

Effects of Nanoclay on the Properties of Cardanol-Modified-Resol-Epoxy-Novolac Composite Material

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ABSTRACT: A nanocomposite based on nanoclay and resol that was modified with cardanol, a natural alkyl phenol, shows improvement for the glass-fiber-reinforced epoxy-composite system. Dispersion of the nanocomposite was investigated by X-ray, showing good results obtained by the *in situ* polymerization method. The mechanical properties of the final composites were improved by doping a 6 wt% of nanoclay in cardanol-modified-resol (CMR) into the epoxy matrix. The results show that a 15 wt% of CMR in epoxy is a most suitable ratio. Using polyamide as

a curing agent instead of other traditional systems, such as anhydrides or amines for epoxy resin, overcame important limitations, further allowing for improved processability. The overall composite performance was enhanced. Additionally, the thermal stability of the system was investigated by thermal gravimetric analysis. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 3238–3242, 2007

Key words: polymer-matrix composites; particle-reinforcement; resins; nanoclay

INTRODUCTION

Epoxy resins are routinely used as adhesives, coatings, encapsulate, casting materials, potting compounds, and binders. Some of their most interesting applications are found in the aerospace and recreational industries, where resins and fibers are combined to produce complex composite structures.

Glass-fiber-reinforced composite based on epoxy-novolac resin is of great interest because of its low cost and wide applications, especially in the car, ship, aviation, and sporting industries. Epoxy resins, once cured, are thermoset polymers and tend to be both stiff and brittle and require some degree of modification to achieve acceptable physical properties in the processed resin.

Epoxy-novolac resin has good mechanical properties and heat resistance,¹ but it also has several drawbacks. Epoxy-novolac has difficulties in wetting the fiber surface due to its high viscosity; therefore, processing composite materials is not applicable in large-scale productions. As a result of low interfacial bindings between resin and fibers its composites have low mechanical properties and tend to be brittle after curing. Improving the flexibility as well as performance properties was the aim of this study.

In the system studied, polyamide was used as a curing agent² and reactive diluent for the epoxy-novolac resin, which reduces the polymer viscosity, consequently improving the wetting and therefore performance properties. This specific curing agent may also impart toughness and flexibility to the cured epoxy resin. However, it has an unwanted side effect by lowering thermal stability. Finding a balance of these properties for a specific application was the goal of the study. To address this problem, the approach of using nanocomposites based on clay and resol modified with cardanol to increase thermal stability and flexibility was developed. Resol, which is known for high thermal stability and good mechanical properties, is synthesized from phenol and formaldehyde. Cardanol extracted from cashew nut shell liquid is a natural alkyl phenol with a C₁₅ unsaturated sidechain.³ The presence of cardanol with the long alkyl sidechain in cardanol-resol can improve the flexibility of the brittle matrix.⁴ Adding nanoscale fillers into the polymer to enhance the overall performance and thermal stability shows perspective. Polymer-clay-nanocomposites are a class of composite materials in which clay as a layered silicate is dispersed on a nanoscale in a polymer matrix. The resulting materials can exhibit significantly improved properties.^{5,6}

Based on this property, we investigated the influence of nanoclay on the properties of epoxy-novolac utilizing clay-modified-resol (CMR) and its influence on the mechanical properties of glass-fiber-reinforced

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composites. Various methods to prepare polymer-clay nanocomposites have been developed by several groups.^{7–10} In our study the *in situ* method was used to prepare the nanocomposites. One of the goals was to understand the parameters allowing homogeneous dispersion of clay in the polymer matrix without agglomeration. This was studied by X-ray.

Consequently, the nanocomposite is expected to overcome the above-mentioned limitations for fiber-reinforced composite applications based on epoxy-novolac.

