

## Mechanical and Thermoviscoelastic Behavior of Clay/Epoxy Nanocomposites

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### ABSTRACT

The study of organic-inorganic nanocomposites has become relevant in recent years since these materials exhibit synergistic properties derived from the two components. Thermosetting polymers like epoxies that have high mechanical properties provide a baseline for further improvement with the addition of nanoclay particles. These nanocomposites can be used as the matrix of a fiber reinforced composite and lead to higher matrix dominated mechanical properties including elastic modulus, strength and fracture toughness. This study concentrates on the mechanical and thermoviscoelastic properties in the glassy regime of nanocomposites prepared by direct mixing. The elastic modulus of the nanocomposites was found to improve with respect to the pure epoxy modulus at the expense of both tensile strength and ductility regardless of clay content. The glass transition temperature was also found to decrease as well. The morphology of the nanocomposites was studied and correlated with the aforementioned properties.

### INTRODUCTION

Nanocomposites formed by the intercalation or exfoliation of inorganic fillers of the order of 1-100 nm into polymers are of particular interest because of their demonstrated improvement of the physical and mechanical properties relative to the unmodified polymer. Microfillers are used quite extensively but the use of nanofillers is limited because of dispersion problems and viscosity build-up related to strong interparticle interactions. Layered silicate/polymer nanocomposites and clay/epoxy nanocomposites in particular have been studied over the last decade [1]. The morphology of these materials plays a key role and many papers have been written about the characterization of nanocomposites in the nanoscale describing the different layer separations. However, a characterization in the mesoscale and microscale is necessary to determine the orientation and content fluctuations. According to Vaia and Liu [2], the spatial characterization of nanocomposites over six orders of magnitude is a challenge and inconsistencies are likely to appear among different techniques such as scattering spectroscopy and electron microscopy. From the structural point of view, there exist two types of nanocomposites, the intercalated one where the polymer is inserted between the silicate layers forming well-ordered multilayers and the exfoliated one where the silicate layers break into single platelets and orient themselves forming a random pattern. A detailed study of the intercalation and exfoliation behavior of clay/epoxy materials was performed by Lü et al [3].

Several studies on the mechanical behavior of clay/epoxy nanocomposites have been performed. Lan and Pinnavaia [4] reported more than a 10-fold increase in both elastic modulus and strength of an exfoliated nanocomposite consisting of a diglycidyl ether of bisphenol A (DGEBA) epoxy of subambient glass transition temperature ( $T_g$ ) with 5% weight of montmorillonite. The authors showed that no big improvements were obtained for epoxies with

higher  $T_g$  in the glassy region. Giannelis et al. [5] reported the formation of nanocomposites with epoxies cured with different anhydrides and amines, and dynamic mechanical analyses (DMA) showed an improvement of the storage modulus of 58% below  $T_g$  and 450% above  $T_g$ . Zilg et al. [6,7] performed tests with anhydride cured epoxy and montmorillonite particles and they report almost no improvement for four different particle contents. There was a slight decrease in the elastic modulus of about 10 % and a decrease of the strength of about 50%. However, for 10 wt % of clay the elastic modulus increased by 116 % and the strength decreased slightly. Although  $T_g$  was not determined for these nanocomposites, a decrease was observed for mica nanocomposites.

This paper intends to provide a detailed characterization of the mechanical properties of clay/epoxy nanocomposites in the glassy regime at room temperature. Montmorillonite clay particles and an anhydride-cured epoxy were the selected materials and the nanocomposites with 2 to 20 % clay content were formed by a direct mixing method. Special emphasis was placed on the optimization of strength and toughness by way of careful processing.

