Interface-tuned epoxy/clay nanocomposites

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Though interface has been known for a critical role in determining the properties of conventional composites, its role in polymer nanocomposites is still fragmented and in its infancy. This study synthesized a series of epoxy/clay nanocomposites with different interface strength by using three types of modifiers: ethanolamine (denoted ETH), Jeffamine M2070 (M27) and Jeffamine XTJ502 (XTJ). XTJ created a strong interface between clay layers and matrix because it bridged the layers with matrix by a chemical reaction as proved by Fourier transform infrared spectroscopy; M27 produced an intermediate interface strength due to the molecular entanglement between grafted M27 chains and matrix molecules; the interface made by ETH was weak because neither chemical bridging nor molecular entanglement was involved. The studies of mechanical and thermal properties and morphology at a wide range of magnification show that the strong interface promoted the highest level of exfoliation and dispersion of clay layers, and achieved the most increment in Young’s modulus, fracture toughness and glass transition temperature (Tg) of matrix. With ~1.3 wt% clay, the critical strain energy release rate G1c of neat epoxy improved from 179.0 to 384.7 J/m, 115% improvement and Tg enhanced from 93.7 to 99.7 °C, 6.4% improvement.

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1. Introduction

The interface of composites is a well-known factor posing a significant effect on the composite properties due to its role of transferring stress or electrons across matrix and filler. Polymer nanocomposites offer significant improvements in material properties, such as modulus, strength, toughness, scratch resistance, optical properties, electrical conductivity, gas and solvent transport, with much lower fractions of nanoparticles than the conventional composites. Despite the large volume of nanocomposite research published over the past 15 years, the understanding of the role of interface in morphology and properties remains in its infancy. This is mainly due to the lack of reliable experimental data from a series of comparable nanocomposites of tailored interface strength.

Of thermosets, epoxy has been widely used across industries owing to its high chemical resistance against severe corrosive conditions, good thermal and mechanical properties, excellent adhesion to a wide range of materials and easy processability. However, it is inherently brittle and thus attracted increasingly more interest from both industries and universities for toughening. Essentially, there are two common approaches to toughen brittle epoxy resin: to modify epoxy structure [1–3] and to introduce toughening agents [4–6]. The latter has been the focus, in specific using nanoparticles in recent years as the tougheners because of significantly improved fracture toughness with no loss of other desired properties at low fractions [7–11]. Nanocomposites are generally classified by the geometries of the nanoparticles-particulate (e.g. silica), layered (silicate layers), and fibrous geometries (nanotubes)—of which layered polymer nanocomposites have shown the greatest mechanical and barrier properties, and attracted the most extensive research and development due to the fillers’ high specific surface area, functionality and cost-effective fabrication [12–15].

Based on the arrangement of silicate layers in polymer matrixes, two types of morphology are formed in nanocomposites: intercalated or exfoliated. The exfoliated morphology is always preferred because it produces better performance, despite the fact that exfoliation is difficult to achieve. Three key factors to achieve exfoliation...
include: increase in the silicate interlayer spacing through suspension in solvent/water or polymerization prior to compounding with polymers [16]; the adoption of reactive modifier bridging the layers with polymer matrix [17,18]; and the creation of physical entanglement between silicate modifier and matrix [19]. Epoxy/clay nanocomposite research was pioneered by Messersmith and Gianelli [20] who produced merely intercalated nanocomposites. Curing was then proved helpful to promote the exfoliation layers [21,22]. A few studies justifed the ameliorated mechanical properties by the highly exfoliated, uniformly dispersed silicate layers in epoxy matrix based upon just one or two high magnification micrographs, rather than observation made on low magnification TEM micrographs [18,20–23]. In fact, clusters of silicate layers were found at low magnification [24,25], an important factor in studying epoxy/clay nanocomposites since phase separation often occurs during fabrication.