EXPERIMENTAL

Materials

Epoxy-novolac resin DEN438 was supplied by Dow Chemical (Midland, MI) with an epoxide equivalent of 176–181 g/eq. Nanoclay Cloisite 15A was supplied by Southern Clay Products (Gonzales, TX). Cloisite 15A is a natural montmorillonite modified with a quaternary ammonium salt. It contains dimethyl dehydrogenated tallow ammonium as an organic modifier. Hydrogenated tallow is composed of C18 of 65 wt %, C16 of 30 wt %, and C14 of 5 wt %.

Phenol and formaldehyde was supplied by Fluka (Buchs, Switzerland). Cardanol was obtained by direct vacuum distillation at 5–6 mbar and 190–210°C under nitrogen from cashew nut shell liquid (Tai Loi, Vietnam). The curing agent Versamid 125 polyamide (Henkel, Dusseldorf, Germany) was used at a ratio of 50 wt % compared to epoxy-novolac. Glass fiber mats (CS-Interglas, Germany) were used for manufacturing the glass-fiber-reinforced polymer composites.

Preparation of CMR nanocomposite by the *in situ* method

Resol, a phenol-cardanol-formaldehyde resin type, was prepared as published previously¹¹ using a 1 mol mixture of phenol and cardanol with a phenol/cardanol ratio of 9 : 1 by weight and 1.2 mol of formaldehyde in the presence of 25 wt % ammonia as catalyst at 50–60°C for 3 h. During the methylol generation process, nanoclay Cloisite 15A was slowly added in several amounts of 6, 10, 16, and 20% by weight and mixed well. CMR was used as obtained.

Composite fabrication

CMR was mixed with the polyamide at a speed of 8000 rpm for 6 h at room temperature. Then the mixture of CMR and polyamide was mixed with epoxy resin for 5–10 min at room temperature using CMR/epoxy ratios of 5, 10, 15, and 20% by weight. Then the glass fiber mat was wetted with the resin-mixtures at a resin/fiber weight ratio of 6 : 4. After that a pressure of 200 kg/cm² was applied on the samples

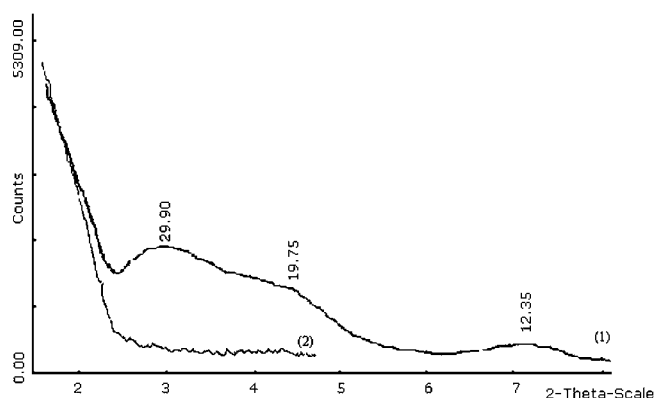


Figure 1 XRD patterns for the pristine Cloisite 15A (curve 1) and for CMR with 6 wt % of clay (curve 2).

at room temperature for 4 h. The mechanical properties of the composite samples were measured after postcure for 12 h at 60–70°C.

Measurements

The dispersion quality was measured using X-ray diffraction (XRD) to investigate the intercalated structure. In such nanocomposites the repetitive multilayer is well preserved, allowing the interlayer spacing to be determined. The intercalation of the polymer chains usually increases the interlayer spacing in comparison to the spacing of the pristine organoclay, leading to a shift of the diffraction peak toward lower angle values. CMR samples were scanned at a rate of 0.05°/min with a Shimadzu XD-5 X-ray diffractometer (XRD; 30 kV, 0.01A) with copper target and $\lambda = 1.55414 \text{ \AA}$.

Dynamic mechanical thermal analysis (DMTA) of the cured CMR/epoxy nanocomposite samples was performed on a Rheometric Scientific DMTA-V (New Castle, DE). Glass transition temperatures of films in a bending mode at a frequency of 0.2 Hz and strain level of 1 were determined using the DMTA with a heating rate of 5°C/min in the temperature range of 30–150°C.

