

# Synthesis and Characterization of Epoxy Based Nanocomposites

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**ABSTRACT:** Epoxy-clay nanocomposites were synthesized to examine the effects of the content and type of different clays on the structure and mechanical properties of the nanocomposites. Diglycidyl ether of bisphenol-A (epoxy) was reinforced by 0.5–11 wt % natural (Cloisite Na<sup>+</sup>) and organically modified (Cloisite 30B) types of montmorillonite. SEM results showed that as the clay content increased, larger agglomerates of clay were present. Nanocomposites with Cloisite 30B exhibited better dispersion and a lower degree of agglomeration than nanocomposites with Cloisite Na<sup>+</sup>. X-ray results indicated that in nanocomposites with 3 wt % Cloisite 30B, *d*-spacing expanded from 18.4 Å (the initial value of the pure clay) to 38.2 Å. The glass

transition temperature increased from 73°C, in the unfilled epoxy resin, to 83.5°C in the nanocomposite with 9 wt % Cloisite 30B. The tensile strength exhibited a maximum at 1 wt % modified clay loading. Addition of 0.5 wt % organically modified clay improved the impact strength of the epoxy resin by 137%; in contrast, addition of 0.5 wt % unmodified clay improved the impact strength by 72%. Tensile modulus increased with increasing clay loading in both types of nanocomposites. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1081–1086, 2005

**Key words:** epoxy resin; mechanical and thermal properties; montmorillonite; nanocomposite

## INTRODUCTION

The major problems with polymers in engineering applications are the low stiffness and strength when compared with metals. To offset these deficiencies, reinforced particles or fibers may be added to the resin.<sup>1</sup> Layered silicates, such as montmorillonite (MMT), are increasingly being used as reinforcement in polymer systems owing to their high aspect ratio and platy morphology.<sup>2,3</sup> Clay particles have large specific surface area and exhibit strong interactions with the matrix. Since the space between the layers of the silicates is in the nanometer range, new materials composed of a polymer matrix and layered silicates are called nanocomposites.<sup>4</sup> Nanocomposites display markedly improved mechanical, thermal, optical, and physicochemical properties when compared with conventional composites and neat polymers.<sup>5</sup> Initial research on nanocomposites was performed by the Toyota group,<sup>6</sup> utilizing nylon-6 as the matrix. Since the 1980s, the structure and properties of nanocomposites have been investigated by many researchers.<sup>7–12</sup>

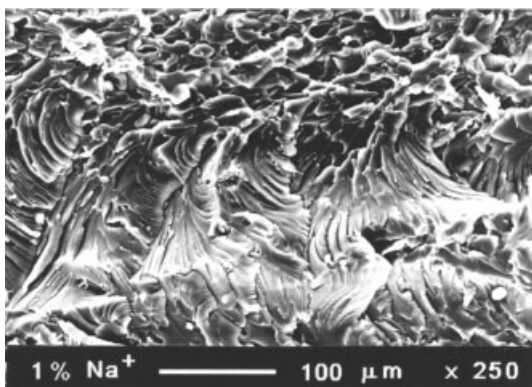
The three basic methods to synthesize polymer-clay nanocomposites are melt intercalation, the solution approach, and *in situ* polymerization. *In situ* polymer-

ization is a convenient method for thermoset-clay nanocomposites.<sup>7</sup> In this method, first organoclay is swollen in the monomer, then a curing agent is added and nanocomposites are formed.<sup>8</sup> In the present study, the *in situ* polymerization method is used since the polymer matrix is an epoxy resin.

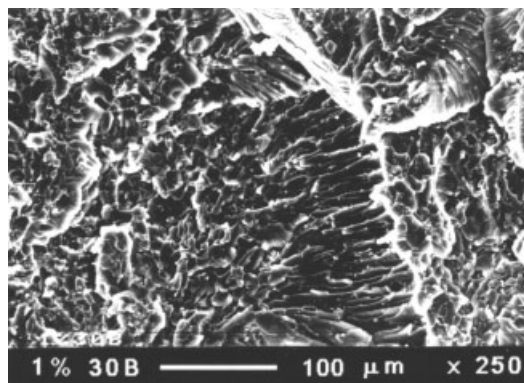
Pinnavaia and coworkers<sup>9</sup> synthesized epoxy-clay nanocomposites. By using different curing agents, both glassy and rubbery epoxy matrices were obtained. The mechanical reinforcement provided by the exfoliated clay layers was found much more significant with the rubbery matrix than the glassy matrix. Kornmann and colleagues<sup>8</sup> studied the influence of the nature of the curing agent on the structure of epoxy-clay nanocomposite systems. It was found that the curing agent has a major effect on the synthesis of exfoliated nanocomposites. Tolle and Anderson<sup>10</sup> studied the role of processing temperature on the morphology development of organically modified montmorillonite-epoxy nanocomposites. A higher degree of exfoliation was observed at higher temperatures. Zerda and Lesser<sup>11</sup> studied intercalated clay nanocomposites and examined the morphology, mechanics, and fracture behavior. They observed that the fracture toughness of intercalated nanocomposites with modified MMT was improved by 200% over the unmodified resin.