## **EXPERIMENTAL**

### **Materials**

#### *Epoxy*

Epoxy was selected because it is a low creep polymer with high mechanical properties, high heat distortion temperature and excellent dimensional stability. For these reasons, it is also the most common polymer used in fiber and filler reinforced polymers for structural applications. The epoxy system considered here is an anhydride-cured epoxy consisting of a DGEBA epoxy resin cross-linked by methyl tetrahydrophthalic anhydride (MTHPA) with the help of a 1-methylimidazole accelerator. All chemicals were purchased from Vantico Inc. and used in proportions of 100:90:1 (phr) respectively.

#### *Clay*

Montmorillonite/smectite (Hydrated Sodium Calcium Aluminum Magnesium Silicate Hydroxide) was selected because it is a relatively inexpensive clay with good intercalation capabilities. It consists of very small platy crystals and it is a subgroup of the clays which are a group of the phyllosilicates which are silicate rings of tetrahedrons, linked by shared oxygen to other rings in two dimensional planes that produce a sheet-like structure, that contain varying amounts of water and allow substitution of their cations. The selected clay particles for this study were Nanomer I.28E from Nanocor and Cloisite 30B from Southern Clay Products (table I). In order to allow dispersion of the clay in an organic medium like an epoxy polymer, a surface modification of the clay is necessary to make it organophilic. Rendering the normally hydrophilic inorganic host surface into a hydrophobic host requires ion exchanging the hydrated inorganic gallery cations with cationic organic surfactants such as alkylamines. Both types of particles used for this study had been treated with quaternary amines and they were dispersed as received. However, it has been shown that protonated amines in contrast to quaternary amines react with epoxy resins thus enhancing both swelling and compatibility [4]. The length of the alkyl chain plays also a key role in increasing the basal spacing of the particles [4].

**Table I.** Properties of clay particles.

	Nanomer I.28E	Cloisite 30B
Specific density	1.9	1.98
Mean particle size ( $\mu\text{m}$ )	8-10	6
Basal spacing ( $\text{\AA}$ )	24	18.5

### **Nanocomposite formation**

A direct method like curing agent dispersion [8] was employed to disperse the particles in the epoxy matrix to form the nanocomposite. It consisted of mixing the clay particles with the hardener for 15 h followed by the addition of the epoxy resin and the accelerator and subsequent mixing for 1 h. The mixing was carried out with a magnetic stirrer in a hot plate at 50°C. The resulting mixed material was degassed under deep vacuum until no bubbles were observed and then cured in a Teflon mold at 150°C for 1 h. Several curing cycles with varying temperature and time were also considered and it was found that extending the curing cycle for more than 1 h at 150°C would not improve the mechanical properties substantially. Different amounts of clay were added to the epoxy: 1, 2, 5, 10, 15 and 20% by weight. Interfacial adhesion of the layered silicates results from adsorption, i.e. the binding of polymer molecules to the platelet surface. The motion of the polymers in the interlayer is the process that dictates the intercalation kinetics and effective diffusion of the confined polymer inside the platelet is the governing factor [9]. This diffusion becomes increasingly hindered with increasing particle content because of both the viscosity build-up and the catalytic effect of the particles making processing more difficult.

### **Characterization**

Nanocomposite formation is accompanied by increased interlayer distance as evidenced by x-ray scattering and transmission electron microscope (TEM). Small angle x-ray scattering (SAXS) performed in a machine with a solid state detector with  $\text{CuK}\alpha$  radiation was employed to monitor the change in the basal spacing (d-spacing) and intercalation patterns of the particles. Wide angle x-ray diffraction (WAXD) performed on a diffractometer with  $\text{CuK}\alpha$  radiation was used to determine the basal spacing of pure Cloisite. Scanning electron microscopy (SEM) was used to determine the presence of clay aggregates in the nanocomposites.

