Structure-Properties Relationship in Resol/Montmorillonite Nanocomposites

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ABSTRACT: Polymer/layered silicate nanocomposites were prepared, adding modified, and nonmodified montmorillonites to a resol resin. It was observed that the composites exhibited an intercalated disordered structure by means of X-ray diffraction (XRD) and transmission electronic microscopy. The crosslinking density of the resol network was greatly influenced by the presence and type of clay that was added to the resin. The composites filled with the modified montmorillonites showed a lower glass transition temperature value as well as a higher degradation peak at $\sim 400°C$, which is characteristic of the degradation of methylene bridges, indicating a decrease in the crosslinking density of the resol network when modified clays are added. Resol/unmodified montmorillonite composites exhibited different behavior comparing to the other composites and the resol. A higher thermal resistance was observed in the fragmentation zone and a different tan δ response was seen in the DMA analysis. These differences in the behavior of the composites could be because of the interaction between the resol prepolymer and the clay modifiers and as a result of their chemical compatibility. The hardness and elastic modulus of the resol were improved with the addition of clays. However, higher values were obtained for the composite made with the more dispersed montmorillonite. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 3082–3089, 2007

Key words: nanocomposites; clay; structure-properties relations; viscoelastic properties; thermal properties

INTRODUCTION

Polymer/layered silicate nanocomposites are attracting considerable interest in polymer science research because of improvement in some of their properties, such as barrier properties, scratch and abrasive-resistant hard coatings,[1] fire resistance, and an increase in mechanical properties.[2–4]

Phenolic resins are one of the most commonly used thermosetting resins. They have been used in the manufacture of wood products, molding compounds, coatings, structural adhesives, thermal insulation materials, and composites. Most of these applications were made because of their excellent thermal and chemical resistance.[5] However, because of their high crosslinking density, phenolic resins are brittle. There has been much research effort in limiting this disadvantage by modifying phenolics with elastomers or thermoplastics.[5–9] In a previous study,[10] we wanted to improve the toughness of phenolics by adding

plastisols. With the addition of plastisol to the phenolic resin, an increment in the T_g, thermal resistance, and the deformation and load at break was found in a flexural analysis.

The addition of layered silicates to the phenolic resins could increase their thermal resistance and mechanical properties. Of the thermoset polymers studied, a significant amount of research has been performed on nanocomposites with epoxy resins. In those studies, the epoxy polymerization reaction,[11–13] thermal and mechanical properties,[14–16] and the addition of different clay modifiers[17–19] were analyzed. However, phenolic resin/clay nanocomposites have not been studied as much as epoxy resins. The reason could be the three-dimensional structure of the phenolics, even if they are not crosslinked. Their structure makes it more difficult to intercalate the layered silicate galleries than with linear polymers. To overcome this difficulty, the main quantity of work was done on the development of novolac/clay nanocomposites because novolac resin is almost incapable of crosslinking without a curing agent and can be obtained as a linear structure. Usuki et al.[20] tried to synthesize a phenolic resin-layered silicate nanocomposite via intercalative polymerization. They obtained a composite material consisting of novolac resin and montmorillonite from the reaction between phenol and formaldehyde in the presence of oxalic acid and

