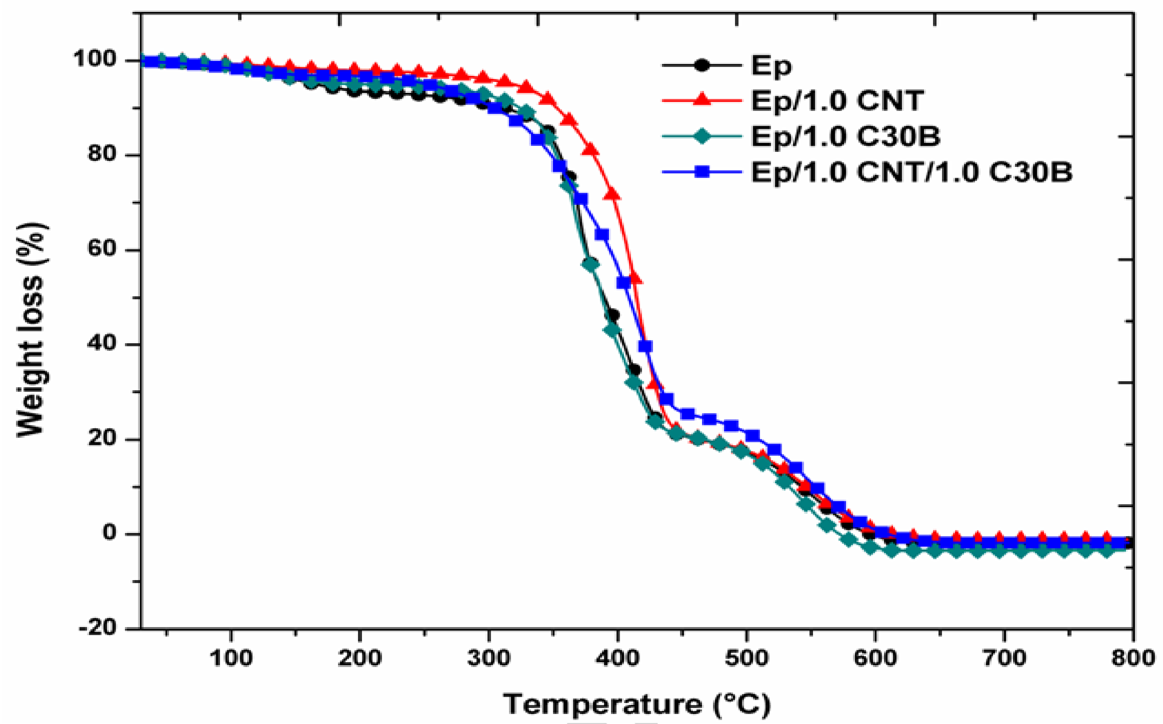

Figure 7: TG thermograms of Ep, Ep/1.0 CNT, Ep/1.0 C30B, Ep/1.0 CNT/1.0 C30B adhesives systems.

The epoxy adhesive starts to degrade as low as 145°C possibly due to the decomposition of lower molecular weight materials (i.e. incompletely cured oligomer) but the maximum degradation or second stage weight loss was between 340°C and 365°C, related to the degradation of the epoxy of higher molecular weight formed after curing. Similar findings have also been observed by Yu et al [22]. On the other hand, the Ep/1.0 CNT adhesive showed degradation occurring at a higher temperature than that of the neat epoxy. The thermal stability increment of the Ep/1.0 CNT adhesive can be attributed to the stabilizing effect of the CNTs owing to their outstanding thermal conductivity [22]. In the case of the nanoclay based epoxy adhesive, the thermal stability shows a marginal increase as compared to the pristine epoxy adhesive. The main reason for the improvement in thermal stability of the Ep/1.0 C30B system will be the barrier action of hard nanoclay layers, which restricts the segmental motion of the polymer chains present in between the layers thus minimizing any potential volatilization effects [19]. Compared with the Ep/1.0CNT and Ep/1.0C30B adhesive systems, Ep/1.0 CNT/1.0 C30B showed a higher thermal stability because nanofiller inclusion forms a hybrid network structure which has combined properties of both CNT and nanoclay. The hybrid filler acts as physical crosslinking point which restricts polymer chain movement and delays the degradation of epoxy by reducing their ability to degrade [35].