Tensile and flexural properties of the glass fiber composites were measured by LLOYD-LR 30 K (UK) using the ASTM D3039-76 and D790-71, respectively.

Thermal gravimetric analysis (TGA) measurements were performed using a Netzsch TG 209 (Germany) with a heating rate of 10°C/min in nitrogen at 100–900°C.

RESULTS AND DISCUSSION

Structure by X-ray diffraction

The diffraction patterns of the pristine Cloisite 15A are shown in Figure 1 (curve 1) and the CMR prepared by the *in situ* method containing 6 wt% of nanoclay (curve 2). The Cloisite 15A shows a peak at

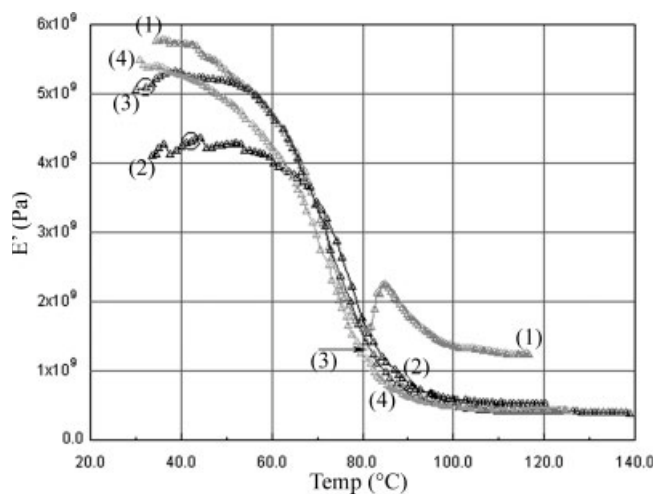


Figure 2 Storage modulus, E' [Pa], of the cured nanocomposites with different loadings of CMR at fixed 10 wt % of clay: (1) 5 wt %, (2) 10 wt %, (3) 15 wt %, and (4) 20 wt % CMR in epoxy resin.

$2\Theta = 3^\circ$ corresponds to a d_{001} layer spacing of 29.9 \AA [Fig. 1(curve 2)]. The X-ray diffractogram of CMR shows no more diffraction peak (curve 2), indicating an exfoliated structure of montmorillonite in the polymer matrix. This can be explained by a too-large layer spacing of the nanocomposite or because it does not appear to be ordered any longer. When the silicate layers are completely and uniformly dispersed in the continuous polymer matrix, an exfoliated or delaminated structure is obtained. Therefore, we conclude that the intercalation of nanoclay in the resol was successful.

Dynamic mechanical analysis of CMR/epoxy nanocomposite

Figure 2 shows the storage modulus, E' , of CMR/epoxy against temperature with various CMR contents

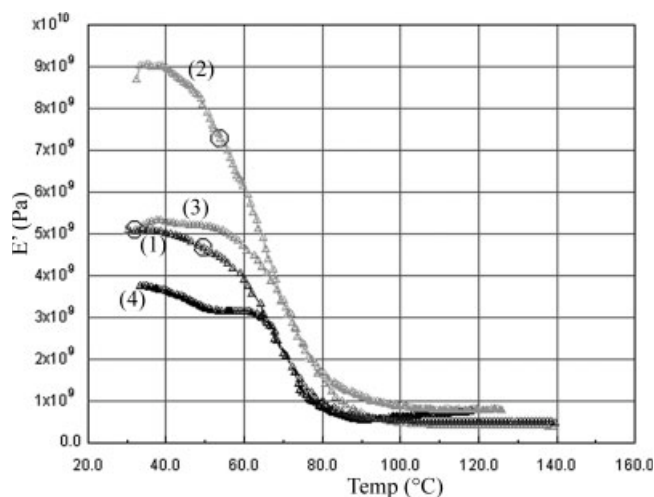


Figure 3 Storage modulus, E' [Pa], of CMR/epoxy nanocomposite at 15 wt% CMR at various clay contents: 0, 6, 10, 16 wt% (curves 1, 2, 3, 4 respectively).