A recent trend is to adopt reactive surfactants to modify silicate which subsequently bridged to matrix molecules [18,23]. Cheng-Yang et al. adopted an epoxide-containing surfactant to modify silicate layers which was then mixed with epoxy and hardener; during curing, the epoxide groups reacted with hardeners to produce links between silicate layers and matrix. Since an epoxy of low modulus was chosen as matrix, no fracture toughness measurement was made. Although the silicate layers obviously improved modulus and strength by adapting the following routes: (1) Molecular entanglement. Matrix molecules physically entangle with surfactants that are grafted into silicate layer surface via ion exchange; and (2) Chemical reaction. The surfactant used for clay contains two end-amine groups: one grafting into the silicate surface via ion exchange and the other reacting with epoxy molecule. Fig. 1 illustrates the proposed routes for improving the interaction between epoxy and silicate. We then investigate the effect of interface on the morphology, mechanical properties, fracture toughness and thermal mechanical properties of these materials. Through this work, an understanding of the interface effect on layered polymer nanocomposites is obtained.

2. Experimental parts

2.1. Materials

Epoxy resin, diglycidyl ether of bisphenol A (DGEBA, Araldite-F) with epoxide equivalent weight 182–196 g/equiv, was purchased from Ciba-Geigy, Australia. Hardener polyoxypropylene (Jeffamine® J230) was provided by Huntsman. Sodium montmorillonite was provided from APS Specialty Chemicals; surfactants Jeffamine® M2070 and Jeffamine® XTJ502 were provided by Huntsman. The chemical structures and molecular weight of these surfactants are shown in Table 1.

2.2. Modification of clay surface

10 g clay was dispersed in 2 kg boiling deionized water through 10 min vigorous stirring using a mechanical mixer. Stoichiometric amount of ethanamine or M27 or XTJ was dissolved in 200 g water, followed by adding 10 g of hydrochloric acid solution (0.83 mol/L). The mixture was stirred by a glass rod and then added slowly to the clay suspension, followed by 10 min vigorous stirring at 90 ºC. The resulting clay was condensed using a rotary vacuum evaporator for 30 min at 80–90 ºC and then separated using a centrifuge. The precipitate was repeatedly washed three times with acetone using a magnetic mixer, an ultrasonic bath and the centrifuge. The final precipitate was suspended in 500 ml acetone to form clay/acetone slurry, which were denoted as eth-clay or m27-clay or xtj-clay depending on the type of surfactant used.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Surfactants used to modify raw clay.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Modifiers</strong></td>
<td><strong>ABBR.</strong></td>
</tr>
<tr>
<td>Ethanolamine</td>
<td>ETH</td>
</tr>
</tbody>
</table>

* Molecular weight of grafted surfactant.
2.3. Preparation of epoxy/clay nanocomposite

An in situ reaction was used, taking advantage of the increased layer spacing in a solvent—a key factor to achieve exfoliation [16]. DGEBA was mixed with a desired amount of the modified clay slurry for 1 h at 55 °C using a mechanical mixer at 400 rpm in a round-bottom flask with a condenser. The mixture was then transferred into a beaker followed by mixing and heating at 300 rpm and 120 °C for 1 h to evaporate acetone, followed by degassing in a vacuum oven at 120 °C. A stoichiometric amount of curing agent J230 (3.3:1 weight ratio of DGEBA to J230) was added to the mixture and mixed for ~2 min at 50 °C. The resultant mixture was highly degassed in a vacuum oven for ~5 min to remove trapped bubbles, followed by pouring into a rubber mould and curing at 80 °C for 3 h and at 120 °C for 12 h.

2.4. Chemical characterization

A Nicolet Avatar 320 Fourier transform infrared spectroscopy (FTIR) was employed to analyze the bonding between matrix and nanoparticles, by recording the spectra of neat epoxy and the nanocomposites from 4000 to 700 cm⁻¹ at 2 cm⁻¹ using a minimum of 32 scans. The FTIR samples were prepared by a solution-casting method on the KBr plate.

2.5. Morphological observation

Transmission electron microscopy (TEM) was performed to provide two dimensional images of internal structure of the nanocomposites. Ultrathin sections of 50 nm were microtomed from bulk samples using Leica Ultracut S microtome equipped with a diamond knife and collected on 200-mesh copper grids. These sections were examined with a Philips CM200 transmission electron microscope at 200 kV accelerating voltage. X-ray diffraction (XRD) was conducted at room temperature using a Mini-Materials Analyzer (MMA). The diffractometer was equipped with a curved graphite monochromator, tuned to Cu Kα radiation, which was applied at a tube voltage of 35 kV and an X-ray power of 1 kW. The diffraction patterns were then collected in reflection mode geometry between 2θ = 1.5°-12° at a scanning rate of 1°/min.

