

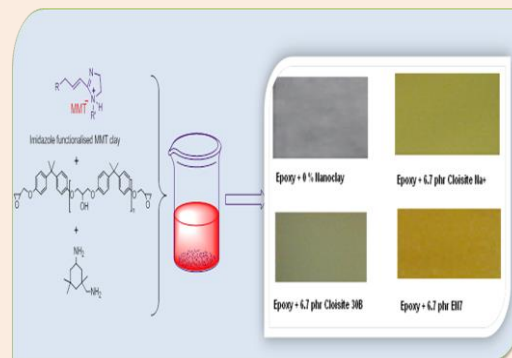
Research Article

Effect of Imidazole Functionalized Nanoclays on Thermal and Mechanical Property of Epoxy Nanocomposites

Sunil Virkar¹ and Atul Chaskar*²¹Pacific Academy of Higher Education & Research University, Udaipur, India.²Department of Dyestuff Technology, Institute of Chemical Technology, Matunga, Mumbai**Abstract**

We have prepared imidazole functionalized clay with better organophilic property and this clay was found to have higher thermal stability than commercially available alkyl ammonium functionalized clays. The imidazole functionaliser intercalated the clay and the clay dispersed well in epoxy matrix resulted into better interaction which leads to enhanced mechanical properties. Epoxy nanocomposites containing 6.7 phr imidazole functionalized clay showed a higher storage modulus and a higher Td_{5%} than unfilled epoxy and epoxy nanocomposites containing the same loading of commercially available clays.

Keywords: Nano-structures, Polymer-matrix composites (PMCs), Mechanical properties, Diglycidyl ether of bisphenol A, Montmorillonite (MMT).

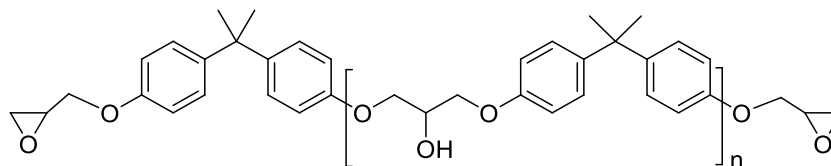
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Introduction

Epoxy resins are polymeric materials bearing epoxy groups with significant properties such as excellent dimensional stability and low shrinkage, outstanding chemical resistance, excellent mechanical stiffness and strength, good electrical and thermal properties. These properties could be tuned for specific applications due to the formulation versatility and low cost of epoxy resins. The formulation versatility is due to the highly strained epoxy ring which is amenable to reactions with a wide variety of curing agents under different conditions. The resins can also be combined with a variety of diluents, fillers, plasticizers, tougheners and solvents which further expands their formulation versatility. As a result they find applications in adhesives, coatings, composites, encapsulants, laminates, polymers, sealants and viscosity modifiers.

**Figure 1** Chemical structure of DGEBA

Diglycidyl ether of bisphenol A (DGEBA), a product of epichlorohydrin and bisphenol A is the most important intermediate in epoxy resin technology. The structure of epoxy resins is responsible for its outstanding performance. Ether linkages provide chemical resistance while bisphenol-A moiety provides toughness, rigidity and high temperature performance **Figure 1**. The resins are cured into solid, infusible and insoluble three-dimensional

thermoset networks. Although various types of curing agent could be used, amines and carboxylic-functional polyesters and anhydrides are the most widely used.