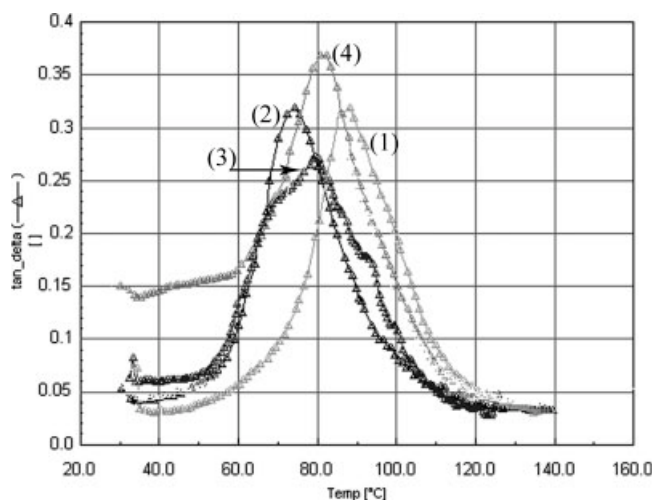


Figure 4 $\tan \delta$ of the cured CMR/epoxy nanocomposites of different clay loadings at 15 wt % CMR: (1) 0 wt % CMR in epoxy (EN 0Re-0); (2) 0 wt% clay in CMR (EN 15Re-0); (3) 6 wt % clay in CMR (EN 15Re-6); (4) 10 wt % clay in CMR (EN 15Re-10).

(5, 10, 15, 20 wt %) at a chosen content of 10 wt % of clay in CMR (termed EN 5Re-10, EN 10Re-10, EN 15Re-10, and EN 20Re-10).

The E' at 5 wt % CMR loading has the highest initial storage (curve 1). But at 85°C one peak appears that can be explained by the lowest content of CMR, resulting in a less closely cured structure. Increasing the CMR content from 10 to 20 wt % improved the initial storage modulus (E') at room temperature. The storage modulus remained nearly constant up to 50°C in the case of 10 and 15 wt % CMR loading (curves 2, 3). This is not the case for 20 wt % loading of CMR. Therefore, 15 wt % CMR loading results in a high and stable storage modulus. This value was chosen for further investigation of the clay content effect in CMR on its nanocomposites.

In Figure 3 the storage modulus E' of CMR/epoxy nanocomposite at 15 wt % CMR with various clay contents (0, 6, 10, 16 wt %) is plotted as a function of temperature. An increase in the storage modulus is observed in the nanocomposite system when adding 6–10 wt % of nanoclay, because the clay plays the role of nanoscale reinforcement in the epoxy matrix, improving its mechanical properties. The highest storage modulus was observed at 6 wt % clay. Over 6 wt % loading the storage modulus tends to decrease. At 16 wt % clay the storage modulus decreases significantly and is even lower than that of CMR without clay. This fact can be explained by the curing quality of the polymer system, a low cross-linking density that was caused by the filler overload. Therefore, loading 6 wt % of clay to the CMR gave the optimum value for the investigated system.

Figure 4 shows $\tan \delta$ of the cured CMR/epoxy nanocomposites with 0, 6, and 10 wt % of clay as

TABLE I
Influence of Clay Content on Glass Transition Temperature (T_g)

No.	Sample	T_g ($^{\circ}\text{C}$)
1	EN 0Re-0	88
2	EN 15Re-0	74
3	EN 15Re-6	80
4	EN 15Re-10	82

well as of virgin epoxy. When a load was applied to the sample the storage modulus E' and loss modulus E'' were measured by DMTA. The ratio E''/E' is defined as $\tan\delta$ which is taken as the glass transition temperature, T_g , at its peak point.