2.6. Mechanical measurement

Tensile test was performed on dumb-bell samples of gauge length 100 mm at 0.5 mm/min according to the ASTM D-638 to determine the elastic modulus, ultimate stress, and ultimate strain of neat epoxy and nanocomposites, by using Instron 5567 testing system with a 30 kN load cell and an extensometer. The average values of all the properties were taken from five repetitions of each test; Young’s moduli were calculated at a strain range 0.05–0.15%.

Fracture toughness measurement requests great care to produce an instantly propagated crack [26]. In comparison with compact tension (CT) or double cantilever beam (DCB), single edge notch bending (SENB) just needs the least volume of materials but it is the most difficult to produce an instantly propagated crack due to its limited cross section area. Therefore, this study tested fracture toughness according to ASTM D-5045 using the compact tension (CT) of ~30 mm in width and ~5 mm in thickness. An instantly propagated crack was produced for each CT by tapping a razor blade to the samples as it is the most cost-effective way to produce a sufficiently sharp crack [26]. It was then tested using the Instron equipped with a 2 kN load cell at 0.5 mm/min. The fracture toughness properties were expressed as stress intensity factor, $K_{1C}$ and critical strain energy release rate, $G_{1C}$. The fracture toughness was calculated using Eqs. (1) and (2).

$$K_{1C} = \frac{P_{0}/(x)}{B W^{1/2}}$$

(1)

$$G_{1C} = \frac{K_{1C}}{E(1 - \nu^2)}$$

(2)

where

$$f(x) = \frac{(2 + x)(0.866 + 4.64x + -13.32x^2 + 14.72x^3 - 5.6x^4}{(1 - x)^{3/2}}$$

and (0.2 < x < 0.8):

$$x = \frac{a}{W}$$

where $P_0$ is the maximum load, $B$ is the thickness, $W$ is the width, $E$ is Young’s modulus and $\nu$ is Poisson’s ratio 3.4.

2.7. Dynamic mechanical measurement

Dynamic Mechanical Analyzer 2980 (TA Instruments, Inc., USA) was utilized at 1 Hz to determine the glass transition temperatures of neat epoxy and its nanocomposites. A single cantilever clamp with a supporting span of 20 mm and torque of 1 Nm was used to clamp rectangular specimens of 3.0 x 6.0 x 40.0 mm which were scanned from 50 to 120 °C and recorded at 2 s/point.

3. Results and discussion

3.1. Reactions for interface

Fourier transform infrared spectroscopy (FTIR) was employed to analyze the interaction and bonding between silicate surface and epoxy molecules during fabrication. Fig. 2 shows the FTIR spectra of epoxy, raw clay, the clay modified by ethanolamine (eth-clay), and the washed mixture of epoxy/eth-clay. The dominant absorption from 991 cm⁻¹ to 1045 cm⁻¹ is ascribed to the Si–O band in-plane stretching of clay [27,28]. The absorption of raw clay at 1636 cm⁻¹ is due to the O–H deformation of entrapped water and the absorption at 3620 cm⁻¹ is created by the O–H stretching of structural

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**Fig. 2.** FTIR spectra of sodium clay, eth-clay, the washed mixture of epoxy/eth-clay and neat epoxy (Graphs are vertically shifted for clarity).
as shown in Section 2.2, absorption bands for epoxy should be mixed with epoxy followed by thoroughly washing using acetone existence of epoxide groups at 910 cm

Fig. 4. FTIR spectra of sodium clay, m27-clay, and the washed mixture of epoxy/m27-clay.