The molecular weight of DGEBA, the type of curing agent, the degree of cross-linking, etc govern the properties of the cured resin. In recent years enormous efforts have been concentrated on making epoxy nanocomposites in order to improve the properties. The epoxy nanocomposites offer significant improvements in mechanical, thermal, electrical and flame properties. Although a wide variety of nanoparticles is available, naturally occurring montmorillonite (MMT) based nanoclays have attracted the most attention due to their inherently high modulus (~ 270 GPa), high aspect ratio (~ 100), ease of surface modification and low cost [1]. MMT is a 2:1 layered silicate with lamellae made up of octahedral alumina sheets sandwiched between two tetrahedral silicate sheets. It exhibits a net negative charge on the lamellae when aluminum is substituted by magnesium. The negative charge is balanced by Na^+ , K^+ or Ca^{++} [2, 3]. The nanoclays are however hydrophilic and do not disperse well in polymers. Their dispersion in polymers can be improved by organically modifying the nanoclays. The modifier increases the basal spacing between nanoclay platelets and allows insertion of polymer molecules into the gallery between the nanoclay platelets. The nanoclay platelets can thus have polymer molecules residing inside the galleries (intercalation) or the whole stack of clay layers can be completely delaminated (exfoliation) [4]. However, due to impurities and non-uniform charge distribution on clay surface, the resultant morphology is a combination of clay tactoids, intercalation and exfoliation [1]. Nanocomposites of various polymers such as epoxy [1-4], polyamide [5], polyimide [6], polyethylene [7], polystyrene [8] and polyurethane [9] have been prepared using such functionalized clays.

The organic modifiers are usually alkyl ammonium salts of long chain fatty acids. A drawback associated with these modifiers is their poor thermal stability. The thermal degradation of alkyl ammonium modifiers is initiated at 150 °C which is well below the processing temperature of many industrially important polymers [10]. In spite of this, a number of these modifiers have been used as surface treatments in nanocomposites with varying degrees of success. Shah et al. [11] showed that the thermal degradation of alkyl ammonium modifiers limits the extent of exfoliation/intercalation thereby limiting performance improvements that would otherwise be possible. On thermal degradation, the ammonium ions dissociate to form primary amines which react with free epoxide groups of resin. The resulting linear epoxy chains reduce cross-link density while the unreacted primary amines plasticize the epoxy matrix [12, 13]. This reduces mechanical properties like modulus and thermal properties like glass transition temperature (T_g) and heat distortion temperature (HDT).

The thermal stability of organically functionalized nanoclays can be improved by selecting other modifiers like alkyl phosphonium, alkyl stibonium or alkyl imidazolium [7, 14-18]. In alkyl imidazolium, the thermal stability depends on substituents on the imidazole ring, counter ion, alkyl chain length and substituents on the alkyl chain. There is, however, scant work on the use of imidazolium salts as a replacement for the commercially available alkyl ammonium salts.

Experimental

Materials and Reagents

Materials

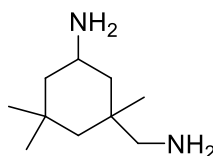


Figure 2 Chemical structure of IPDA

2-Ricinyl-1-hydroxy ethyl-4,5-dihydro imidazole, Cloisite Na⁺, Cloisite 30B, Cloisite 20A, and the epoxy resin DGEBA were used as it obtained. The curing agent was isophorone diamine (IPDA) which is a clear liquid with a boiling point of 247 °C. The structure of IPDA is shown in **Figure 2**.

Nanoclay Modification with Imidazole

MMT clay (Cloisite Na⁺) was used as received for modification with imidazole. The cation exchange capacity (CEC) of this clay is 92.6 meq/100 g. A 10% excess of stoichiometrically required quantity of imidazole was added to 100 ml distilled deionised water. The mixture was sonicated for 3 minute. A water miscible imidazole salt was prepared by addition of 4 ml of 0.5 N hydrochloric acid and it further used for ion exchange with the Na⁺ ions of the hydrophilic unfunctionalised MMT clay. The resulting imidazole salt is soluble in water and gives a clear solution. The pH measured at this point was 6 to 7.

1 gm MMT clay was dispersed in 100 ml distilled deionised water by sonication for 5 min. This dispersion was stirred in a beaker at 150 rpm for 5 min. Imidazole salt solution, prepared above, was added to the MMT dispersion dropwise with continuous stirring. The mixture was stirred at 150 rpm for 6 hours at room temperature. The salt preparation and ion exchange with MMT clay are shown in **Figure 3**. After stirring, the mixture was kept undisturbed for 12 hours. During this period the clay settled down in the beaker. The supernatant water was removed and fresh distilled deionised water was added to wash the clay to remove any unreacted imidazole. The washing step was repeated three times. The clay was then filtered and dried under vacuum at 105 °C for 8 hours.