Table 4: Data obtained from DTG thermograms and activation energy (E) calculated using Kissinger method.

Sl No.	Samples	Heating rate (β) (°C/min)	Temperatures		Activation energy of degradation (E) (kJ/mol)
			T_{md} (°C)	T_{fd} (°C)	
1.	**Ep**	10	349	550	141.9 [44]
2.	**Ep/1.0 CNT**	5	336.5	600	155.7
		10	350.9	622	
		15	357.3	650.7	
3.	**Ep/1.0 C30B**	5	330.06	602.7	151
		10	349.4	608	
		15	358.04	623.5	
4.	**Ep/1.0 CNT/1.0 C30B**	5	343	600	223.2
		10	353.01	616.3	
		15	358.04	626.3	

The DTG curves of the Ep/1.0 CNT, Ep/1.0 C30B and Ep/1.0 CNT/1.0 C30B adhesive systems at heating rates of 5, 10 and 15°C/min are depicted in Figure 8(a-c). The DTG peaks show similar trend as that of curing peaks of adhesive systems: they shift towards higher temperature with increasing heating rates. The activation energy of degradation (E) for Ep/1.0 CNT, Ep/1.0 C30B and Ep/1.0 CNT/1.0 C30B were calculated using the Kissinger method (Eq.5) as reported in Table 4 and depicted in Figure 8(d). The E values obtained for the Ep/1.0 CNT, Ep/1.0 C30B and Ep/1.0 CNT/1.0 C30B adhesives were 155.7, 151 and 223.2 kJ/mol respectively and are compared with the activation energy of the pristine epoxy from the literature. The activation energy for the Ep/1.0 CNT system was found to be higher as compared to that of the pristine epoxy which can be attributed to the stabilizing effect and degree of dispersion of the CNTs. The well-dispersed CNTs can also restrict the deformation of the epoxy matrix, thus enhancing the thermal stability of the system [45]. In the case of the Ep/1.0 C30B adhesive, the improvement in the E value can be ascribed to the existence of well-organized clay platelets which can inhibit the breakage of chemical bonds between nanoclay and epoxy matrix. Similar results have been observed by other researchers [46]. On the other hand, the adhesive system filled with both nanofillers shows a substantial increase in E value as compared to the virgin epoxy resin. This behavior can be attributed to the formation of a hybrid network structure in which hybrid filler acts as physical barrier that can retard easy polymer degradation [35].