In the present study, the aim is to synthesize new nanocomposite materials composed of epoxy resin as the matrix and natural or organically modified clay

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**Figure 1** SEM micrograph of the fracture surface of the nanocomposite with 1 wt % Cloisite Na<sup>+</sup>.



**Figure 2** SEM micrograph of the fracture surface of the nanocomposite with 1 wt % Cloisite 30B.

MMT as the filler, to examine the effects of content and type of clay on the mechanical and thermal properties and structure of the nanocomposites.

## EXPERIMENTAL

### Materials

Natural Na-Montmorillonite (Na-MMT, Cloisite Na<sup>+</sup>) and organically treated MMT (Cloisite 30B) from Southern Clay Products, Texas, were used as the fillers. Cloisite 30B is clay treated organically by methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium chloride (MT2EtOH) by the manufacturer. The epoxy resin, diglycidyl ether of bisphenol A (DGEBA, Araldite M), and the aliphatic amine curing agent, triethylenetetramine (TETA, HY 956), were purchased from Vantico Chemical Products.

### Preparation of nanocomposites

The epoxy resin was mixed mechanically in a reaction kettle with the desired amount (0.5, 1, 3, 5, 7, 9, or 11 wt %) of clay at 50°C for 2 h. Then, it was further mixed in an ultrasonic bath for 20 min to disperse the clay in the resin. Later, the mixture was degassed by a vacuum pump to remove the air bubbles and cooled to room temperature in 30 min. Then, a stoichiometric amount of the curing agent (curing agent to epoxy resin ratio was 1 : 5 by wt) was added. After mixing mechanically for 10 min, the mixture was degassed again and poured into aluminum molds. The composites were cured for 16 h at 75°C and postcured for 3 h at 130°C.

### Characterization

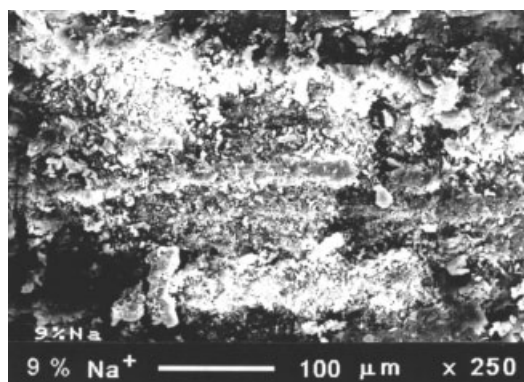
Impact fractured surfaces were investigated at various magnifications by using a JEOL JSM-6400 Scanning Electron Microscope (SEM). X-Ray diffraction patterns

of powdered samples were recorded by monitoring the diffraction angle  $2\theta$  from 1° to 10° on a Rigaku Miniflex Diffractometer using CuK<sub>α</sub> radiation (40kV, 30 mA). The scanning speed and the step size were 5°/min and 0.02°, respectively. DSC analyses were performed by using a 910 S Dupont-TA instrument. The measurements were carried out, from 20 to 220°C with 20°C/min heating rate, under nitrogen atmosphere. A Bandelin Sonorex RK 100 H Ultrasonic Bath was used for ultrasonic mixing at a frequency of 35 kHz. Tensile tests were performed by using a Lloyd 30K Universal Testing Machine according to ASTM D638M-91a standard. Samples were M-II type. The extension rate was 5 mm/min. The pendulum impact tester of Coesfeld Material Testing was used for the Charpy impact tests. The dimensions of the impact specimens were 50 mm × 6 mm × 4 mm.

