Resol/Montmorillonite Nanocomposites Obtained by *In Situ* Polymerization

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ABSTRACT: Nanocomposites based on resol resin and layered silicates were obtained by in situ polymerization. An increment in the viscosity and in the content of free formaldehyde in the prepolymer with the addition of clay was observed. It could be attributed to the entrance of small phenol molecules into the galleries modifying the concentration of reagent enabled to react outside the clay galleries. The composites were cured by temperature and it was observed that the type of clay affect their dispersion in the polymer. The unmodified Cloisite® Na+ montmorillonite (CNa) was the best dispersed in the polymeric matrix, whereas the modified montmorillonites (MMTs) showed an interlayer contraction after curing. It seems to be due to the loss of modifiers from the clay or to the different rate of curing inside and outside the galleries. In addition, the composite containing CNa presented higher crosslinking density than the others with modified MMTs. More adhesive strength was observed in that composite as well. It was related with the void content and the polarity of the samples. These results were compared with the ones obtained when the nanocomposites were synthesized by mixing the clay with the prepolymer. The nanocomposites with the addition of CNa showed similar properties independent of the way of synthesis used. However, it seems that the modified clays are better dispersed by mixing with the prepolymer than by in situ polymerization. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 32–39, 2009

Key words: nanocomposites; clay; thermosets; structure–property relations; adhesion

INTRODUCTION

Phenolic resins are thermosetting resins used in many different applications since 1907 when they were first synthesized.[1] The principal advantages of these resins are their excellent chemical and thermal resistance. The application field of different polymers was widened with the emergency of nanotechnology. It was proved that the use of low percentages of nanoparticles as reinforcement of polymer matrices is an effective way to improve some properties such as mechanical, adhesive, barrier, and thermal.[2] Layered materials such as montmorillonite (MMT), saponite, and mica are widely used clay nanoreinforcements because of their availability and low cost.[3] To reach an improvement in the properties of the material, the layers of the clay must be dispersed throughout the polymer matrix phase. When the layers are fully separated, the clay is considered to be exfoliated. On the other hand, when polymer resin is inserted into the gallery between the adjacent layers and the interlayer gallery expands, it is known as intercalated composite. Surface modification of the layers should favor the entrance of the polymer into the clay galleries. Functionalized clays with quaternary alkylammonium salts containing long carbon chains and compatible groups with the polymer matrix were selected.[4]

Different synthesis methods have been proposed to obtain nanocomposites: intercalation of polymer from solution, in situ intercalative polymerization, or melt intercalation. Different ways of synthesis were used to obtain nanocomposites based on clay and phenolic resins, both novolacs and resols. It was reported the synthesis of phenolic resins by melt intercalation,[5–9] in situ polymerization,[10–13] and intercalation of prepolymer.[14,15] In those works, different conditions of synthesis and curing, formaldehyde to phenol molar ratio, type of clay, and organic modifiers were used. It was stated that the experimental conditions as well as the surfactant selected to compatibilize the clay with the polymer and the intrinsic properties of the polymer are crucial to control the dispersion. The aim of this work is to obtain phenolic/MMT nanocomposites synthesized by in situ polymerization maintaining similar

TABLE I
Organic modifiers and Interlayer Distance of the clays

Type of clay	Organic modifier	Concentration of organic modifier [meq/100 g clay]	Interlayer distance (d_{001}) [Å]
Cloisite® 30B (C30B)	H_2C—CH_2—OH, H_3C—N^+—T, H_2C—CH_2—OH	125	18.5
Cloisite® 10A (C10A)	H_3C, H_3C—N^+—CH_2—(phenyl), HT	90	19.2

conditions of synthesis and curing than those used in a previous work.[15] Although in the previous work the resol nanocomposite was obtained by intercalation of the prepolymer, in this study, in situ polymerization was used. It will allow us to compare the results obtained from the characterization of the materials and to choose the way to obtain the material with the best properties.