The T_g of the samples (Table I) shifted to lower temperatures from unfilled epoxy (EN 5Re-0) to filled epoxy (EN 15Re-0). The T_g of CMR/epoxy nanocomposites was elevated at an increasing clay content (curves 2, 3, 4), but in all cases still lower than the T_g of virgin epoxy resin. That is the consequence of the presence of flexible cardanol-resol in the system. A loading 15 wt % of CMR increased the flexibility of the system, and therefore the T_g decreased.

Mechanical properties of glass-fiber composites based on CMR/epoxy nanocomposites

Nanocomposites consisting of polymer and nanoclay frequently exhibit improved material properties compared to those of pristine polymer. Here we report on the tensile and flexural properties of glass-fiber-reinforced composite based on CMR/epoxy nanocomposites.

Table II shows the influence of various CMR contents (5, 10, 15, 20 wt %) on the mechanical properties of the composites. The 10 wt % of clay in CMR was chosen (also for comparing with the DMTA results in Fig. 2) for all samples EN 5Re-10, EN 10Re-10, EN 15Re-10, and EN 20Re-10. The mechanical properties of the composites were greatly affected by the nature of the resin. Loading 5–15 wt % CMR

TABLE II
Influence of CMR Content in Epoxy on the Mechanical Properties of Glass-Fiber Composites

Sample	Tensile		Flexible	
	δ_t (N/mm^2)	E_t (N/mm^2)	δ_f (N/mm^2)	E_f (N/mm^2)
EN 5Re-10	133.2	2250.0	220.8	12,376.7
EN 10Re-10	134.9	2086.7	185.2	9968.2
EN 15Re-10	161.2	1441.5	200.6	11,650
EN 20Re-10	144.4	1772.2	257.8	13,470

δ_t and δ_f , tensile and flexible strength.
 E_t and E_f , tensile and flexible modulus.

TABLE III
Influence of Clay Content in CMR on the Mechanical Properties of Glass-Fiber Composites

Sample	Tensile		Flexible	
	δ_t (N/mm^2)	E_t (N/mm^2)	δ_f (N/mm^2)	E_f (N/mm^2)
EN 15Re-0	143.6	1490.7	217.6	9667.0
EN 15Re-6	166.1	1562.4	249.5	14,515.0
EN 15Re-10	161.2	1441.5	200.5	11,650.0
EN 15Re-16	149.3	1512.0	209.9	10,642.5

exhibited an increase in tensile strength and showed a peak at 15 wt % (EN 15Re-10), while its flexible strength remained near the maximum value obtained from 20 wt % CMR (EN 20Re-10). Both mechanical properties increased with the addition of CMR from 5 to 15 wt % (EN 5Re-10 to EN 15Re-10). This may be due to the fact that the presence of the long alkyl chain of cardanol in CMR improved the flexibility as well as the fracture toughness of the rigid epoxy matrix; therefore, the tensile strength increased. The 15 wt % of CMR in CMR/epoxy nanocomposite can be considered the best choice for the mechanical properties of the fiber-reinforced composite, providing good crosslinking density, high tensile strength (Table II), and improved flexibility.

Based on the above results, 15 wt % of CMR in epoxy was chosen for investigating the effects of nanoclay in CMR on the mechanical properties of the final glass-fiber composites. Table III shows the results of mechanical properties of glass-fiber composites at various clay contents (0, 6, 10, and 16 wt %) in CMR itself at 15 wt % in the epoxy.