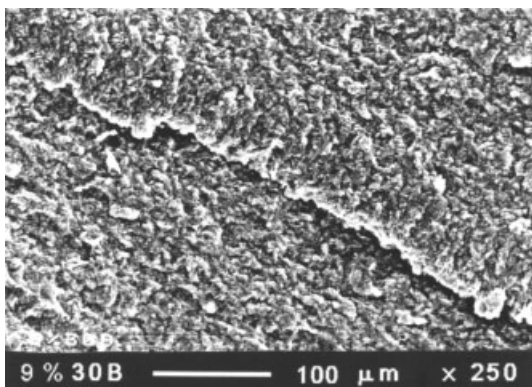
## RESULTS AND DISCUSSION

### SEM analysis

Figures 1–4 illustrate the SEM micrographs of the nanocomposites with 1 and 9 wt % Cloisite Na<sup>+</sup> (Figs.



**Figure 3** SEM micrograph of the fracture surface of the nanocomposite with 9 wt % Cloisite Na<sup>+</sup>.



**Figure 4** SEM micrograph of the fracture surface of the nanocomposite with 9 wt % Cloisite 30B.

1 and 3) and with 1 and 9 wt % Cloisite 30B (Figs. 2 and 4). SEM micrographs show that as the clay concentration in the nanocomposites increases, larger agglomerates of particles are observed and the average distance between the agglomerates decreases. At high clay loadings, owing to the difference in the scattering density between the clay and epoxy, large clay aggregates can be easily observed. When the micrographs of the nanocomposites with Cloisite Na<sup>+</sup> (Figs. 1 and 3) and with Cloisite 30B (Figs. 2 and 4) are compared, it can be seen that at the same clay content, nanocomposites with Cloisite 30B exhibit better dispersion and a lower degree of agglomeration than nanocomposites with Cloisite Na<sup>+</sup>. Agglomerates give rise to lower clay-polymer surface interactions and higher stress concentrations. In general, both of these factors lead to lower mechanical properties of the nanocomposites. On the other hand, smaller agglomerate size and exfoliation of the clay result in highly improved mechanical properties.

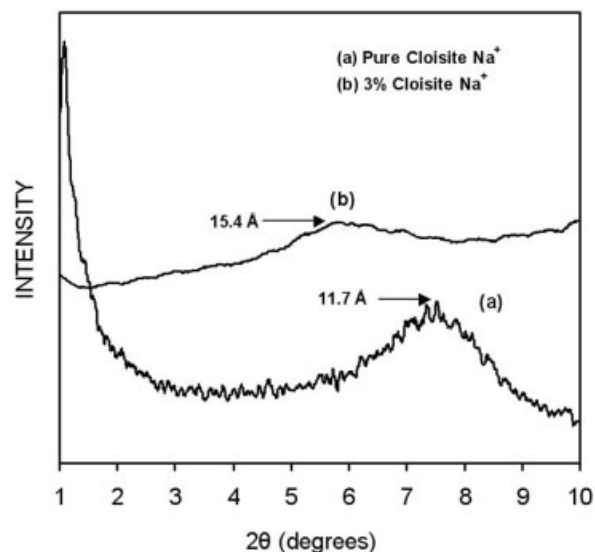
### X-ray diffraction analysis

X-ray diffraction is the most useful method to evaluate the *d*-spacing between the clay layers.<sup>12</sup> The angle and *d*-spacing values are related through Bragg's Law,<sup>13</sup> stated in eq. (1):

$$n\lambda = 2d\sin\theta \quad (1)$$

where *n* is an integer,  $\lambda$  is the wavelength,  $\theta$  is the glancing angle of incidence, and *d* is the interplanar spacing of the crystal.

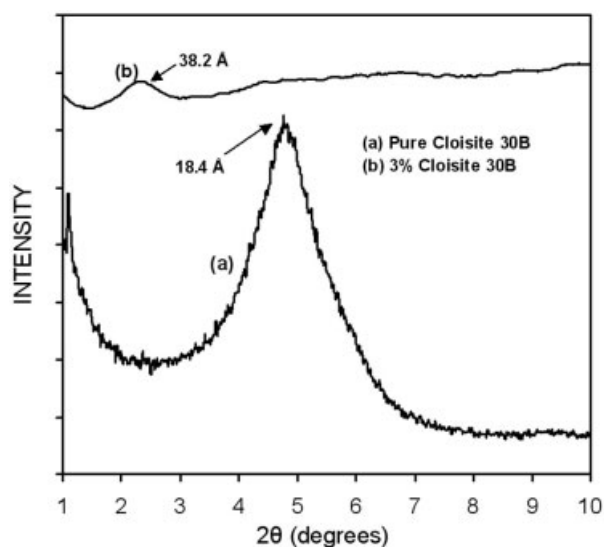
To verify that the epoxy resin entered between the clay layers, the diffractograms of pure materials are compared with the diffractograms of the nanocomposites with 3 wt % Cloisite Na<sup>+</sup> and Cloisite 30B in Figures 5 and 6. The original clay powders of Cloisite Na<sup>+</sup> and Cloisite 30B have XRD patterns corresponding to *d*-spacings of 11.7 Å at  $2\theta = 7.54^\circ$  and 18.4 Å at