hydroxyl group of the clay. Upon modification with ethanolamine (ETH), new absorption bands are expected in FTIR. Actually, absorption at 1456 cm\(^{-1}\) and 2900 cm\(^{-1}\) are observed due to the presence of \(-\text{CH}_2-\) groups \([29]\) and \(-\text{CH}-\) groups \([30]\), and this confirms the graft of ethanolamine into the clay layer surface. For epoxy, the absorption from 1450 cm\(^{-1}\) to 1600 cm\(^{-1}\) corresponds to the benzyl groups; the C–H band stretching of SP2 is observed at 3048 cm\(^{-1}\), the C–H band stretching of SP3 at 2965 cm\(^{-1}\), 2927 cm\(^{-1}\) and 2873 cm\(^{-1}\), C–O band stretching 1246 cm\(^{-1}\), and the existence of epoxide groups at 910 cm\(^{-1}\) \([31]\). After eth-clay was mixed with epoxy followed by thoroughly washing as shown in Section 2.2, absorption bands for epoxy should be observed if epoxy molecules react or attract to the grafted ethanolamine. Indeed, there is just little characteristic bands of epoxy observed (at 910 cm\(^{-1}\)), indicating traces of epoxy molecules between the clay layers, which is caused by the incomplete removal of epoxy during washing due to the interaction between the hydroxide group of ETH and that of epoxy.

In Fig. 3, new absorption bands are found for the clay modified by M27 (m27-clay): the absorption at 1456 cm\(^{-1}\) is contributed by the \(-\text{CH}_2-\) groups \([29]\) and the absorption at 2900 cm\(^{-1}\) by the \(-\text{CH}-\) groups of the M27 molecules \([30]\), and C–O band stretching is found 1246 cm\(^{-1}\), all of which confirms the graft of M27 into the clay layers. The washed mixture of epoxy/m27-clay shows a similar spectrum to the m27-clay, indicating that neither chemical reaction nor strong physical interaction combines epoxy molecules with m27-clay.

The spectra of the xtj-clay and its washed mixture are shown in Fig. 4. The spectrum of xtj-clay shows a similar feature to M27 in Fig. 3, indicating the graft of XTJ chains into the clay layers as XTJ has similar chemical composition to M27 except the number of end-amine groups as shown in Table 1. Upon mixing with epoxy followed by thoroughly washing as shown in Section 2.2, the mixture shows intensive characteristic absorption which is similar to neat epoxy in Fig. 2, and this confirms the reaction of epoxy molecules with the grafted XTJ chains. The absorption at 910 cm\(^{-1}\) corresponds to epoxide groups, implying that only one of the two end-groups of each epoxy molecule between the layers reacted with the grafted XTJ chains. When xtj-clay was further mixed and cured, the free end-group NH\(_2\) of a grafted XTJ chain reacted with hardener J230, building up a bridge linking the clay layers with matrix to produce a strong interface.

In summary, the interface strength between clay layers and epoxy increases in the order of raw clay < eth-clay ≠ m27-clay < xtj-clay, based on the interaction of the surfactants with epoxy molecules.

### 3.2. Morphology

The structure analysis of these nanocomposites were performed not only using the XRD, but TEM as it is the only method to identify the distribution of individual silicate layers in matrix \([32]\).

#### 3.2.1. XRD spectra

Fig. 5 presents the XRD patterns of raw clay and the modified clay in 2\(\theta\) = 1.5–10\(^{\circ}\). A diffraction peak assigned to the [001] lattice spacing of raw clay at 2\(\theta\) = 7.36\(^{\circ}\), corresponds to a d-spacing of

<table>
<thead>
<tr>
<th>Type of clay systems</th>
<th>(2(\theta)) Peak angle, (deg)</th>
<th>(001) Basal spacing, (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium clay</td>
<td>7.36</td>
<td>12.0</td>
</tr>
<tr>
<td>eth-clay</td>
<td>7.10</td>
<td>12.4</td>
</tr>
<tr>
<td>m27-clay</td>
<td>5.36</td>
<td>16.5</td>
</tr>
<tr>
<td>xtj-clay</td>
<td>5.36</td>
<td>16.5</td>
</tr>
</tbody>
</table>

Table 2: Interlayer distance of various types of clay system.
Upon modification, the diffraction shifts left to lower angles, revealing an increase in the layers’ spacing. This result confirms the grafted surfactant into the layers through cationic exchange between layers and surfactants as supported by FTIR analysis in Figs. 2–4.

