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RESEARCH ARTICLE

Epoxy – clay nanocomposites – effect of curing temperature in mechanical properties

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Abstract

Diglycidyl ether of bisphenol – A (DGEBA) epoxy resin – clay nanocomposites was synthesized with diamino-diphenyl methane (DDM) curing agent. Nanocmposites were synthesized at different curing temperatures (60°C, 80°C, 100°C and 120°C), at various level of clay content in matrix (1–3% and 5%). The aim of this work is to study the effect of curing temperature on nanocomposite structure and properties. It is observed that property and structure of nanocomposites is governed by curing temperature and clay content in the matrix. Higher curing temperature shows increased mechanical properties over low temperature curing. Maximum increase in tensile properties is observed for 2 wt% nanoclay concentration irrespective of curing condition.

Keywords: Polymer – Clay Nanocomposites • Epoxy – Clay Nanocomposites • Nanoclay • Nanocomposites

Introduction

The reinforcement of inorganic clay minerals in organic polymers have attracted researchers in recent years due to the presence of silicate layers of clay with thickness 1mm. The dispersion of individual nano layer in polymer matrix exhibit improved performance properties when compared with conventional micro-scale filled composites, because of their unique phase morphology shown by layer intercalation or exfoliation. Toyota R & D group first synthesized the nylon-6/montmorillonite nanocomposites, and later the studies have been extended to other polymer/clay nanocomposites. These nanocomposites show improved mechanical (40% higher tensile strength, 68% higher tensile modulus, 60% higher flexure strength and 126% higher flexure modulus than pure nylon matrix polymer), thermal (HDT increase from 65°C to 152°C, decreased mass loss) and physical (barrier, optical) properties when compared with the respective polymer matrices [1–5].

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Thermoset epoxy system is unique polymeric materials with a wide range of physical and chemical properties. Wide range of monomer and curing agents are now commercially available and tailor-made properties can be obtained from the well designed combination of monomer materials and curing agents. Thermoset epoxy can be tailored to meet the highly diversified demands of modern technologies such as coatings, adhesives, laminates, electrical insulation etc [6–10]. Some researchers [11–15] have studied different types of epoxy and curing agents containing silicate layers and examined morphology, thermal, mechanical and physical properties. These composites have exhibited significant improvement in elasticity, barrier and thermal properties. It is reported that good exfoliated and intercalated structure can be achieved in epoxy-clay nanocomposite system. The reactants of epoxy systems have a suitable polarity to diffuse in to the clay layers and favour exfoliated or intercalated nanocomposite structure. The alkyl ammonium ions of organo clay that are present in the gallery region generate protons and attack the epoxy ring, causing acid catalysed ring opening homo-polymerization. The ammonium ions of organo clay polymerize the epoxy resin that are in the interlayer gallery region, and as the curing progresses further, the interlayer space is increased due to additional entry of polymer matrix in the gallery region. The uniform curing rate at inter-gallery (inter layer region of clay) and extra-gallery region (matrix) favours the exfoliated nanocomposite structure [16–20].

Although several types of amine curing agents are available in the literature, the study of curing of epoxy-clay system with diamino-diphenyl methane (DDM) is relatively unexplored. In this work, emphasis is given to study the structure and properties of epoxy-clay nanocomposites cured with DDM hardener. The influence of curing temperature on intercalation and exfoliation mechanism of these nanocomposites is studied. The synthesis of epoxy-clay nanocomposites with the addition of DDM curing agent is an important phenomenon to be considered as many composite structures, consisting of fibre [glass, kevlar, carbon etc] reinforced epoxy, are prepared and applied in many applications [21, 22]. Recent study shows that fibre reinforced polymer filled with nano layered clay, improves the matrix dominant properties attributed to 44, 24 and 23% improvement in interlaminar shear strength, flexural strength and fracture toughness in comparison to conventional S2-glass/epoxy composites [23]. The improvement of mechanical and thermal properties depends on the curing agent, curing rate and curing time. The present work is to study the structure and property of epoxy-clay nanocomposites by varying the curing temperature.

Experimental details

Materials

The matrix material used is DGEBA epoxy resin system and curing agent is diamino-diphenyl methane (DDM), both obtained from CIBA Ltd, Basel (Switzerland). The organoclay is alkyl ammonium modified montmorillonite clay (Garamite®-1958) obtained from Southern Clay Products Inc, Gonzales, Texas (USA).