**Figure 5** The X-ray diffraction pattern of: (a) pure Cloisite Na<sup>+</sup> and (b) nanocomposite with 3 wt % Cloisite Na<sup>+</sup>.

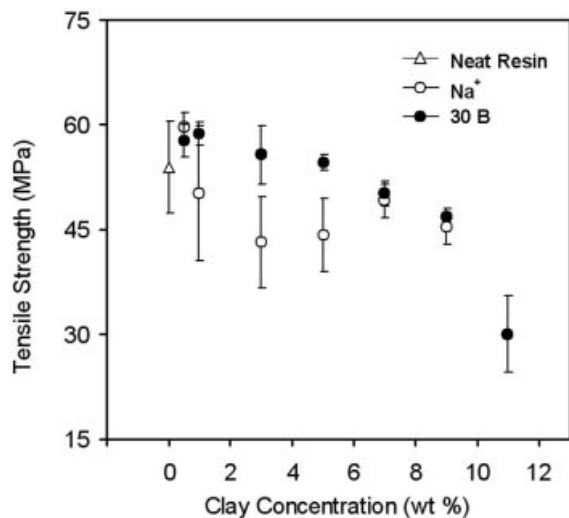
$2\theta = 4.81^\circ$ , respectively. The *d*-spacing of the Cloisite 30B powder is higher than the *d*-spacing of the Cloisite Na<sup>+</sup> powder owing to the intercalation of methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium chloride in Cloisite 30B.

Incorporation of clay into the epoxy matrix affects the *d*-spacing as follows: In Figure 5, there is a broad diffracted peak at  $2\theta = 5.75^\circ$  corresponding to a *d*-spacing of 15.4 Å in the nanocomposite with 3 wt % Cloisite Na<sup>+</sup>. Since the original *d*-spacing of the Cloisite Na<sup>+</sup> powder is 11.7 Å, it is seen that the *d*-spacing of this clay increases slightly when it is used as filler. It can also be seen in Figure 6 that *d*-spacing



**Figure 6** The X-ray diffraction patterns of: (a) pure Cloisite 30B and (b) nanocomposite with 3 wt % Cloisite 30B.





**Figure 7** The tensile strength of the neat resin and nanocomposites with Cloisite Na<sup>+</sup> or Cloisite 30B.

in the nanocomposite with 3 wt % Cloisite 30B increases from 18.4 Å to 38.2 Å, owing to intercalation of the epoxy and the hardener in the nanocomposite. The increase in the *d*-spacing of Cloisite 30B in the nanocomposite is much higher than the corresponding increase in the *d*-spacing of Cloisite Na<sup>+</sup>. Thus, the degree of intercalation in the nanocomposites with Cloisite 30B is higher than the intercalation in the nanocomposites with Cloisite Na<sup>+</sup>. It can also be concluded that the presence of the diffracted peaks indicated by the symbol (b) indicates that the nanocomposites are not totally exfoliated. However, the mechanical properties analyzed later imply that there is a certain degree of exfoliation, especially at low clay contents.

#### Differential scanning calorimeter (DSC) analysis

The glass transition temperature values increased from 73°C in the unfilled epoxy resin to 83.5°C in the nanocomposite with 9 wt % organically modified MMT (Cloisite 30B) and to 75°C in the nanocomposite with 9 wt % natural clay (Cloisite Na<sup>+</sup>). This is a typical effect for the inclusion of clay in a polymer system.<sup>14</sup> Addition of clay decreases the mobility of the polymer-clay system owing to clay-polymer interactions. The epoxy group may react with the hydroxyl groups on the clay surface. The level of interaction is higher in the case of Cloisite 30B, owing to the higher degree of intercalation.