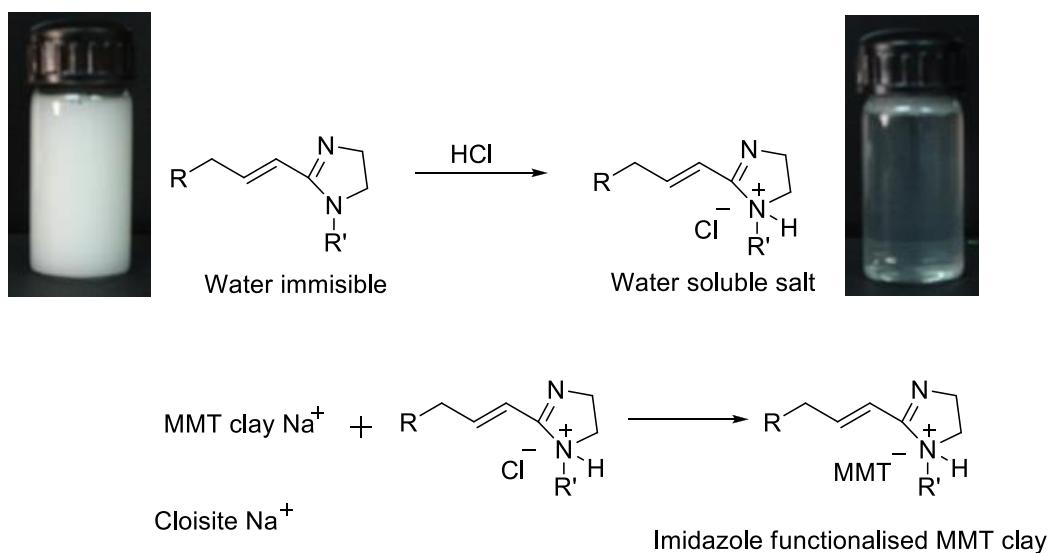


Figure 3 MMT clay modifications

Composite Preparation

Epoxy nanocomposites were prepared with various loadings of Cloisite Na⁺, Cloisite 30B and imidazole functionalized clays. Acetone was used as a dispersing medium to enhance the dispersion of these clays in epoxy. Weighed quantity of clay (5 phr and 6.7 phr calculated for 100 parts of epoxy + IPDA) was added to 20 ml of acetone in a beaker. The mixture was sonicated for 5 minutes. Epoxy resin (DER 331) was added to the mixture and mixed well with a glass rod until visually consistent, viscous paste was obtained. The mixture was kept under vacuum at 105 °C for 3 hours to remove acetone. IPDA (24 phr calculated for 100 parts epoxy) was added and mixed for 2 minutes with a glass rod. The viscous mixture was poured in rectangular trays made of a aluminum foil. The trays were left

undisturbed overnight for room temperature curing and further post cured at 100 °C for 4 hours. The post cured samples were cut and machined for mechanical testing.

Differential Scanning Calorimetry

The glass transition temperature (T_g) of epoxy nanocomposites was measured using Q2000 DSC under nitrogen atmosphere. The DSC was run from room temperature to 200 °C at 10 °C/min and the T_g was measured from the second heating run.

Thermogravimetric Analysis

The thermal stability of various types of nanoclay and epoxy nanocomposite was studied using Q500 TGA under nitrogen atmosphere. The samples were heated at 20 °C/min from room temperature to 105 °C and held at 105 °C for 5 minutes to remove any moisture present. Eventually the samples were heated at 10 °C/min to 800 °C. The weight loss due to thermal degradation of the organic modifiers was calculated after subtracting the weight loss due to loss of moisture at 105 °C.