montmorillonite (MMT) modified with 4-aminophenol hydrochloride. Lee and Giannelis[21] were the first to prepare phenolic resin-layered silicate nanocomposites via melt intercalation, using organically modified MMT. Choi et al.[22,23] synthesized linear novolac-layered silicate nanocomposites prepared by means of melt intercalation as well. In the first study,[22] they concluded that the resulting interaction between the organic modifier of organosilicate and phenolic resin played an important role in determining the stable nanostructure and final morphology of the nanocomposite. In the second part of the study,[23] they examined their mechanical properties and thermal stability. The nanocomposite with 3% clay, containing an organic modifier with hydroxyl groups showed better mechanical properties and their thermal stability was slightly improved or decreased compared to that of the neat phenolic resin, depending on the silicate content. Pappas et al.[24] obtained novolac/MMT nanocomposites by *in situ* polymerization. They argued that intercalation and exfoliation can be achieved by premixing the untreated MMT with the modifier in a solution of phenol at a reduced pH. An improvement in the thermal degradation, stiffness, and strength was obtained for the composites containing up to 5% clay compared to the neat resin. Wu et al.[25] prepared both novolac/MMT and resol/MMT nanocomposites by means of suspension condensation polymerization. They concluded that MMT is easier to exfoliate or intercalate in novolac than in resol since novolac usually has a linear molecular structure. Wang et al.[26,27] reported that the polymerization of phenol and formaldehyde can be catalyzed by protons inside the galleries of an acid-modified montmorillonite (HMMT). Thereafter, they introduced HMMT to the reaction system of formaldehyde and phenol, with ammonia as a catalyst. Intragallery reactions catalyzed by protons and extragallery polymerization catalyzed by ammonia went on simultaneously. The exfoliated clay layers were effective in increasing the T_g and improving impact strength in the nanocomposites with 5% clay content.[27] In addition, resol resin/layered silicate nanocomposites were studied. Byun et al.[28] synthesized resol/MMT nanocomposites by means of melt intercalation with ω-amino acid modified MMT. They observed an improvement in the mechanical properties with the addition up to 3% clay but the thermal stability of the nanocomposites was similar to that of the neat resin. Kato et al.[29] successfully prepared resol/clay nanocomposites by means of melt intercalation using octadecyl ammonium modified MMT. In spite of the fact that resol/silicate nanocomposites were studied, the influence of hydrophobic and hydrophilic clay modifiers in the final properties of the nanocomposites was not analyzed.

The aim of this work was to study the influence of the nanoreinforcement in the curing process and in the final properties of the cured nanocomposites. A nonmodified and two modified MMTs were used to compare their behavior.

EXPERIMENTAL

Materials

A resol-type phenolic resin was prepared with a formaldehyde to phenol molar ratio (F/Ph) = 1.3. Samples of phenol and a formaldehyde aqueous solution (37% w/w) (Cicarelli) were placed in a 1-L stainless steel reactor with a low velocity stirrer, thermometer, and reflux condenser. The pH was kept at 9.0 with a solution of NaOH 40% (w/w) and the mixture was allowed to react for 2 h at 90°C. Thereafter, the mixture was neutralized with a solution of boric acid until a pH value of 6.8–7.0 was reached. After synthesis, the resol was kept at −10°C until it was used.

Clays were supplied by Southern Clay Products (Texas). Three types of MMT were used: purified Cloisite® Na+ and organically modified Cloisite 30B and Cloisite 10A. The characteristics of each are shown in Table I.

The composites were obtained by adding 5% (wt/wt) clay to the resol resin whereafter it was sonicated for 30 min. After that, the mixture was dehydrated in a vacuum at 75°C until the water had been totally extracted. Thereafter, the composite was cured in an oven for 150 min at 90°C, with a prior addition of 2.5% sulfuric acid (25% water solution). The curing cycle used had already been used in a previous study,[10] where resol–plastisol blends were investigated.

Method

X-ray diffraction (XRD) analyses of the composites were performed in a Philips PW 1710 diffractometer (45 kV and 30 mA) at 2°/min with a radiation of Cu Kα (λ = 1.54 Å).

The determination of the dynamic–mechanical properties of the blends was carried out with a Perkin-Elmer DMA-7 at a fixed frequency of 1 Hz and a heating rate of 5°C/min in a three-point bending mode. The specimens used for the test were cut from 2-mm thick plaques, obtained from curing the blends between two glass plates, previously treated with a silicone release agent supplied by Siliar S.A. (Argentina).

Dynamic degradation measurements were carried out using a Seiko Instruments SII Exstar 6000. Tests were performed in a dynamic mode to cover a wide range of thermal conditions under nitrogen environment. Temperature programs were run from room temperature to 900°C at a 10°C/min heating rate. TGA tests were performed in platinum crucibles, where samples had been placed without any prior treatments and experiments were run immediately. The sample weight in all the tests was ~ 10 mg.