Table 2 contains the peak angles and interlayer distance for each type of clay. eth-clay shows the lowest value of spacing due to its short chain length. When clay is modified with the long-chain surfactants XTJ and M27, the diffraction peak moves to lower angle, corresponding to a layer spacing of 1.65 Å. XTJ-clay and m27-clay show similar diffraction pattern and the same basal spacing because of their similar chain length.

The XRD patterns of the nanocomposites containing nominal 2.5 wt% clay are presented in Fig. 6. In comparison with Fig. 5, the diffraction moves to lower angles and all diffraction intensity reduces, indicating the expansion of layer spacing due to the intercalation of epoxy molecules into the clay gallery. Epoxy/eth-clay nanocomposite shows a broad peak at 2θ = 6.2° relative to 14.2 Å layer spacing. By contrast, the diffraction of epoxy/m27-clay nanocomposite appears at 2θ = 4.98°, corresponding to a layer spacing 17.7 Å; the diffraction intensity is much smaller. This indicates that the layer spacing of m27-clay is further increased and most layers may have exfoliated as more epoxy molecules migrate into the clay interlayer space through compounding with epoxy. The chain length of M27 is over 40 fold longer than that of ETH, and thus the grafted M27 molecules are much more effective in entangling with and migrating epoxy molecules into the interlayer space of clay. Although m27-clay and xtj-clay were modified by similar molecular weight surfactants, epoxy/xtj-clay nanocomposite demonstrates a lower angle diffraction with much smaller intensity than the epoxy/m27-clay. This is caused by the reactivity of the graphed XTJ chains, each of which has two amine end-groups: one grafting into clay layers and the other reacting with epoxy molecules as discussed in FTIR, thus creating a strong interface between layers and matrix. The reaction of XTJ with epoxy brought a great amount of epoxy molecules into the interlayer space, significantly increasing the layer spacing and probably causing a higher level of exfoliation than the epoxy/m27-epoxy. This explains why xtj-clay is of the best capacity for exfoliation.

Therefore, the three types of clay follow the following sequence to exfoliate in epoxy: eth-clay < m27-clay < xtj-clay.

### 3.2.2. TEM micrograph

The exfoliation and dispersion of clay layers are two critical factors determining the mechanical and functional properties of polymer/clay nanocomposite. While exfoliation is proved by XRD and high magnification TEM micrographs, the uniformly dispersion of clay layers can only be certified by low magnification TEM micrographs, although a number of research claimed a homogeneous nanostructure of epoxy-clay without sufficient TEM evidence [23,33].

Figs. 7–9 present the TEM micrographs of these nanocomposites at magnification 500–50000×. At the lowest magnification micrographs “a” in these figures, all types of clay form clusters of 2–10 μm in...
diameter in the matrix. The dark lines consist of the single or multiple layers of inorganic clay, while the organic matrix appears light. From XRD analysis, the clay exfoliation follows the sequence: eth-clay < m27-clay < xtj-clay, leading to a prediction that eth-clay should have the lowest degree of dispersion. However, epoxy/eth-clay nanocomposite shows many clay layers dispersed separately in addition to the clusters in Fig. 7a and by contrast, this is not the case for the other two nanocomposites. The contradiction is explained in light of phase separation and compatibility. The surfactant ETH grafted on the clay layer surface is \(\sim 0.5\) nm in length, while the chains of the surfactants M27 and XTJ are as long as \(\sim 20\) nm. During curing, the long-chain surfactant molecules just phase-separated, a phenomenon similar to liquid rubber-toughened epoxy where rubber molecules phase-separate to create micron-sized particles [34]. By comparing Fig. 9a with Fig. 8a, smaller clusters’ size is found for epoxy/xtj-clay nanocomposite than the epoxy/m27-clay, and this is caused by the cluster composition: epoxy molecules were combined with clay layers by the reaction between grafted XTJ and matrix, which improved the compatibility between clay and matrix and thus reduced the cluster size and produced more separated layers in matrix.
In Figs. 7–9, representative zones in micrographs “a” are magnified in micrographs “b” which typically contain a cluster and a few separately dispersed silicate layers; each cluster is then magnified in micrographs “c” and further in “d”; the separately dispersed layers are magnified in micrographs “e” and further in “f”. The micrographs “a–c” in Figs. 7 and 8 all show a number of voids which occurs at the interface between layers and matrix. The voids were produced by a diamond knife during microtoming, indicating a weak interface. The micrographs “a–c” in Fig. 9 show less quantity of voids in comparison, possibly indicating an improved interface strength by the grafted XTG chains which bridge the clay layers with the matrix. In Fig. 7d, white arrows indicate intercalated layers while black arrows refer to exfoliated arrows; most layers remain intercalated. In Fig. 8d, most layers are orderly exfoliated; that is, the layer spacing is too large to be detected by XRD but the layers still remain stacked. In contrast, most layers in Fig. 9d are disorderly exfoliated. In spite of the co-existence of intercalation and exfoliation for these nanocomposites, an exfoliation degree is sequenced from these micrographs: eth-clay < m27-clay < xtj-clay, which is in agreement with XRD analysis.