Dynamic Mechanical Analysis

The storage modulus (E') of epoxy nanocomposites was measured using RSAIII DMA. Specimens 45 mm X 10 mm X ~2 mm were machined from epoxy plaques. The three point bend geometry with a span of 40 mm was used. A prestress of 3.3 MPa was applied on all the samples. The measurements were carried out at 0.2 % strain in the linear viscoelastic region at 40 °C and in a frequency range of 0.1 Hz to 10 Hz.

Results and Discussion

The present work is devoted towards modification of MMT clay, investigation of degradation temperature of functionalised clays and epoxy composites, microstructure of functionalised clays and epoxy composites, and modulus of epoxy composites. A recinoloyl imidazole has been used to modify MMT clay. The imidazole functionalised MMT clay has been characterized using wide-angle X-ray scattering (WAXS) and thermogravimetric analysis (TGA) and its performance has been compared with commercially available Cloisite Na⁺, Cloisite 30B and Cloisite 20A clays. Cloisite Na⁺ is unfunctionalised MMT clay while Cloisite 30B and Cloisite 20A are natural MMT functionalised with quaternary ammonium salts. The structures of the modifiers are shown in **Figure 4**. Cloisite 30B was selected for comparison as its exfoliating performance in amine cured epoxy resin was shown to be better than that of Cloisite Na⁺, Cloisite 6A and Cloisite 25A [3, 19]. The different clays have also been dispersed in a standard epoxy resin to make epoxy composites. These composites have been characterized using TGA, differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA).

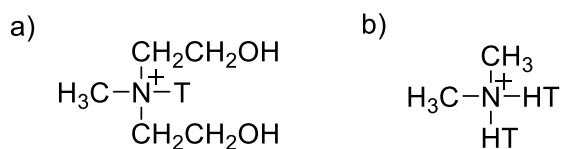


Figure 4 Chemical structure of alkyl ammonium modifiers used in commercial clays: (a) Cloisite 30B and (b) Cloisite 20A

Characterization of Nanoclays

The nanoclays (Cloisite Na⁺, Cloisite 30B and imidazole functionalised clay) were characterized using TGA and WAXS. Results of the TGA, in terms of weight loss with temperature, are shown in **Figure 5**. Cloisite Na⁺, shows a

very small weight loss which is expected as it does not have any organic modification. Interestingly imidazole functionalised clays (EN4 and EN5) show lower weight loss than the commercially available clays Cloisite 30B and Cloisite 20A upto 350 °C.

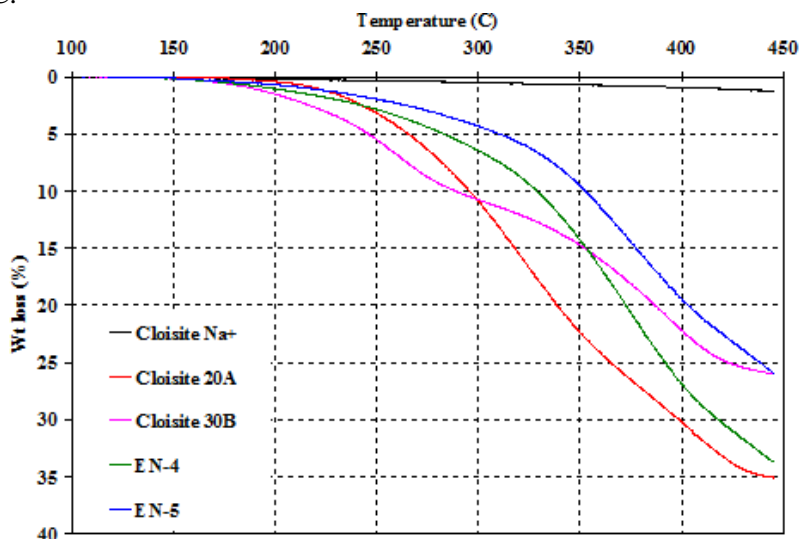


Figure 5 TGA of clays: weight loss with temperature

The rate of weight loss with temperature for the various nanoclays is shown in **Figure 6**. Cloisite 30B and Cloisite 20A undergo maximum degradation at a much lower temperature than the imidazole functionalized clays indicating that the alkyl ammonium modifiers used in the commercially available clays are more prone to thermal degradation than the imidazole modifier used in the current work.