EXPERIMENTAL

Materials

Nanocomposites based on resol and montmorillonite were obtained in situ, by adding 5% of clay during the polymerization reaction. The resol-type phenolic resin was prepared using a formaldehyde to phenol molar ratio equal to 1.3 under basic conditions, as explained in the following. Melted phenol was mixed with the clay and then sonicated at 25°C for 1 h to enhance the dispersion. The mixture was placed in a 1-L stainless steel reactor with a low velocity stirrer, thermometer, and reflux condenser. Formaldehyde was added, 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. The prepolymer was dehydrated under vacuum at 80°C until total extraction of water.

Resol was synthesized without the addition of clay, placing phenol and formaldehyde in the reactor. Then, the same procedure explained earlier was followed. After synthesis, resol and nanocomposites were kept at –18°C until they were used.

Purified montmorillonite Cloisite® Na⁺ and the organically modified Cloisite® 30B and Cloisite® 10A, supplied by Southern Clay Products (TX), were used as polymer nanoreinforcement. The organic modifiers and the interlayer distance of the clays are shown in Table I to account the structural modifications of the functionalizations.

Thereafter, resol and composites were placed over aluminium plaques and cured in an oven maintain-ing 1 h at the following temperatures: 50, 80, 100, 110, 130, 150, and 190°C.

Method

Free formaldehyde content in the resins was measured by the hydroxylamine method.[16] Viscosity of the prepolymers was measured in a cone-plate Brookfield HBTDV viscometer at 25°C. Solid content was determined by curing the resol and nanocomposites at 135°C until constant weight. Refractive index was measured by means of a refractometer Abbe NAR-2T.

X-ray diffraction analyses (XRD) of the composites were performed in a Philips PW 1710 diffractometer (45 kV and 30 mA) at 2°/min, with a CuK$_\alpha$ radiation ($\lambda = 1.54$ Å).

Fourier transform infrared (FTIR) spectra of the cured materials were acquired in attenuated total reflection (ATR) mode using a Matson Genesis II spectrometer. A spectral width of 400–4000 cm⁻¹, 16 accumulations, and 2 cm⁻¹ resolution was used in the analyses. The spectra were normalized using the band at 1610 cm⁻¹, corresponding to the stretching C=C of the benzene ring that was expected to remain constant in all the samples.[17]

Transmission electron microscopy (TEM) images of the samples were obtained with a JEOL 100 CX II at 80 kV of acceleration voltage. All samples were ultramicrotomed at room temperature to give sections with a nominal thickness of 100 nm.

The void content of the samples were determined from scanning electron microscopy (SEM) images obtained with a JEOL JSM-6460LV. Polished lateral surfaces of the samples coated with a 300 Å gold layer were analyzed.

Single Lap-Shear test (ASTM D-1002-94) was used to measure the adhesive strength of the polymer/aluminium joint. Tests were carried out at ambient temperature with an Instron 4467 machine at a crosshead speed of 1.25 mm/min. The aluminium surface was abraded using grid 500 and 1000 sandpapers and cleaned with acetone before the polymer application. The assemblies were joined and fastened

TABLE II
Characterization of Liquid Resol and Nanocomposites

Simple	Free formaldehyde [%]	Viscosity [Pa s]	Solid [%]	Refractive index
Resol	4.88	1520	53.67	1.5775
Resol + CNa	7.80	3608	65.45	1.5755
Resol + C10A	7.14	4060	60.97	1.5705
Resol + C30B	6.46	2063	52.35	1.5705

between two glasses, and the curing cycle was applied. Spacers were used to ensure the bond thickness of 0.60 mm.

Contact angles were measured by the sessile drop method in a goniometer using high purity water as reference liquid.

RESULTS AND DISCUSSION

Resol and nanocomposite prepolymers were characterized in the liquid state measuring the refractive index, viscosity, free formaldehyde, and solid content (Table II). The composite with CNa contained the highest percentage of solid content. This result could be related with the resin crosslinking density studied by FTIR and discussed later. The composite that showed the highest crosslinked structure after curing should have the highest solid content. It was observed an increment in the viscosity and free formaldehyde content of the resol with the addition of clay. Nanocomposite prepolymers were obtained by first mixing the phenol with the clay, and then, formaldehyde was added. The formaldehyde to phenol molar ratio outside the galleries should change if part of the phenol is able to go into the interlayer space of the clay then, the free formaldehyde should be higher than in the polymer obtained without the addition of clay.