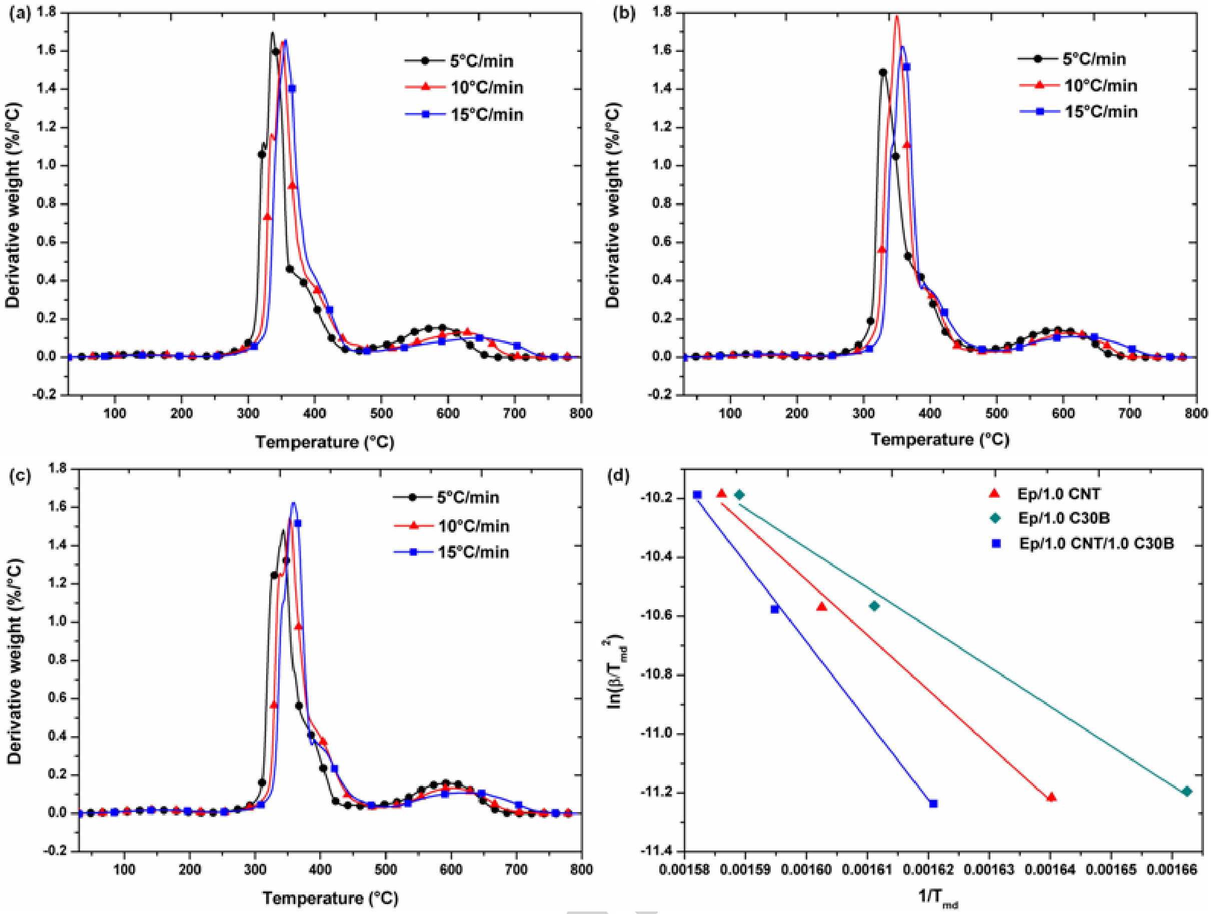

Figure 8: DTG curves for Ep/1.0 CNT (a), Ep/1.0 C30B (b), Ep/1.0 CNT/1.0 C30B (c); Kissinger plot for determination of E for Ep/1.0 CNT, Ep/1.0 C30B, Ep/1.0 CNT/1.0 C30B (d)

4. Conclusions

In the present work, epoxy adhesive systems modified with various nanofillers (such as MWCNTs and nanoclays) were developed and the effects of nanofiller inclusion on both adhesive and morphological properties together with curing and degradation kinetics of the epoxy adhesives were investigated. The Ep/1.0 C30B adhesive system showed optimum shear strength (52% in comparison with the unmodified adhesive) as compared with other adhesive systems such as Ep/1.0 CNT (48%) and Ep/1.0 CNT/1.0 C30B (4.69%). The SEM micrographs reveal that nanomaterials with different shapes and dimensions provide distinct features on the fracture surfaces due to their different energy dissipation mechanisms. TEM images and statistical analysis showed good dispersion of MWCNTs along with less agglomerates and XRD spectra confirmed a high degree of exfoliation of nanoclay within the epoxy matrix. However the Ep/1.0 CNT/1.0 C30B adhesive system consists of distinct regions where either CNTs or nanoclays are present which was confirmed by TEM micrographs. Non-isothermal DSC and TGA techniques were used to study the influence of nanofillers on the curing and degradation kinetics of the epoxy adhesive systems, respectively. The activation energies for curing (E_a) and degradation (E) were calculated by adopting Kissinger's method. The addition of nanofillers reduce the total heat of cure (ΔH_{Total}) of the epoxy adhesive suggesting that reaction rates increase at lower temperatures. The activation energies (E_a) obtained from DSC were 46 (19.6%), 45 (21.3%) and 93.1 (62.8%) kJ/mol for Ep/1.0 CNT, Ep/1.0 C30B and Ep/1.0 CNT/1.0 C30B respectively as compared with that of the pristine epoxy (57.2 kJ/mol). The activation energies of degradation (E) showed increments of 9.7%, 6.4% and 57.3% for Ep/1.0 CNT, Ep/1.0 C30B and Ep/1.0 CNT/1.0 C30B respectively as compared with the virgin epoxy adhesive (141.9 kJ/mol) indicating improved thermal stability with nanofillers inclusion.

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