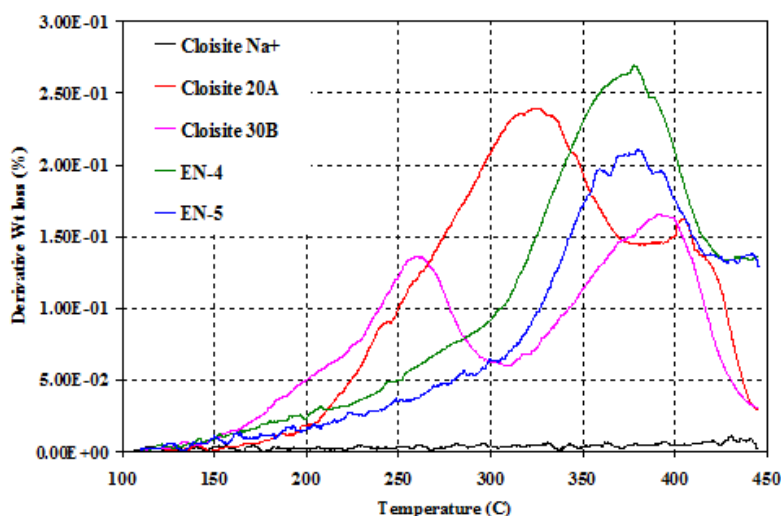


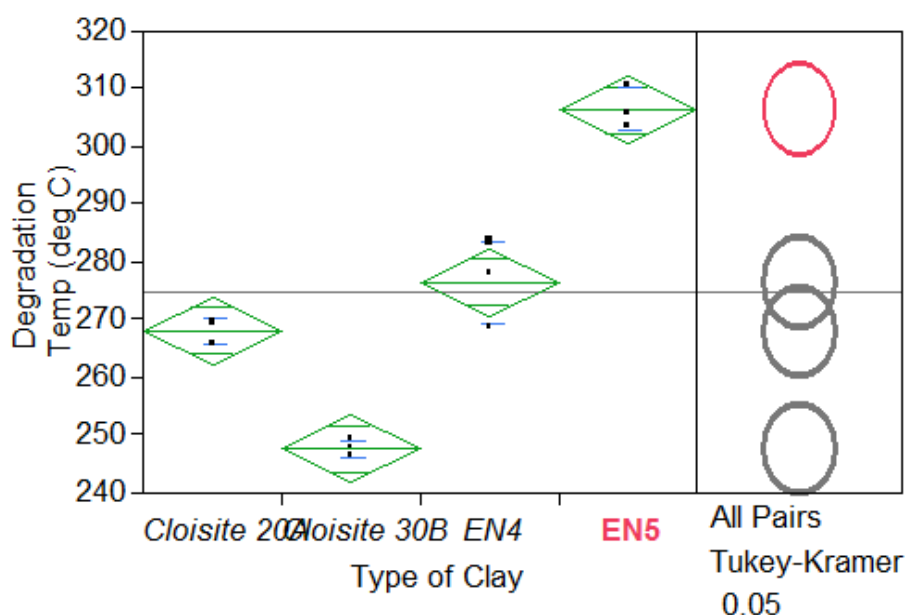
Figure 6 TGA of clays: rate of weight loss with temperature

The TGA data were also used to calculate the moisture content of the clays (**Table 1**). The unfunctionalised Cloisite Na⁺ has the highest moisture content indicating its high hydrophilicity. On organic modification of MMT clays, both commercially (using alkyl ammonium salts) and imidazole functionalized (EN4, EN5), the moisture content has decreased indicating that the clays have become less hydrophilic or more organophilic. The organically functionalized clays were also found to disperse well in organic solvents like acetone whereas the unfunctionalised Cloisite Na⁺ settled down in acetone.