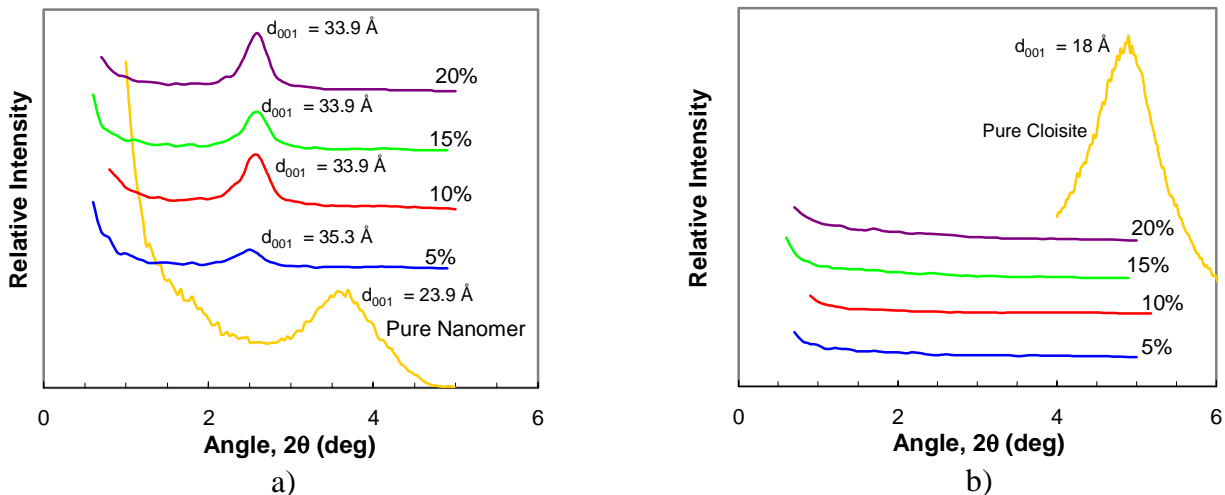
### **Testing**

Nanocomposite specimens for testing under uniaxial tension were prepared according to ASTM standards. They were bonded to fiberglass tabs with an epoxy-based adhesive (Hysol<sup>TM</sup> EA9430) and cured at room temperature under vacuum. The mechanical properties were determined through quasi-static tests performed in a servo-hydraulic testing machine under displacement control. It was found that the strain gage instrumentation would damage the surface of the specimens by generating thermal cracks that would trigger early failures. Extensometers were used instead to record the strains. The elastic modulus, strength and ultimate strain were measured. The thermoviscoelastic behavior was studied in a DMA with double cantilever specimens sweeping across a temperature range of 30-200 °C and for a single frequency (1 Hz). The storage and loss moduli and the glass transition temperatures were recorded.

## RESULTS AND DISCUSSION

### Morphology

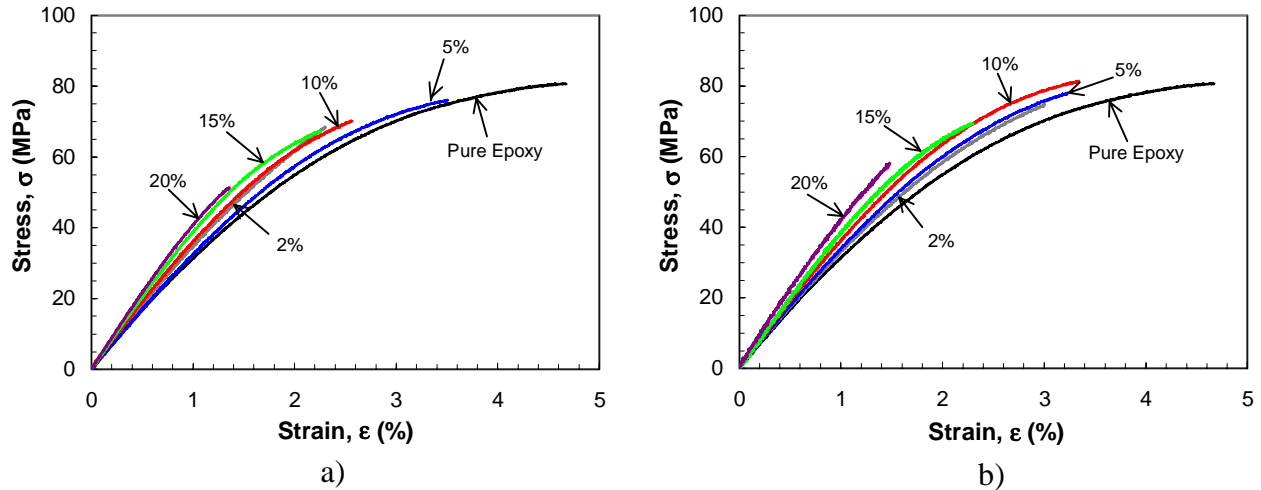
The diffraction patterns of the cured nanocomposites for various clay contents can be seen in figure 1. It can be seen that the epoxy wets completely the Nanomer particles and increases their initial d-spacing of 24 Å to 34 Å for all nanocomposites regardless of clay content. The nanocomposites with Cloisite particles show complete exfoliation regardless of particle content. Kornmann [9] argues that the lack of peaks could rather be attributed to a large distribution of basal spacings as confirmed by TEM analysis. Large aggregates as observed in SEM (bigger than 10 μm) can act as load-concentrating defects leading to a reduction in ductility.