Regarding the clay layers separately dispersed in matrix, similar exfoliation degree sequence can be reached by comparing micrographs “e” and “f” through Figs. 7–9. The incomplete exfoliation of xtj-clay is attributed by either the inconsistent of clay layers charge varied from layer to layer or the inadequacy of alkylammonium ions in the clay galleries, as supported by Chen [35] and Kornmann [36].

### 3.3. Mechanical analysis

#### 3.3.1. Mechanical properties

The mechanical properties of neat epoxy and its nanocomposites are shown in Table 3. Young’s modulus of neat epoxy significantly increases with the clay addition, whereas the tensile strength drops. The significant improvement of stiffness is explained as the inorganic clay layers share a portion of load and restrict the polymer chain mobility through transferring stress and creating shear deformation.

Since the values of Young’s moduli are determined and affected by testing speed and the initial strain range chosen for calculation, we hereby compare the moduli of the nanocomposites with that of neat epoxy, rather than with previous data. Of these nanocomposites, epoxy/xtj-clay nanocomposite demonstrates the most significant increase of Young’s modulus and the least reduction of tensile strength followed by the epoxy/m27-clay and the epoxy/eth-clay. This is explained in light of the interface modification. ETH grafted on the clay layers is short in length and thus cannot interact effectively with matrix molecules, while M27 is a long-chain molecule surfactant which entangles with matrix molecules and thus produces a high level of interface strength. As a result, the ~1.4 wt% (absolute fraction) epoxy/m27-clay nanocomposite demonstrates higher increment in modulus and lower reduction in strength than the ~2.4 wt% epoxy/eth-clay. With a similar chain length to M27, XTG molecules that grafted on the clay layers reacted with matrix molecules, bridging nanolayers with matrix—creating the strongest interface of these nanocomposites. This explained why the 1.3 wt% epoxy/xtj-clay nanocomposite achieved the most significant modulus increment with the least loss of strength.

#### 3.3.2. Fracture toughness

The fracture toughness and critical energy release rate listed in Table 3 were obtained in the presence of an instantly propagated crack as described in Section 2.6. Overall, the fracture toughness of epoxy improves obviously upon the addition of the modified clay. Epoxy/xtj-clay nanocomposite shows the most significant toughness improvement, 58% for KIC and 115% for GIC, followed by the epoxy/m27-clay and the epoxy/eth-clay. It is worth to note that the fracture toughness improvement by ~1.3 wt% of xtj-clay surpasses all the previous effort [37,38] in the condition that the toughness measurement was conducted with the presence of a sufficiently sharp crack because the crack sharpness poses a huge effect on the toughness values for stiff materials [26,37]. Interface debonding is generally accepted as the major toughening mechanisms for epoxy/clay nanocomposites [37]. As aforementioned, xtj-clay obtained the highest interface strength and m27-clay had the lowest upon compounding with epoxy. When loaded, the xtj-clay layers are able to carry and transfer the highest portion of stress to relieve stress concentration on the crack and absorb fracture energy. This is in agreement with the TEM analysis—the least quantity of voids in Figs. 7–9 is found for the epoxy/xtj-clay. The chain length of M27 is ~40 times longer than that of ETH and thus the M27 chains entangle with matrix molecules, providing a thicker and more flexible interface than ETH, and this explains why epoxy/m27-clay nanocomposite shows a higher fracture toughness than the epoxy/eth-clay.