Table 1 Moisture content of clays

Clay type	Moisture content (%)
Cloisite Na+	3.9
Cloisite 30B	1.2
Cloisite 20A	1.3
Imidazole functionalized clay EN4	1.1
Imidazole functionalized clay EN5	0.8

An important parameter that is measured from TGA thermograms is the temperature at 5 % weight loss ($Td_{5\%}$). This parameter was measured on three samples and a statistical analysis was performed using the all pairs Tukey-Kramer test to compare the various types of clay. Results from the Tukey-Kramer test are shown in **Figure 7** and **Table 2**. The test shows that $Td_{5\%}$ of imidazole functionalized clay, EN5 is statistically significantly higher than that of commercially available functionalized clays Cloisite 30B and Cloisite 20A.

**Figure 7** Tukey-Kramer test**Table 2** Tukey-Kramer test

Clay type	Level	$Td_{5\%}$ (°C)
Cloisite 30B	C	247.5
Cloisite 20A	B	267.9
Imidazole functionalized clay EN4	B	276.4
Imidazole functionalized clay EN5	A	306.3

The imidazole functionalized clays and commercially available clays were also characterized using wide angle X-ray scattering (WAXS). These data are summarized in **Table 3**. The experimentally measured d-spacings for the commercially available clays agree well with the reported d-spacings [20]. The d-spacings of all the organically functionalized clays are higher than that of the unfunctionalised Cloisite Na⁺ which is due to intercalation of the organic modifiers. The imidazole modifier has also intercalated the MMT clay as indicated by the increase in d-spacing in EN4 and EN5. Based on the TGA and WAXS data, EN5 was chosen for dispersion in epoxy resins to make nanocomposites.

Table 3 WAXS data on clays

Clay type	2 θ (°)	d-spacing (°A)	
		Measured	Datasheet
Cloisite Na ⁺	7.4	11.9	11.7
Cloisite 30B	5.0	17.7	18.5
Cloisite 20A	3.8	23.2	24.2
Imidazole functionalized clay EN4	5.1	17.4	----
Imidazole functionalized clay EN5	5.5	16.2	----

Characterization of Nanocomposites

Epoxy nanocomposite plaques were prepared by dispersing various types of clay at 5 parts per hundred (phr) loading in epoxy and curing using IPDA. **Figure 8** shows these plaques. These plaques are 2 to 2.5 mm thick. The unfilled epoxy is transparent and there has been a reduction in transparency on addition of clays. It is important to note that the epoxy containing 5 phr imidazole functionalized clay has higher transparency and lower haze than the epoxy containing 5 phr Cloisite Na⁺ and Cloisite 30B. This may be attributed to the better dispersion of the imidazole functionalized clays in epoxy than the commercially available clays which in turn indicates better interaction between the imidazole functionalized clays and epoxy resin. The higher interaction is expected to give higher mechanical properties in epoxy nanocomposites. Modulus measurements on these nanocomposites containing 5 phr clay, however, did not support this. The clay loading was therefore increased to 6.7 phr. **Figure 9** shows these plaques. These plaques are 3.5 to 4 mm thick and are therefore less transparent than those in Fig. 8. However, the epoxy nanocomposite containing 6.7 phr imidazole functionalized clay is still more transparent than those contains 6.7 phr Cloisite Na⁺ and Cloisite 30B supporting the observation of improved interaction between the imidazole functionalized clay and epoxy resin.