**Figure 1.** X-ray diffraction patterns of epoxy nanocomposites: a) Nanomer; b) Cloisite.

### Mechanical and thermoviscoelastic behavior

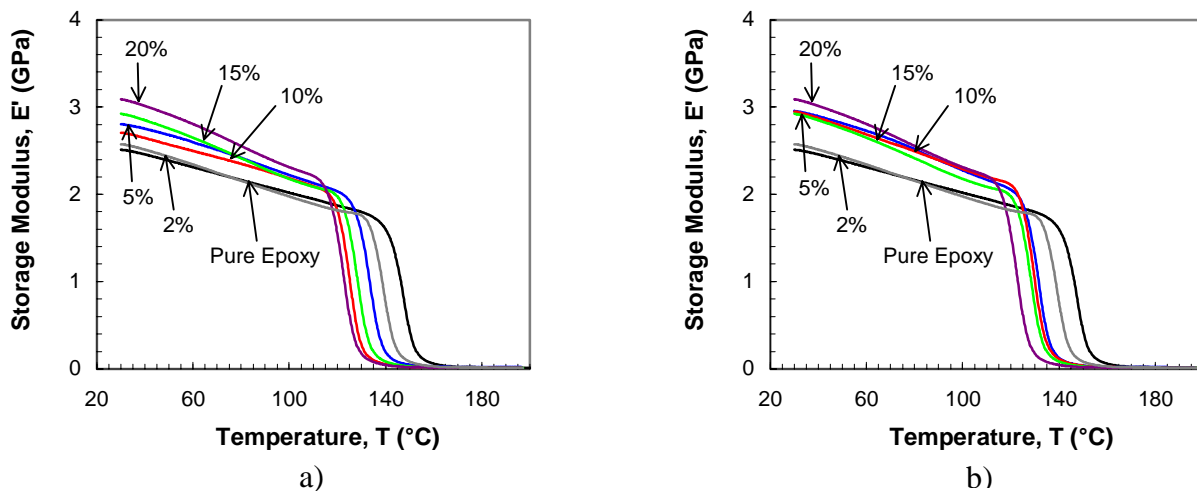
The stress-strain behavior of the Nanomer/epoxy and Cloisite/epoxy nanocomposites under uniaxial tension is presented in figure 2. The pure epoxy shows a linear behavior up to 0.7% strain followed by a stress-softening region that approaches a tensile strength plateau. All nanocomposites behave similarly compared to pure epoxy. The tensile behavior of Nanomer nanocomposites approaches the behavior of pure epoxy while Cloisite nanocomposites show a stronger behavior. Their elastic moduli increase continuously with clay content and this rate of variation increases also with clay content. Cloisite particles consistently give higher modulus nanocomposites than Nanomer particles but this difference decays markedly with increasing clay content. The nanocomposite strengths decrease with clay content. Although all measured tensile strengths were lower than the pure epoxy strength, it was the particle clusters as evidenced by SEM pictures that prevented Cloisite/epoxy from reaching higher strengths. The nanocomposites with 2% clay content did not follow the trend and showed higher elastic modulus and lower ductility than the nanocomposites with 5% clay content. Yasmin et al. [11] reported higher improvements of elastic moduli for low clay contents of nanocomposites prepared by mixing in a roll mill. The d-spacings of both particles after nanocomposite formation were identical to the corresponding ones for nanocomposites prepared by the direct method employed here. This suggests that the microstructure rather than the nanostructure determines the elastic behavior of these materials.