TABLE I
Characteristics of the Used Montmorillonites

Clay	Organic modifier	Modifier concentration	Interlayer distance (d_{001}) [Å]
Cloisite® Na$^+$(ClNa)	None	–	11.7
Cloisite 30B (Cl30B)	H$_2$C—CH$_2$—OH / H$_3$C—N$^+$—T / H$_2$C—CH$_2$—OH	125 meq/100g clay	18.5
Cloisite 10A (Cl10A)	H$_3$C / H$_3$C—N$^+$—CH$_2$—C$_6$H$_5$ / HT	90 meq/100g clay	19.2

Where T is tallow ($\sim$ 65% C18; $\sim$ 30% C16; $\sim$ 5% C14); anion: chloride and where HT is hydrogenated tallow ($\sim$ 65% C18; $\sim$ 30% C16; $\sim$ 5% C14); anion: chloride.

Fourier transform infrared (FTIR) spectra (drift mode) were acquired with a Mattson Genesis II spectrometer. Each spectrum was obtained with a spectral width of 400–4000 cm^{-1}, 32 accumulations, and 2 cm^{-1} resolution. For comparison purposes, the spectra were normalized with the intensity of the band at 1610 cm^{-1}. This band was assigned to the stretching C=C of the benzene ring and its intensity was expected to remain constant for all the samples.[30]

Transmission electron microscopy (TEM) was performed on a JEOL 100 CX II, using an acceleration voltage of 80 kV. The specimens were sectioned into ultrathin slices (100 nm) at room temperature, using a microtome.

Hardness measurements were performed with a NanoTest nanoindentation module manufactured by Micro Materials. The specimens used for the tests were cut from 2-mm thick plaques. The measurements were made at a depth of 1000 nm and five independent indentations were carried out on each sample.

RESULTS AND DISCUSSION

To investigate the dispersion of the MMT layers, XRD analyses were performed on the composites. Figure 1 shows the XRD patterns obtained for the different composites, the resol and the MMTs. The 001 diffraction peaks of the MMTs were shifted to lower angles and appeared as a broad band in the pattern of the three composites studied. An increase in the spacing between the layers is termed as an increase in degree of exfoliation. These results could indicate the good dispersion of the clay in the polymer and an increment in the interlayer distance of the clay, without reaching complete exfoliation, forming a disordered intercalated structure.[3] The composites with Cl10A and Cl30B seemed to have structures that were better dispersed than the composite with ClNa.

Generally, however, an XRD technique was used together with the TEM to determine the interlayer spacing and the clay layer arrangement in polymer/clay nanocomposites.[4] TEM is usually chosen to visualize the exfoliation of silicate layers because it allows direct observation of the microstructure of the material. TEM photographs of the samples (Fig. 2) revealed a disordered intercalated structure for the nanocomposites made of modified MMTs [Figs. 2(b,c)]. Upon comparing them, the composite that contained Cl30B showed a higher clay interlayer distance than the one with Cl10A. It was also observed that many clay layers are curved in the photograph. The flexibility of the layers is because of the very low thickness and very large aspect ratio of the clay sheets.[26] The addition of the unmodified MMT formed an agglomerated structure without a clear separation of the layers [Fig. 2(a)], inspite of the considerable shift of the 001 diffraction peak in the XRD
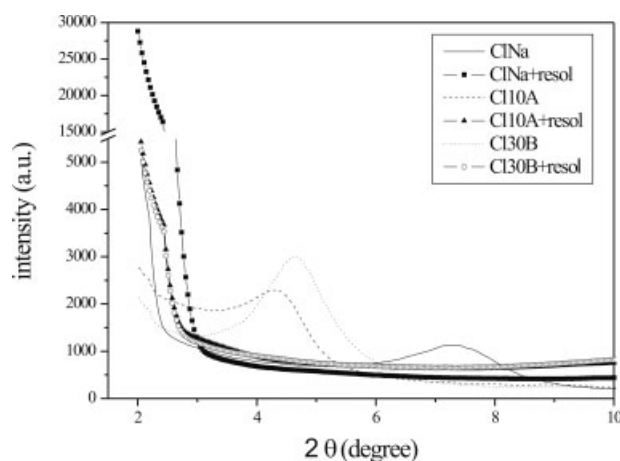