Nanocomposite synthesis

Composites are cured in the closed mold "resin casting method". Two 35cm X 35cm square glass plates are used as moulds to fabricate composites. The 3 mm rubber gasket is used between the glass plates and fastened by pin clips. The rubber gasket covers the three sides of the mold and the remaining one side is used to pour the resin-clay mixture through the runner made in the mold. The mold releasing agent is applied at faces of glass plates and rubber gasket for easy removal of cast product. Wax is used as the mold releasing agent. Initially the epoxy resin (300g) was heated at 120°C for 1 hour. The clay with different weight concentrations [1 to 5%] was gently added in the resin bath and mixed by electrical driven shear mixer rotating at ~1000rpm, until uniform dispersion of clay was obtained. Then 25wt% of DDM hardener was added to the resin-clay mixture and then it was cast in the mold at different temperatures. After mixing, the solution in poured in the mold. Once it is done, the mold is kept in an oven for desired curing temperature [60°C, 80°C to 120°C]. A total of four different batches of nanocomposites were obtained by curing at different temperatures [60°C, 80°C, 100°C and 120°C]. The curing time was maintained four hours for all the specimens. The specimens synthesized by this method were subjected to different tests for characterization.

Characterization and property studies

X-ray diffraction study was performed on clay and nanocomposites with a scanning rate of 2°/min with CuKα radiation (λ = 1.541Å) operating at 30KV and 15mA. Thin specimens of 100–200nm were made using ultra-microtome and Transmission Electron Microscopy (TEM) studies were carried out on these specimens using Philip electron microscopy operating at 120KV. Tensile test was performed on the Instron machine (4301) with cross head speed of 1 mm/min according to the ASTM D638. Five samples were taken from each concentration of clay for testing and the results are averaged. It gives the tensile modulus, tensile strength of the ECN for different concentration of clay.

Results and discussion

Structure and Morphology of Nanocomposite

Figure 1 shows the XRD pattern of organo clay (OC). A reflection peak is noticed at 5.2° (2θ) and it corresponds to the interlayer distance of clay, 17Å. Fig. 2 shows the XRD pattern of epoxy filled with OC series cured at 120°C. It is observed that 001 basal reflection peak of OC is absent for clays up to 2%OC in epoxy polymer matrix. This suggests that the nanolayers are randomly oriented in polymer matrix leading to an exfoliated structure and hence the x-ray diffraction peak is absent, or the interlayer distance is more than 75Å (7.5nm) so that the Bragg's diffraction condition is not satisfied [10]. As the clay content further increases in the matrix (3% and more), XRD shows a sharp reflection peak and suggests that the intercalated nanocomposite structure has formed due to the parallel arrangement of clay nanolayers in stack. The sharp reflection peaks have occurred at 2.6° and 2.8° of 2θ values for 3%OC and 5%OC, and these correspond to interlayer spacing of 33.9Å (3.39nm) and 31.54Å (3.15nm) respectively. Table 1 illustrates the interlayer spacing of epoxy with different OC content that are cured at different temperatures. It is observed that nanocomposites, up to 2%OC, show complete exfoliated structure for all curing conditions. At higher clay content (>2%OC) the interlayer spacing is varies when nanocomposites are processed at different curing conditions. Epoxy with