With the *in situ* method the results show that increasing the clay content from 0 to 10 wt % (sam-

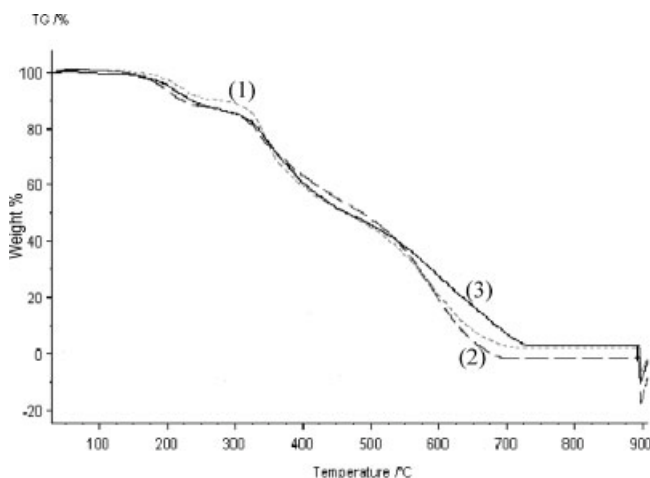


Figure 5 Thermal analysis of pure epoxy resin (1) and of epoxy modified with 15 wt % of CMR containing 0 wt % (2) and 6 wt % (3) of clay.

TABLE IV
TGA Results of the CMR/Epoxy Nanocomposite

No.	Sample	T _{onset}	T ₅ (°C)	T ₁₀ (°C)	T ₁₅ (°C)	T ₂₀ (°C)	T ₃₀ (°C)	T ₅₀ (°C)
1	EN 0Re-0	186	217.9	282.8	325.9	338.6	358.6	464.3
2	EN 15Re-0	162.7	192.1	222.9	305.0	329.6	368.4	487.2
3	EN 15Re-6	179.0	203.4	237.0	304.8	342	365.5	466.2

ples EN 15Re-0 and EN 15Re-10) causes improved tensile strength while the flexibility decreased only slightly (Table III). The main reason for the tensile gain is the stronger interfacial interaction between matrix and layered silicate compared to conventional filler-reinforced systems. The nanocomposites exhibit higher stiffness (confirmed by the DMTA). The presence of nanoclay limits the mobility of polymer chains, including the long alkyl sidechains of cardanol; therefore, the flexibility of the composite decreased (confirmed by T_g measurements, see Table I). The results show the maximum tensile and flexible strength of the glass-fiber composites was obtained with 6 wt % clay in CMR. This was also confirmed by DMTA measurements (see Fig. 3).

Thermal stability of CMR/epoxy nanocomposites

Figure 5 shows the TGA results for pure cured epoxy (EN 0Re-0), and for epoxy with 15 wt % of CMR containing 0 and 6 wt % of nanoclay EN 15Re-0, EN 15Re-6, respectively. Table IV shows onset and decomposition temperatures at 5, 10, 15, 20, 30, and 50% of weight loss (T_{onset}, T₅, T₁₀, T₁₅, T₂₀, T₃₀, T₅₀) of the three above samples (EN 0Re-0, EN 15Re-0, EN 15Re-6). The results indicate that loading CMR into the system reduces its thermal stability because the long alkyl side chains of cadanol have low thermal stability (EN 15Re-0). The presence of nanoclay compensates for this problem (EN 15Re-6). Hence, the overall thermal stability of the CMR/epoxy nanocomposite reduced slightly in comparison to the pure epoxy, while its mechanical properties increased remarkably.

CONCLUSION

Doping nanoclay by the *in situ* method while synthesizing phenol-cardanol-formaldehyde allows good dispersion of nanoclay in the final polymer matrix, enhancing the composite materials overall performance. Using polyamide as a curing agent and CMR (nanoclay/phenol-cardanol-formaldehyde nanocomposite) overcame important limitations, further allowing for improved processability. The results show that the best mechanical properties were obtained with 15 wt % CMR (at 6 wt % clay) used to modify epoxy-novolac; the flexibility of the composites especially improved, while the thermal stability was maintained as in the pristine epoxy resin.

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