Figure 1 XRD patterns for the clays and the composites of resol and 5% of (a) ClNa; (b) Cl30B; and (c) Cl10A.
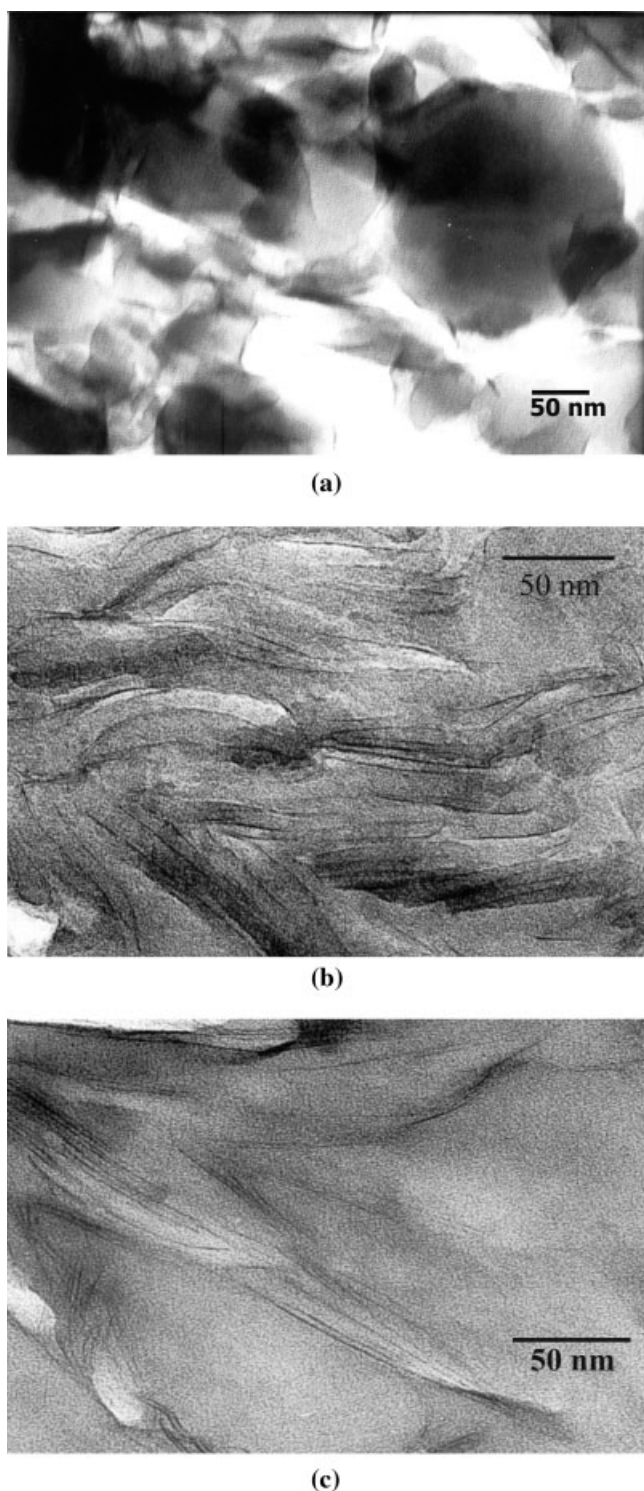
Figure 2 TEM photograph of the composites of resol and 5% of (a) ClNa; (b) Cl30B; and (c) Cl10A.

pattern. This could be because of the irregular distribution of the clay in the specimen, observed with the TEM, that showed both zones with agglomeration of clay and zones with a very low quantity of MMT.

Choi et al.[23] also observed a higher gallery expansion in the novolac/MMT nanocomposite with the

clay containing an organic modifier with hydroxyl groups. In both the novolac and resol systems, modifiers containing benzyl groups were observed to be more compatible with phenolic resin than those modified with alkyl groups because of their similar structures.[26]

Consequently, the modified MMTs resulted in better dispersion of the clay in the polymeric matrix. This behavior is certainly because of the higher interlayer distances of the modified MMTs compared to the unmodified one and also because of the chemical structure of the organic modifiers. The chemical composition of the clay modifiers allows the prepolymer resol to migrate between the layers. The driving force for this mechanism is controlled by the affinity between the prepolymer and the modifiers, as explained hereinafter.