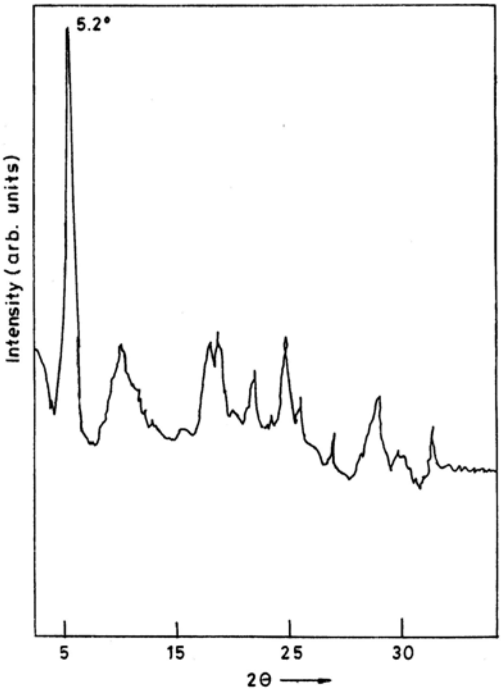

Fig. 1 XRD of organoclay

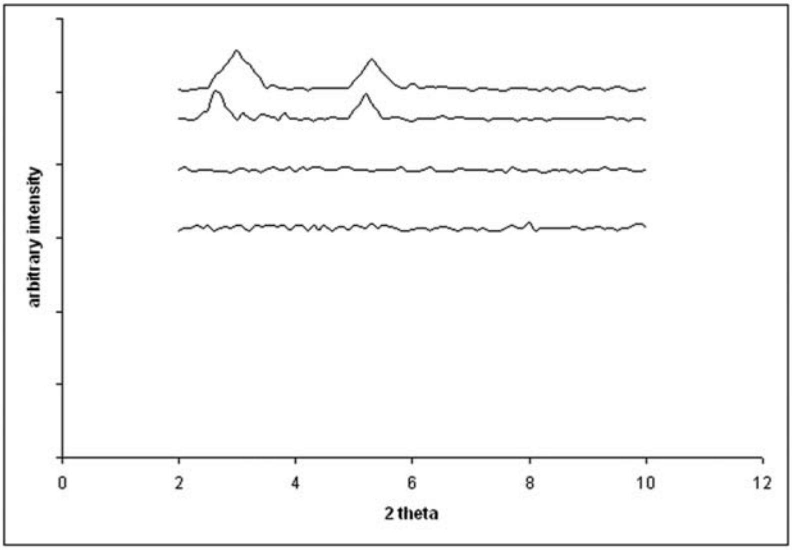

Fig. 2 XRD of epoxy with organoclay series

Table 1. Effect of curing temperature on clay interlayer spacing of nanocomposites

Material	Interlayer spacing (nm) of clay in matrix cured at 60°C	Interlayer spacing (nm) of clay in matrix cured at 80°C	Interlayer spacing (nm) of clay in matrix cured at 100°C	Interlayer spacing (nm) of clay in matrix cured at 120°C
E + 1% OC	>7.5	>7.5	>7.5	>7.5
E + 2% OC	>7.5	>7.5	>7.5	>7.5
E + 3% OC	2.49	2.51	2.79	3.39
E + 5% OC	2.28	2.33	2.66	3.15

3%OC and 5%OC cured at 60ºC, shows the interlayer distance of 2.49nm and 2.28nm respectively. These values are lesser than that cured at 120ºC for the same clay content. The nanocomposites (>2% OC) cured at 80ºC and 100ºC also show lesser interlayer spacing than that cured at 120ºC. This result shows that the curing temperature affects the nano structure morphology particularly for higher clay content (>2%OC).

Figure 3a shows the TEM of epoxy with 2%OC cured at 120ºC. It shows the presence of random arrangement of nanolayers (exfoliated structure) Fig. 3b shows the TEM of epoxy with 3%OC cured at 120ºC. It shows the regular arrangement of nanolayers (intercalated structure). From these results, it is further observed that the nanolayers of clays are better exfoliated in nanocomposites at low clay concentration (≤2 wt.%). TEM picture of the tested specimens also shows good interfacial bonding between the matrix and filler irrespective of the synthetic condition. If the interfacial strength is poor, then the particles will peel

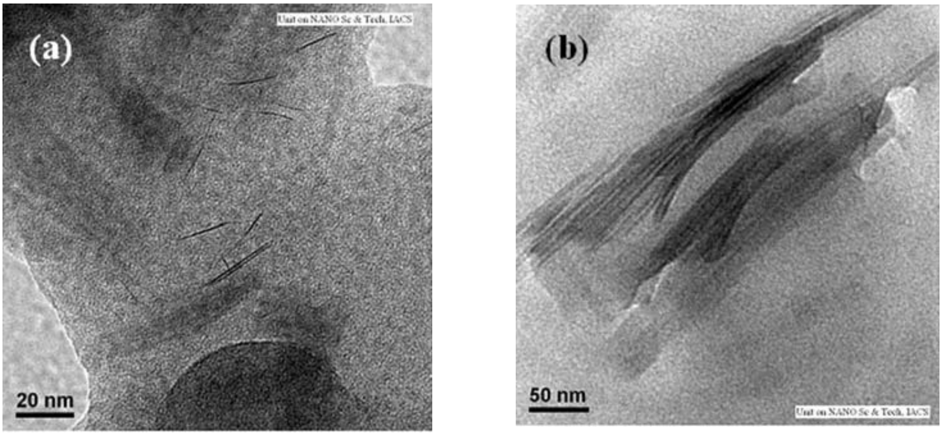

Fig. 3 TEM of epoxy with (a) 2% OC and (b) 3% OC

off from the material when sample preparation is made for TEM. TEM pictures do not show any such failure (22, 24–25).