On the other hand, it was expected a higher increment in the viscosity of the prepolymer, where the nanoparticles were better dispersed. Then, the samples containing the highest free formaldehyde content showed a higher increase in the viscosity, which should indicate that phenol molecules have migrated inside the galleries favoring the separation of the clay layers. Despite the lower initial interlayer distance of the unmodified MMT, it seems that it was dispersed in the liquid resol as far as the organically modified clays. It could be due to the hydrophilic OH groups contained in the surface of the CNa layers that are compatible with the hydrophilic character of species in the resol prepolymer. The dispersion of the modified MMTs should be favored by the organic modifiers containing OH groups and a benzene ring in the C30B and C10A, respectively. At the beginning, phenol was the unique molecule that

could enter into the galleries and then, when formaldehyde was added, part of the formaldehyde could react with the phenol that is both outside and inside the galleries. Thereafter, the oligomers that are formed in the medium are also able to enter in the interlayer spacing.

In a previous work,[15] we synthesized resol nanocomposites by mixing the clay with the prepolymer, instead of using in situ polymerization. Only the modified MMTs were observed to be better dispersed in the liquid prepolymer in that work. The in situ polymerization allows a better dispersion of the unmodified MMT because it seems to be easier to introduce the phenol than the prepolymer in the lower initial interlayer spacing. The affinity of the polymer segments for the silicate surface is a key factor to understand the polymer–clay interaction. In this case, the OH groups in the surface of the unmodified clay layers are chemically compatible with the phenol groups contained in the polymer matrix.

X-ray diffraction analyses were performed in the samples to study the dispersion of the different clays in the polymer. The XRD patterns are showed in Figure 1. It was observed that the nanocomposite containing CNa was the one that showed the higher intergallery distance due to the displacement of the basal peak of the clay from $2\theta = 7.3$ to 4.7. This behavior could be attributed to the interaction between the ─OH groups of the clay layers and the polymer, allowing their entrance in the galleries. On other hand, nanocomposites containing modified MMTs showed an interlayer contraction because the basal peaks were displaced to higher angles compared with the pristine clays. The same behavior was observed in other nanocomposites,[18–21] and it was attributed to loss of clay modifiers from the galleries, degradation of surfactants, and/or to the
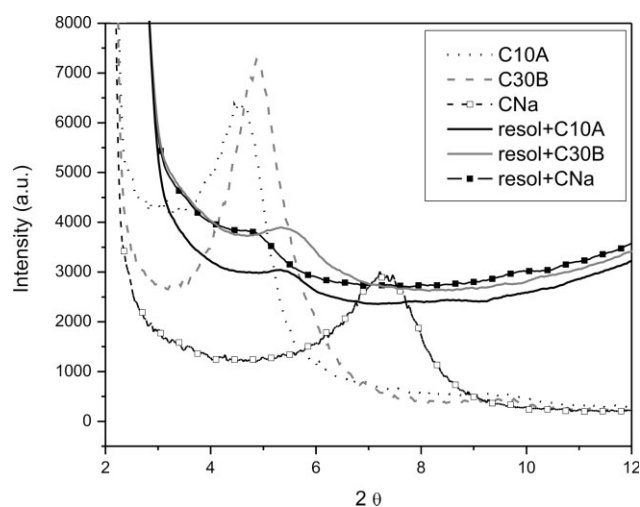

Figure 1 XRD patterns of the resol and nanocomposites.

different rate of polymer curing inside and outside the galleries. As these processes may occur simultaneously, it is difficult to interpret the results. It was proposed[22] that the exfoliation mechanism in epoxy resins occurred in a first step by the diffusion of the resin in the clay galleries due to the high surface energy of the clay, which attracts the polar resin molecules. Then, the reactions that involve resin polymerization could occur inside and outside the galleries at the same time. The cure outside the galleries inhibits migration of more monomers and oligomers into the galleries producing a different curing rate in both places. Then, both balance between inter- and extragallery reactions and monomers, oligomers and resin diffusion are the key factors, which control the clay exfoliation. The results obtained about the dispersion of the different clays in the polymer were not similar from those observed when the synthesis of the nanocomposites was not made in situ. In the previous work,[15] where the prepolymer was mixed with the clay, the modified clays were better dispersed in the polymer than the CNa. It was attributed to the affinity between the resin and the modifiers containing compatible groups with the chemical structure of the resol. It seems that the better dispersion observed in the liquid state was kept for the CNa, but the modified MMTs contract during curing. It could be due to the lower crosslinking density of the polymer network when the modified clays are present, observed by FTIR and explained later.