It is well known that resols are obtained from the reaction between formaldehyde and phenol under basic conditions and usually when using an excessive amount of formaldehyde. In an aqueous alkaline medium, phenol and formaldehyde are present in the form of phenolate and methylene glycol, respectively. The initial reaction is created by the addition of formaldehyde to phenol [Fig. 3(a)] and thereafter, condensation between the substituted phenol rings [Fig. 3(b)] occurs. Consequently, methylolphenols are initially the predominant intermediate compounds. At this stage, the resol was mixed with the clay and these condensation reactions took place. Therefore, the chemical structure of the resol reveals that it is a hydrophilic compound with reactive OH groups as well as with free reactive positions in the benzene ring. These reactive groups could interact with the modifiers of the clays because of the affinity between them. The modifier with Cloisite 30B had OH groups at the end of the chains and the modifier with Cloisite 10A had a benzene ring. The Cloisite Na$^+$ also had OH groups in the interlayer region but the smaller interlayer distance at the beginning of the reaction certainly did not allow the polymer to enter the galleries as easily as the modified MMTs did.

Dynamic–mechanical analyses were performed to determine the influence of the clay on the viscoelastic behavior of the polymer. Figure 4 shows the tan δ curve for the different composites. It was observed that the T_g, determined as the maximum of the tan δ peak, was lower for the composite with Cl30B than for the composite with Cl10A and the T_g of both of them were lower than that of the resol without clay (Table II). Furthermore, the height of the tan δ peak increased with a decrease in the T_g value. These results indicate that the presence of the modified clays in the reaction medium affect the formation of the resol network during curing. According to the decrease in the T_g value and the higher tan δ peak, which is related to the damping of the polymeric
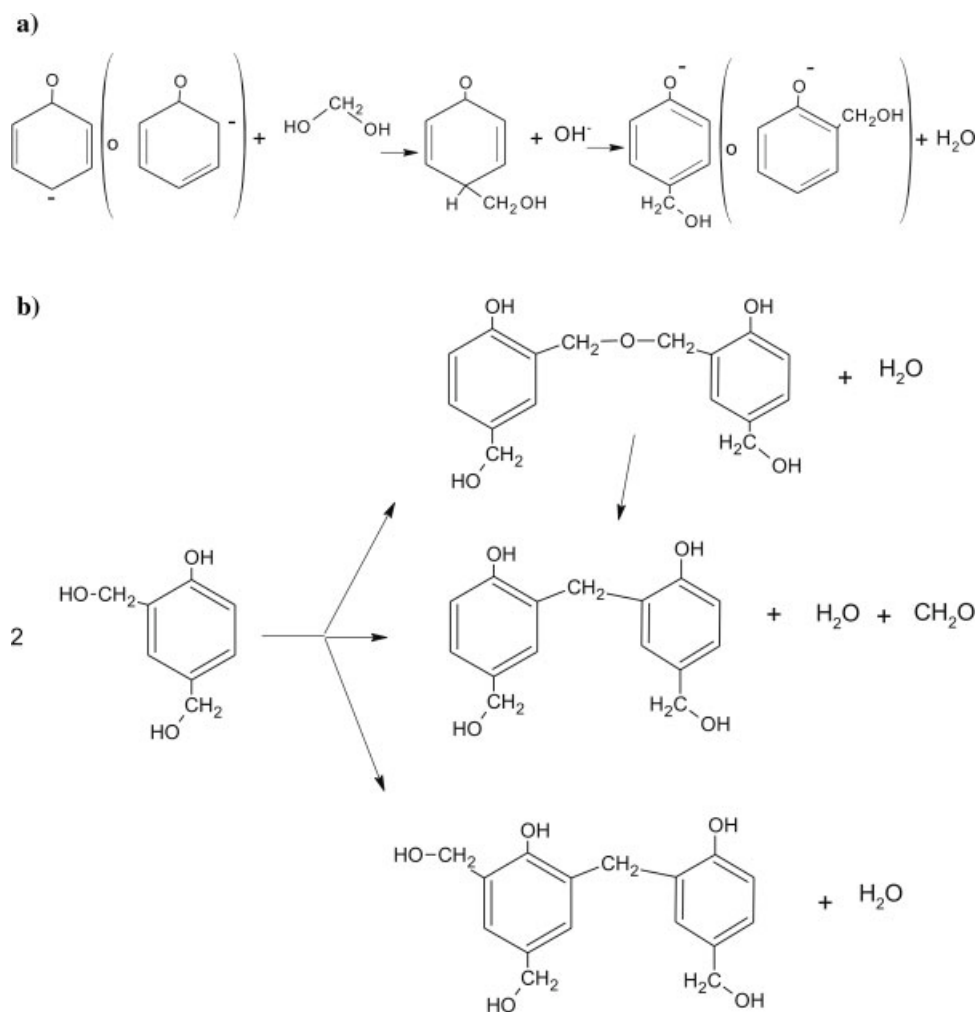
Figure 3 Diagram showing the addition (a) and condensation (b) reactions between phenol and formaldehyde.