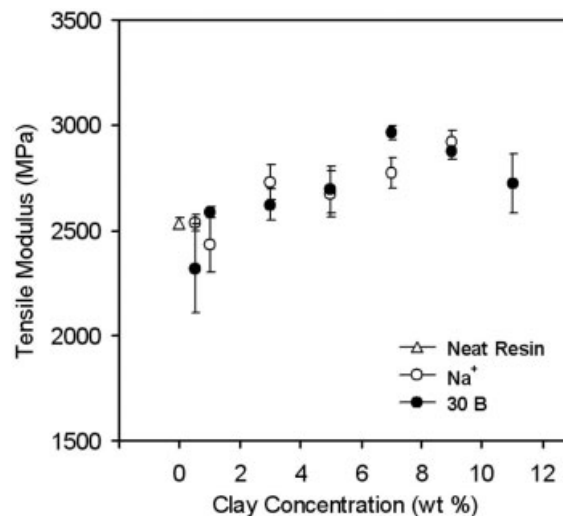
#### Mechanical properties

Figure 7 shows the tensile strength of the pure epoxy resin and nanocomposites with Cloisite Na<sup>+</sup> and Cloisite 30B. Tensile strength values of Cloisite 30B

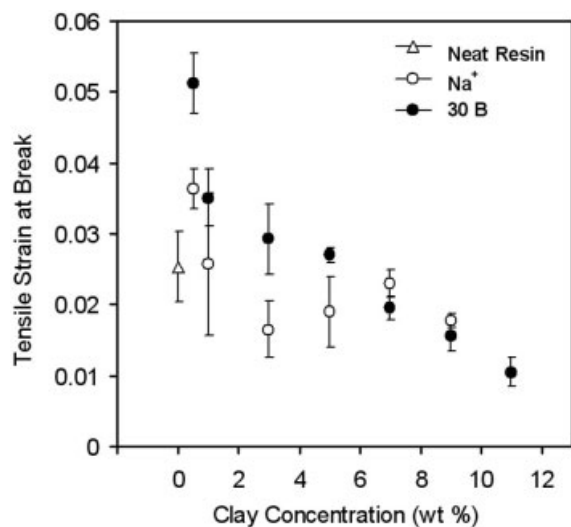
and Cloisite Na<sup>+</sup> nanocomposites exhibit a maximum at 1 and 0.5 wt % of clay, respectively. Addition of 1 wt % Cloisite 30B improves the tensile strength from 53 MPa in the neat resin to 59 MPa, indicating the reinforcing capability of the intercalated clay particles. The decrease in tensile strength values at higher clay contents is a result of the stress concentration effect of the agglomerated clay particles. The agglomeration of the clay particles at high clay loadings also results in lower tensile strength owing to lower filler surface area and lower polymer-clay surface interactions.

Figure 8 illustrates the changes in modulus with respect to the clay type and content. Tensile modulus of the nanocomposites increases with the clay content in both types of clay, since clay is more rigid than the matrix. This response is characteristic for materials reinforced with stiff fillers. At high filler contents, modulus does not increase as expected, owing to agglomeration that decreases the polymer-clay surface interactions. Agglomerates also prevent entering of the matrix resin in between the layers. Addition of 7 wt % Cloisite 30B or Cloisite Na<sup>+</sup> increases the tensile modulus by 17.2% and 9.6%, respectively. Considering that the spatial orientation of the particles is random in the production method of the present study, the improvements in the tensile modulus and strength are reasonable.

Figure 9 shows the tensile strain at break values with respect to the type and content of the MMT. Nanocomposites with both types of MMT give a rise in the strain at break values at 0.5% MMT loading, owing to the crack stopping nature of the exfoliated clay at low clay contents. However, starting from this point, the strain at break values decrease with increasing clay loading, since in these composites the rigid fillers cannot elongate much, and the actual elongation