**Figure 2.** Stress-strain behavior of nanocomposites under uniaxial tension: a) Nanomer/epoxy; b) Cloisite/epoxy.

The thermoviscoelastic behavior of all nanocomposites is characterized by an increase of storage modulus in the glassy region with respect to the pure epoxy and by a decrease of  $T_g$ , both for increasing clay content (figure 3). The storage modulus at room temperature varies with clay content similarly to the elastic modulus. Although it was not experimentally confirmed, the reduction in  $T_g$  could be attributed to a disruption of the crosslinks making the polymer more flexible at higher temperatures.

The modeling of all the described mechanical and thermal properties in terms of the filler volume fraction is an important task. It can be said that the elastic modulus follows the Reuss model for low clay fractions (less than 0.07) and models such as Halpin-Tsai or Mori-Tanaka with low aspect ratios appear to describe better its behavior for higher filler volume fractions. Table II gives the mean thermomechanical properties for all nanocomposites ( $T_g$  calculated from  $\tan \delta$ ).



**Figure 3.** Storage modulus-temperature behavior of nanocomposites: a) Nanomer/epoxy; b) Cloisite/epoxy.

**Table II.** Thermomechanical properties of clay/epoxy nanocomposites.

	Nanomer I.28E				Cloisite 30B			
	E (GPa)	F <sub>t</sub> (MPa)	ε <sub>ult</sub> (%)	T <sub>g</sub> (°C)	E (GPa)	F <sub>t</sub> (MPa)	ε <sub>ult</sub> (%)	T <sub>g</sub> (°C)
0%	3.4	81	4.85	152.4	3.4	81	4.85	152.4
2%	3.7	64.1	2	144.7	3.65	74.8	3.0	140.7
5%	3.5	76.1	3.5	137.6	3.55	78.1	3.5	137.5
10%	3.6	70.1	2.6	131.2	3.85	81.4	3.4	133.9
15%	3.95	67.4	2.25	133.3	4.05	69.2	2.3	135.9
20%	4.35	62.1	2	129.2	4.45	58.2	1.5	129.6

## SUMMARY AND CONCLUSIONS

A study of the mechanical and thermoviscoelastic behavior of clay/epoxy nanocomposites and their corresponding morphologies was performed. Two different types of clay particles were intercalated as received in the epoxy matrix by a direct mixing method. It was found that the elastic modulus of the nanocomposites increases and their tensile strength and ductility decrease with increasing clay content. The modulus improvements are more pronounced for higher clay contents. Cloisite particles exfoliate and give nanocomposites with slightly higher mechanical properties than nanocomposites with Nanomer particles that intercalate and increase their basal spacing. These results are in agreement with previous observations on particulate-filled glassy epoxies and semicrystalline polymers, where increased stiffness leads to a decrease of ductility and toughness. It has been reported that nanocomposites from the same materials with identical basal spacing but formed by applying extensive shear loading produces nanocomposites with much higher elastic modulus. This fact reinforces the idea that the microstructure rather than the nanostructure determines the elastic behavior of these nanocomposites.

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