chains, it seems that the density of crosslinking of the polymer network was lower for the composites that were made with the modified clays.
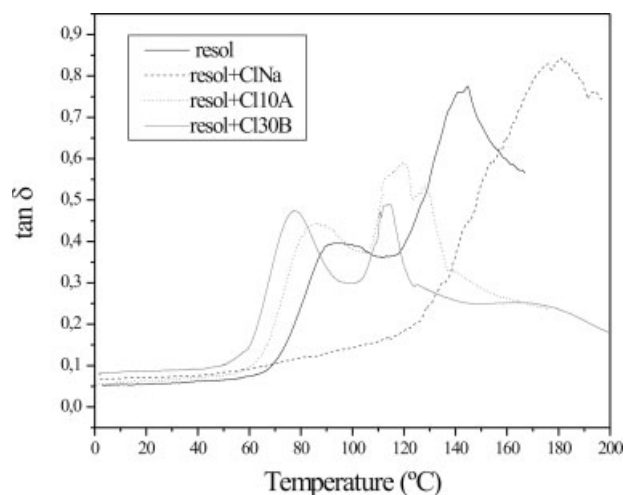

Figure 4 Dynamic–mechanical analysis of the polymer/clay composites.

The composite with the unmodified MMT, on the other hand, showed different behavior to the others. The shape of the tan δ curve is very similar to that obtained when the resol was cured by temperature without the addition of an acid catalyst.[31] This behavior could be explained by taking into account the pH value of the clays. The pH measured in a solution of ClNa was 8.7, which is a basic solution. Therefore, this basic solution could neutralize at least part of the sulfuric acid added, giving a different final network after curing.

To analyze the final network structure of the different composites, FTIR spectra were obtained. Figure 5

TABLE II
T_g **of the Composites from a DMA Analysis**

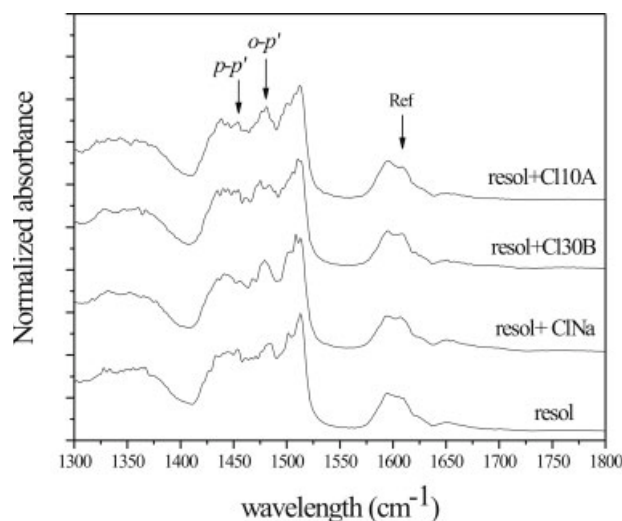| Clay in the composite	T_g (°C)
None	96
Cl10A	86
Cl30B	78

Figure 5 FTIR spectra for the resol and composites.

shows the 1300–1800 cm^{-1} region of the spectra for the resol and their composites. The region between 1500 and 1400 cm^{-1} was identified as a characteristic of the deformation vibrations of —CH— bonds in the —CH$_2$— groups, which formed the methylene bridges. Some differences can be noticed in this region. The band at $\sim$ 1450 cm^{-1} was assigned to methylene bridges in para–para' (p–p') and the band at 1480 cm^{-1} was assigned to the ortho–para' (o–p') position.[30] The relative quantity of methylene bridges in the studied composites is shown in Figure 6. As expected, lesser proportions of methylene bridges were found for the composites made with Cl30B and Cl10A than for the resol and the composite made with ClNa. This concurs with the previous results that showed a decrease in the crosslinking density of the network for the composites made with modified MMTs.