Tensile properties

Figure 4 shows the tensile modulus as a function of OC content for specimens synthesized at different curing cycles. Tensile modulus of epoxy polymer continuously increases as curing temperature increases. The high temperature curing increases the cross-link

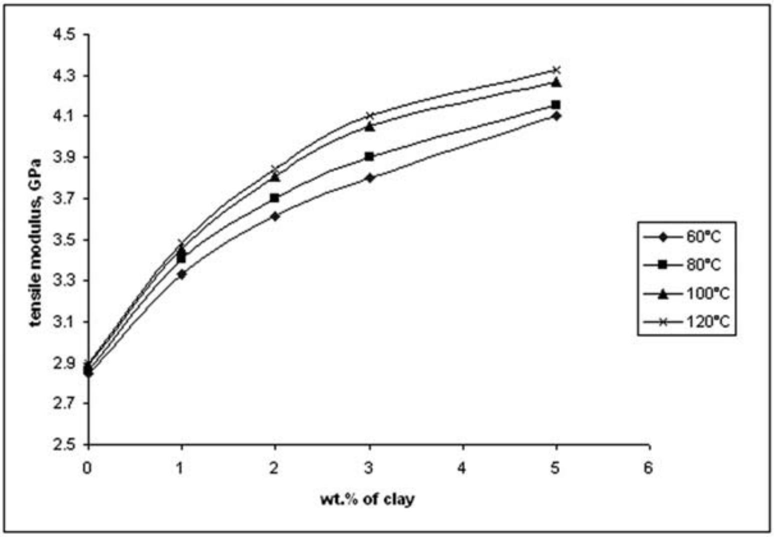

Fig. 4 Effect of clay addition on tensile modulus of epoxy polymer at different curing conditions

density and thereby increases the modulus for pure epoxy [7]. The addition of OC also increases the modulus of epoxy polymer for all curing temperatures. However, the rate of increase in modulus for epoxy-OC series cured at 120°C is higher than that of composites cured at other temperatures.

At higher clay concentration (> 2%), the rate of increase in modulus of nanocomposites has decreased due to the presence of un-exfoliated aggregates and agglomeration of clay particles (Table 2). In general, the properties of epoxy-clay nanocomposites are affected by the nature of curing nature of clay used, types of organo ions and synthetic procedures, clay content in matrix etc. [5, 7, 10, 22, 26, 27]. Fig. 5 shows the Tensile strength of composites for different OC content cured for different curing cycles. It is observed that there is a slight increase in strength of pure epoxy polymer as curing temperature is increased (Table 3). The addition of clay in epoxy polymer increases the strength for OC up to 2%, irrespective of the curing cycle. At low clay content the nanolayers of clays are relatively well separated and have increased the interfacial contact area with matrix polymer, thereby favouring good load transfer, unique phase morphology, etc. For higher clay content (3% and above), the strength decreases but higher than that of the matrix material. It is observed that good enhancement in strength is noticed for the composite series cured at 120°C than that cured at low temperatures. The study of fracture surface analysis also provides additional information for the increased strength in these materials.

Figure 6 shows the tensile fracture surface of the epoxy and epoxy-OC composites that are cured at 120°C. Fig. 6a shows that the fracture surface of pure epoxy polymer is smooth which is due to brittle failure. This indicates that the crack has propagated easily and causes low strength values. Fig. 6b shows

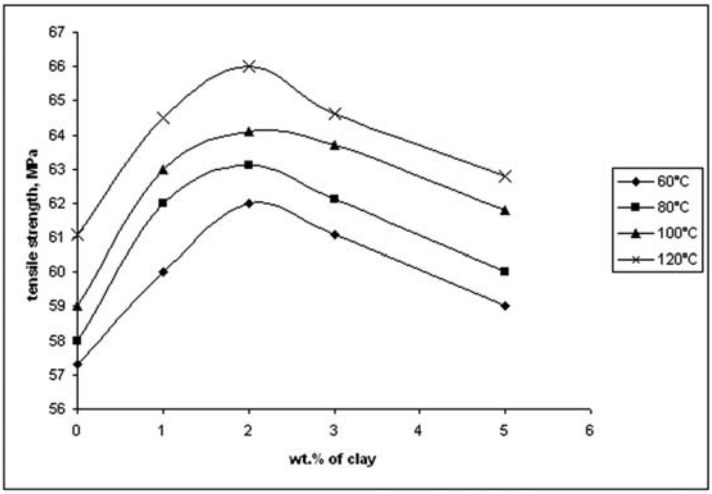

Fig. 5 Effect of clay addition on tensile strength of epoxy polymer at different curing conditions