### 3.4. Thermal dynamic analysis

The glass transition temperature (Tg) of a thermosetting polymer—a temperature at which crosslinked chains start vibrating to
rearrange themselves—is the most important thermal parameter indicating the upper temperature limit for its application. The rate of rearrangement or relaxation process is determined by matrix chain stiffness, crosslink density, reinforcement particles and the interface between particles and matrix. Since matrix chain stiffness and crosslink density are not variable in this study, the change of $T_g$ must be caused by reinforcement particles and the interface between particles and matrix.

Fig. 10 shows the damping behaviour of neat epoxy and the epoxy/m27–clay and epoxy/xtj–clay nanocomposites at the absolute fraction of 1.3–1.4 wt% clay. Determined from the midpoints of the corresponding glass transition regions, the $T_g$s for these materials are 93.7 °C, 96.2 °C and 99.7 °C, respectively. While both nanocomposites show improved $T_g$s, the epoxy/xtj–clay shows a higher value. This is explained by the interface modification. M27 molecules grafted on the clay layer surface have a $M_n$ of ~2000 with a chain length ~20 nm, and thus they are able to entangle with matrix molecules to increase the layer spacing and cause exfoliation, leading to the presence of matrix molecules between the layers; these 1 nm thick layers of extremely high specific surface area poses barriers to the vibration of matrix molecules through the $T_g$ region and thus causes longer relaxation time, implying higher $T_g$. This is supported by previous research [8,24]. XTJ molecules grafted on the layers are of similar chain length to M27, but they build up a strong interface with matrix by reacting with matrix molecules during curing; this creates more significant barriers to the movement of matrix molecules, causing a longer relaxation time and a higher $T_g$. In conclusion, higher interface strength means higher $T_g$ for epoxy/clay nanocomposites.

We have recently showed a number of improved $T_g$s due to the barrier provided by 55 nm rubber particles that are less stiff than matrix [9]. In contrast, clay is a stiff, 1-nm thick layer which produces a significantly restricting effect on the matrix chain movement, leading to improved $T_g$s. However, previous studies regarding the improvement of $T_g$s of epoxy/clay nanocomposites are inconsistent. With addition of clay, some reported an increment of $T_g$ [39–41], while there are reports of reduced [42–44] or no change of $T_g$ [45,46]. This may be caused by inappropriate ratio of epoxy to hardener, variations of curing condition and excessive surfactants left by modification.

4. Conclusion

Although it was proved that polymer nanocomposites demonstrated a significantly higher level of performance compared to conventional composites, no clear understanding has yet emerged regarding the effect of interface on the various properties of polymer nanocomposites. In this study, we designed three levels of interface strength by adopting ethanolamine (denoted ETH), Jeffamine® M2070 (M27) and Jeffamine® XT502 (XTJ) to modify clay. It was remarkable to see how the adopted systems had produce significant outcomes, which demonstrated the effects of different interface strength on the morphology, mechanical properties, fracture toughness and thermal dynamic behaviour of epoxy. The chemical reaction of XTJ–clay with epoxy created a strong interface, resulting in the best dispersion of clay layers and the most increment of Young’s modulus, fracture toughness and thermal property. Upon compounding with ~1.3 wt% clay, the fracture toughness and fracture energy of epoxy were improved at 58% and 115%, respectively. Although no chemical bonding was employed to produce the interface for epoxy/m27 nanocomposite, the long chain of M27 entangled with matrix molecules and thus produced an intermediate interface which explained for relatively good dispersion of clay layers and the moderate improvement of modulus, fracture toughness and thermal property. Epoxy–clay produced a weak interface for epoxy/eth–clay nanocomposite, because neither chemical bonding nor molecular entanglement occurred between eth–clay and matrix.

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