The variation in the chemical structure of the resol could be because of the interaction between the OH
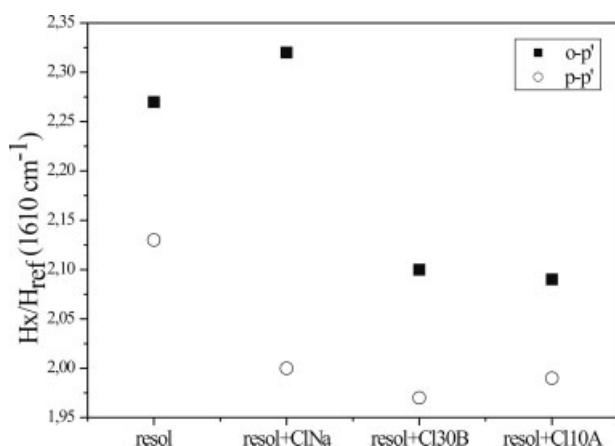
groups of the clay and the prepolymer and because of the hydrophilic character of the resol, as explained earlier. The exfoliation mechanism and the interaction between the clay's modifiers in epoxy nanocomposites were previously studied.[32–34] Park et al.[32] reported that the presence of organic modifiers gives rise to differences in intra- and extragallery polymerization for an epoxy resin because of the acidity of the modifiers inside the galleries. Chen et al.[33] reported that the crosslinking-reaction of an epoxy in the presence of Cl30B was due to the surfactant groups' initiation. It was also reported[34] that the epoxy molecules can adhere to the clay surface because of the polarity of its epoxy groups. In the same way, the phenolic resin can interact with the layers of the clay, modifying the final network. In addition, since free formaldehyde and oligomers are short and have high polarity, they could enter the galleries, modifying the formaldehyde/phenol molar ratio outside the galleries, thereby giving a different final network. A more exhaustive study to understand the type of interaction between the resol, modifiers and clay to achieve the final network structure should be done in the future.

The thermal degradation of the composites was also studied. The thermograms for each composite are reported in Figure 7. In the percentage weight loss curve, it was observed that the thermal stability of the resol was similar to that of the composites made with Cl30B and Cl10A at the beginning of the degradation process. Thereafter, the composites showed a slight increase in the thermal stability when compared with the neat resin up to $\sim$ 400°C but at higher temperatures, the resol degraded in a minor proportion because of their higher crosslinked network. This behavior was observed more clearly in the time derivative of the weight loss (DTG) in Figure 7. The first peak at $\sim$ 200°C was lower and thinner for the composites than for the resol, indicating that the addition of MMT enhances the thermal resistance at this stage
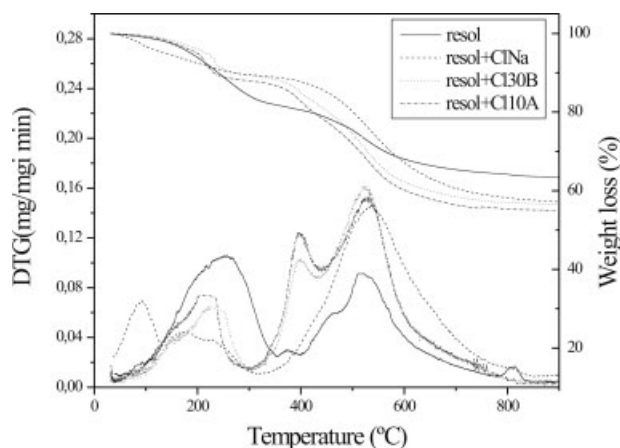

Figure 6 Relative quantity of methylene bridges for the resol and composites.