Figure 8 Epoxy nanocomposites with 5 phr clay

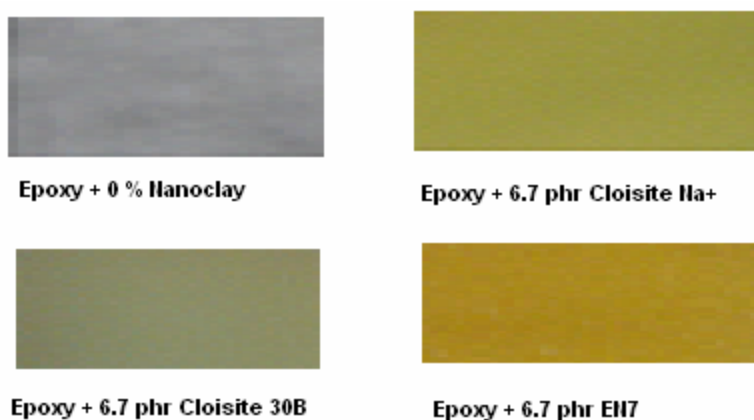


Figure 9 Epoxy nanocomposites with 6.7 phr clay

Results of modulus measurements using DMA on these nanocomposites containing 6.7 phr clay are shown in **Figure 10**. Composites were prepared using acetone to disperse the nanoclays in epoxy resin (acetone is removed before addition of the curing agent) and also without acetone by directly dispersing the nanoclays in epoxy resin. Acetone seems to play a dual role, on one hand, it improves nanoclay dispersion in epoxy (helps improve the modulus) while on the other hand, the residual acetone plasticizes the epoxy matrix (reduces the modulus). Results from the DMA (Fig. 10) show the higher storage modulus in epoxy containing 6.7 phr imidazole functionalized clay compared with unfilled epoxy and epoxy containing 6.7 phr Cloisite Na+ and Cloisite 30B. It is, however, surprising to see a drop in modulus in epoxy containing 6.7 phr Cloisite Na+ and Cloisite 30B compared with unfilled epoxy. This is plausibly due to plasticization of the epoxy matrix by the alkyl ammonium modifiers used commercially.

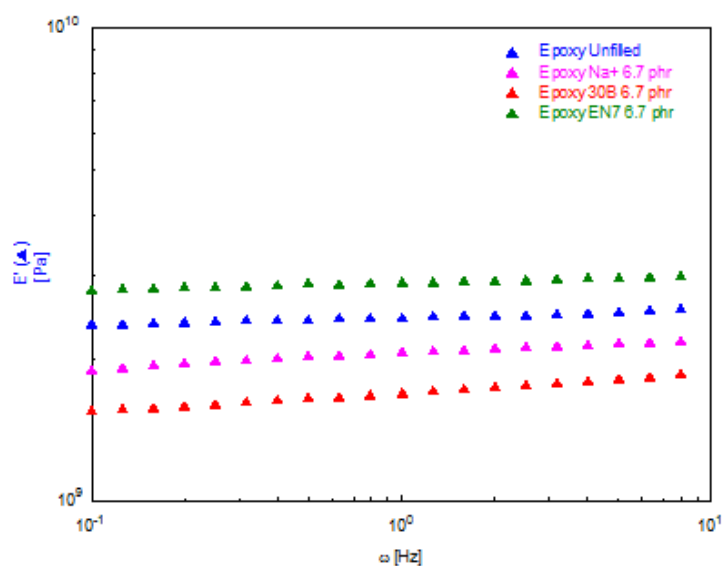


Figure 10 DMA of epoxy nanocomposites with 6.7 phr clay

A statistical analysis was performed using the all pairs Tukey-Kramer test to compare the storage moduli of epoxy nanocomposites containing 6.7 phr of various types of clay. These results are compiled in **Table 4**. The test shows that the storage modulus of epoxy nanocomposite containing 6.7 phr imidazole functionalized clay, EN7 is statistically significantly higher than that of unfilled epoxy and also epoxy containing 6.7 phr commercially available functionalized clays Cloisite Na+ and Cloisite 30B.