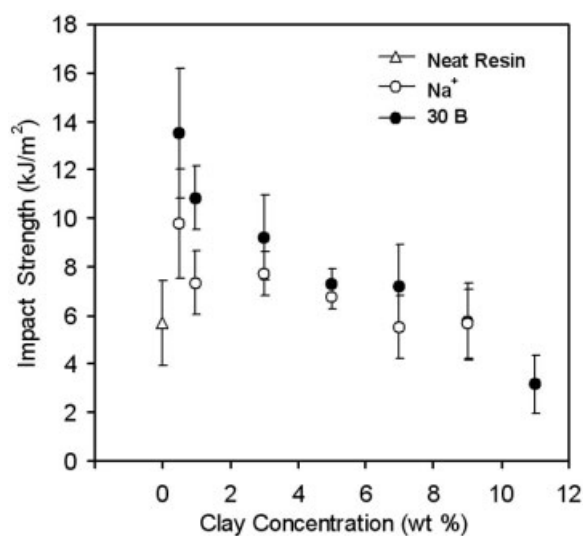
**Figure 8** The tensile modulus of the neat resin and nanocomposites with Cloisite Na<sup>+</sup> or Cloisite 30B.



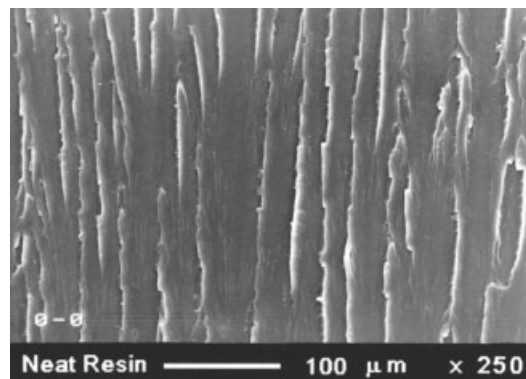
**Figure 9** The tensile strain at break of the neat resin and nanocomposites with Cloisite Na<sup>+</sup> or Cloisite 30B.

in the matrix is higher than the measured one. The clay particles are rigid fillers and make the nanocomposite more brittle at high clay contents.

Impact strength of the composites increases sharply with the clay loading, since exfoliated clay particles act as crack stoppers and form a tortuous crack propagation path, resulting in higher impact energy (Fig. 10). Addition of 0.5 wt % Cloisite 30B improves the impact strength by 137%, which is a significant improvement. An improvement of 72% was observed at the same clay content with Cloisite Na<sup>+</sup>. The impact strength values of the nanocomposites with Cloisite Na<sup>+</sup> are lower than the impact strength values of the nanocomposites with Cloisite 30B, since this clay exfoliates to a lower extent than Cloisite 30B. The clay particles ag-



**Figure 10** The impact strength of the pure epoxy resin and nanocomposites with Cloisite Na<sup>+</sup> or Cloisite 30B.



**Figure 11** SEM micrograph of the fracture surface of the neat polymer.

glomerate with increasing clay content, as seen from SEM; thus, impact strength of the composites decreases with the clay content. As seen in Figure 11, the fracture surface of the neat polymer is quite smooth, showing crack propagation lines that are almost parallel to each other. Thus, the impact strength of the neat resin is quite low.

## CONCLUSIONS

From scanning electron micrographs, it can be seen that clay particles have a tendency to form agglomerates as the clay content increases. A higher degree of agglomeration occurs in nanocomposites with Cloisite Na<sup>+</sup>. As a result of this, mechanical properties of the nanocomposites with Cloisite Na<sup>+</sup> are not significantly improved. Cloisite 30B exhibits better dispersion than Cloisite Na<sup>+</sup>.

From XRD patterns, it is observed that, in nanocomposites with 3 wt % Cloisite 30B, *d*-spacing expands from 18.4 Å (the initial value of pure Cloisite 30B clay) to 38.2 Å, indicating intercalation. However, in nanocomposites with 3% Cloisite Na<sup>+</sup>, the *d*-spacing expands from 11.7 Å to 15.4 Å, exhibiting a lower degree of intercalation in comparison to nanocomposites with Cloisite 30B. In accordance with this observation, DSC data show that the *T<sub>g</sub>* value increases from 73°C in the neat epoxy to 83.5°C and 75°C in the nanocomposites with 9 wt % Cloisite 30B and Cloisite Na<sup>+</sup>, respectively.

The impact strength values of the nanocomposites exhibit marked improvement in both types of clays. Addition of 0.5 wt % Cloisite 30B improves the impact strength by 137%. On the other hand, addition of 0.5 wt % Cloisite Na<sup>+</sup> improves the impact strength by 72% with respect to the impact strength of the neat resin. In general, the mechanical properties of nanocomposites with Cloisite 30B are improved more than those of nanocomposites with Cloisite Na<sup>+</sup>.

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