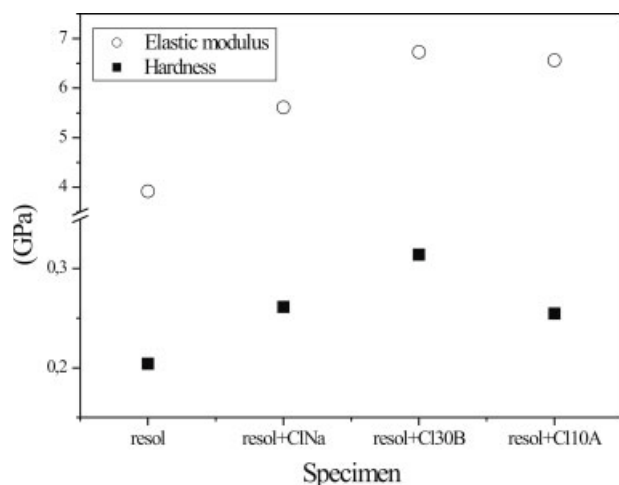**Figure 7** DTG curves of the polymer/clay composites.

Figure 8 Hardness and elastic modulus of the different polymer/clay composites and resol.

of the degradation process. Inspite of the fact that the maximum of this peak appeared at lower temperatures for the composites, the peak for the resol is higher and broader than those of the composites. This effect is because of the fact that the clay acts as a heat barrier.[4] Other authors that have studied the thermal degradation of phenolic resins and their nanocomposites[23,24,28] have also reported that the silicate layers do not play a significant role in enhancing the thermal stability of phenolic resins, since the phenolic resins itself have good thermal stability. The thermal degradation of the neat phenolic resins was widely studied[35–37] and the region between 350 and 600°C was identified as the thermal fragmentation zone, which involved fragmentation reactions and the development of further crosslinking. Thereafter, there was a partial decomposition of the structures previously formed, leading to the formation of a charred aromatic residue at temperatures higher than 600°C. Two peaks were observed in this region and the first one was higher for the composites than for the resol. In a previous study,[37] we looked at the thermal degradation behavior of a series of resols with different crosslinking densities and it was found that the peak at 400°C was lower for the higher crosslinking resol. So, according to the DTG curves in Figure 7, the composites should have a network with less crosslinking density because of the higher peaks at 400°C with respect to resol. These results concurred with the ones obtained by means of DMA and FTIR analyses.

Upon studying the composites, the composites of resol and Cloisite Na^{+} showed different behavior in comparison with the others. The DTG curve shows a peak at ∼ 400°C that appears as a shoulder and is lower than the same peaks of the other composites. However, the second peak in the fragmentation zone is very similar to the peaks of the other composites. It

could indicate more crosslinking in the network, as demonstrated in our previous study[37] and as explained earlier.

Furthermore, the hardness and the elastic modulus of the different composites were compared to that of the resol resin. The results are shown in Figure 8, which shows that these properties were enhanced by the addition of clay to the polymer. However, better results were obtained from the nanocomposites where the clay was better dispersed. The composite with Cl30B showed an increase of 50% in the hardness value and of 70% in the elastic modulus, in comparison with the resol. These results concur with those obtained when adding carbon nanotubes to an epoxy resin.[38] The addition of clay can increase the elastic modulus since clays have an extremely high elastic modulus of 170 GPa,[4] which is important when using the material as a coating.

CONCLUSIONS

Composites of resol resin filled with modified and nonmodified MMTs were studied. From the DMA and TGA analyses, it was found that the structure of the polymer network is greatly influenced by the presence and type of filler added. The addition of modified clays with modifiers containing hydrophilic groups leads to less crosslinked polymer networks than in the case of the resol, because of the interaction between the modifier and the prepolymer. These results concur with the methylene bridge content determined by FTIR, which indicates higher bridge contents for the resol and the composite with Cloisite Na^{+}. However, the network was different when the nonmodified Cloisite Na^{+} was added. This could be because of the interaction between the OH groups present in the surface of the layers of the clay with the hydrophilic groups of resol, modifying the formaldehyde/phenol molar ratio in the bulk.

The polymer filled with a modified clay allows a major increase in the interlayer distance because the long chains of the modifier initially separate the layers more and the prepolymer can easily enter the galleries.

Finally, in comparison with the resol, the composites showed an increase in the hardness and elastic modulus. However, the better results were obtained with the addition of Cl30B that seemed to disperse better in the polymer matrix.

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