Table 4 Tukey-Kramer test

Nanocomposite	Level	Storage modulus (GPa)
Unfilled epoxy	B	2.5
Epoxy + Cloisite Na+	C	2.1
Epoxy + Cloisite 30B	D	1.7
Epoxy + Imidazole functionalized clay EN7	A	2.9

The thermal stability of epoxy nanocomposites was studied using TGA to explore if the improved thermal stability of imidazole functionalized clays translates into improved thermal stability for the epoxy nanocomposites. These data are compiled in **Table 5**.

Table 5 Thermal properties of epoxy nanocomposites

Nanocomposite	Clay loading (%)	Td _{5%} (°C)	T _g (°C)
Unfilled epoxy	0	301.7	153.7
Epoxy + Cloisite Na+	5.0	TBR	151.7
	6.7	TBR	
Epoxy + Cloisite 30B	5.0	289.3	152.4
	6.7	279.1	
Epoxy + Imidazole functionalized clay EN7	5.0	292.2	153.3
	6.7	286.7	

The Td_{5%} of unfilled epoxy and epoxy nanocomposites containing Cloisite Na+ are similar. This is expected as Cloisite Na+ does not have any organic modification. In nanocomposites using organically functionalized clays, however, there is a reduction in Td_{5%} compared with unfilled epoxy due to degradation of the organic functionalizers. The Td_{5%} of epoxy nanocomposites containing imidazole functionalized clays was found to be higher than that of epoxy nanocomposites containing commercially available functionalized clays which have alkyl ammonium functionalisers. The higher thermal stability of imidazole functionalized clays thus does translate into a higher thermal stability of epoxy nanocomposites.

The various nanocomposites were also characterized using WAXS. These data are compiled in **Table 6**. The d-spacings in epoxy nanocomposites are similar to those of clays reported in Table 3. This indicates that the intercalation in nanoclays is preserved even after composite preparation. The data also suggest that the clays are not exfoliated. It is reported in literature that in epoxy nanocomposites, a high degree of exfoliation is achieved only at low clay loadings and at higher loadings a mixed morphology (large intercalated areas with some exfoliated domains) is obtained [3].

Table 6 WAXS data on nanocomposites

Nanocomposites with 6.7 phr clay	2θ (°)	d-spacing (°A)
Epoxy + Cloisite Na+	6.6	13.3
Epoxy + Cloisite 30B	5.3	16.7
Epoxy + Imidazole functionalized clay EN7	6.0	14.9

Conclusions

MMT clay was functionalized using chloride salt of 2-ricinyl-1-hydroxy ethyl-4,5-dihydro imidazoline. The imidazole functionalized clay was found to have statistically significantly higher thermal stability than commercially

available alkyl ammonium functionalized clays. The imidazole modifier also intercalated MMT clays thereby widening the d-spacing between clay platelets. The clay also became more organophilic upon modification as evidenced by its improved dispersion in organic media, e.g., acetone.

Epoxy nanocomposites were prepared using the imidazole functionalized clay and commercial clays at 5 phr and 6.7 phr clay loading. The imidazole functionalized clay was found to have improved dispersion in epoxy as evidenced by the higher transparency of these plaques than that of the plaques of epoxy nanocomposites containing commercially available clays. The intercalation of clays by the imidazole modifier was preserved even in epoxy nanocomposites as evidenced by the d-spacing data on nanocomposites. The data, however, showed that the clays were not completely exfoliated. Comparison of the storage modulus of epoxy nanocomposites containing different types of clay using the Tukey-Kramer test established the statistically significantly higher storage modulus of epoxy nanocomposites containing 6.7 phr imidazole functionalized clay. The storage modulus of this composite was about 16 % higher than that of unfilled epoxy. Surprisingly, however, the alkyl ammonium functionalized clay containing epoxy nanocomposites showed a lower storage modulus than unfilled epoxy plausibly due to plasticization of epoxy matrix by the modifier. Analysis of the degradation behavior of epoxy nanocomposites showed the higher thermal stability of nanocomposites containing imidazole functionalized clays compared to that of nanocomposites containing commercially available clays.

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