Table 2. Tensile modulus of epoxy and its nanocomposites at different curing conditions

Material	Epoxy-clay series cured at 60°C			Epoxy-clay series cured at 80°C			Epoxy-clay series cured at 100°C			Epoxy-clay series cured at 120°C		
	Avg Modulus, GPa	STD DEV	% Change	Avg Modulus, GPa	STD DEV	% Change	Avg Modulus, GPa	STD DEV	% Change	Avg Modulus, GPa	STD DEV	% Change
Epoxy	2.85	0.04	-	2.86	0.03	-	2.89	0.02	-	2.90	0.06	-
E + 1% OC	3.33	0.21	16.8	3.40	0.19	18.8	3.45	0.18	19.3	3.48	0.21	20.0
E + 2% OC	3.61	0.23	26.6	3.70	0.20	29.3	3.81	0.24	31.8	3.84	0.28	32.4
E + 3% OC	3.80	0.38	33.3	3.90	0.32	36.3	4.05	0.39	40.1	4.10	0.41	41.3
E + 5% OC	4.10	0.41	43.8	4.15	0.42	45.1	4.27	0.44	47.7	4.33	0.44	49.3

Table 3. Tensile strength of epoxy and its nanocomposites at different curing conditions

M/1	Epoxy-clay series cured at 60°C			Epoxy-clay series cured at 80°C			Epoxy-clay series cured at 100°C			Epoxy-clay series cured at 120°C		
	Avg strength, MPa	STD DEV	% Change	Avg strength, MPa	STD DEV	% Change	Avg strength, MPa	STD DEV	% Change	Avg strength, MPa	STD DEV	% Change
Epoxy	57.3	4.3	-	58.0	4.4	-	59.0	4.1	-	61.1	4.0	-
E + 1% OC	60.0	5.5	4.7	62.0	5.7	6.8	63.0	5.1	6.7	64.5	4.7	5.5
E + 2% OC	62.0	5.7	8.2	63.1	4.9	8.7	64.1	5.8	8.6	66.0	4.9	8.0
E + 3% OC	61.1	5.4	6.6	62.1	5.6	7.0	63.7	6.0	7.9	64.6	5.7	5.8
E + 5% OC	59.0	4.8	2.9	60.0	4.6	3.4	61.8	7.0	4.7	62.8	6.1	2.7

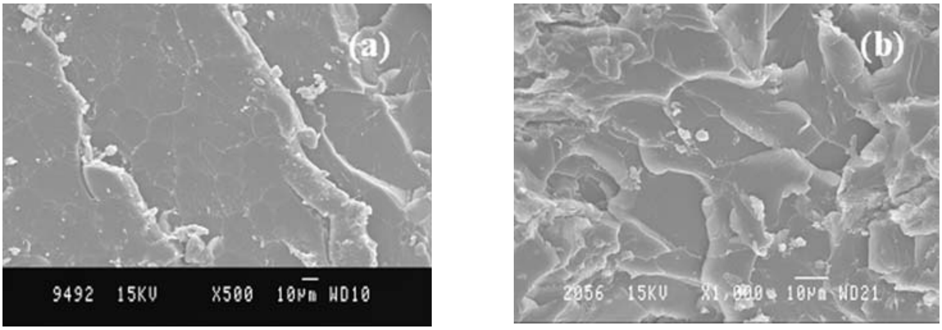

Fig. 6 Tensile fracture surface of (a) neat epoxy and (b) E + 3% OC cured at 120°C

the fracture surface of epoxy-2%OC in which the morphology of crack surface is different from neat epoxy matrix. The crack surface has become rough, which suggests that the crack has taken torturous path to failure. This shows that crack has struggled to propagate under the applied loading conditions and in turn increases the strength to failure [28].

Conclusion

Epoxy-layered silicate nanocomposites based on DGEBA resin system cured with diaminodiphenyl methane (DDM) have been synthesized using alkyl ammonium modified montmorillonite clay. Nancomposites were synthesized at various temperatures ranging from 60°C to 120°C. It is observed that the composites structure, morphology and properties are largely governed by curing temperature and clay concentration. Among the different curing conditions adapted, specimens cured at 120°C show good improvement in nano clay interlayer d-spacing than that cured at other lower temperatures (<120°). It is also observed that the nanocomposite properties are dependent on clay concentrations. Clays of (>2% in matix) tends to decrease the tensile properties due to agglomerations. Maximum increase in tensile properties is observed at 2–3% OC loadings irrespective of curing conditions.

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