The structure of the nanocomposites is typically elucidated using XRD and TEM. Although XRD offers a convenient way to determine the interlayer spacing of the silicate layers in the nanocomposite, it is not possible to obtain conclusive results from this technique. XRD and TEM are often combined to ensure the conclusion derived from separate analysis. TEM allows a qualitative understanding of the microstructure through direct visualization of the nanoreinforcement arrangement. TEM microphotographs of the composites are shown in Figure 2. It was observed that the layers of CNa [Fig. 2(a)] were the better dispersed than the modified clays [Fig. 2(b,c)] in the polymer. The microphotograph corresponding to the composite containing CNa showed a regular distribution of partially aligned clay sheets and small regions of polymeric matrix. However, both the C10A and C30B showed a poor dispersion in the polymer matrix maintaining the alignment of the clay sheets with no appreciable expansion of the galleries. Additionally, an inhomogeneous clay distribution with bigger sections containing only polymeric matrix was observed in Figure 2(b,c). These results were in accordance with XRD results. Also, it was observed that some of the sheets are curved due to their high aspect ratio. It was explained that
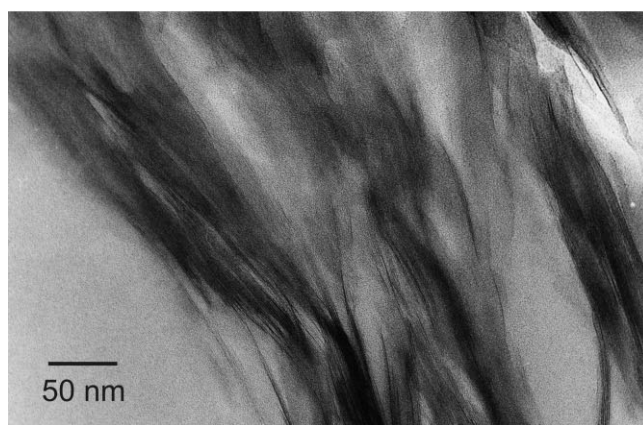
Figure 2 TEM images of the nanocomposites with: (a) CNa; (b) C30B; and (c) C10A.

to take full advantage of the nanoreinforcement, the clay layers must to be oriented in the appropriate direction and not curled or curved.[21]

The influence of the addition of clay in the chemical structure of the resol was studied by FTIR. Normalized spectra of the resol and the nanocomposites are shown in Figure 3. To analyze the chemical structure of the polymer, bands corresponding to
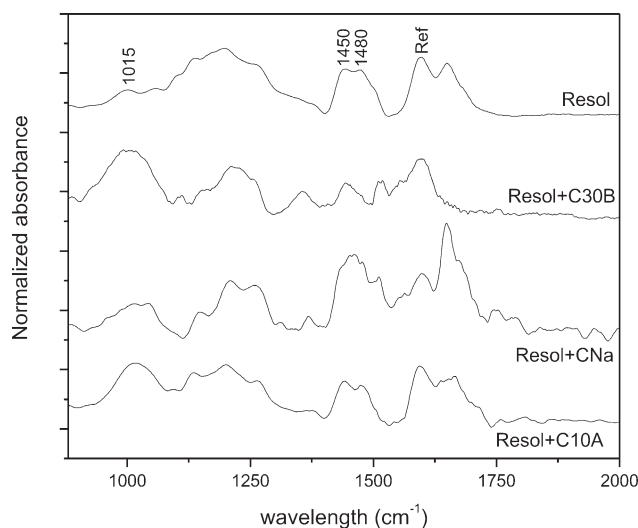
Figure 3   FTIR spectra for the resol and nanocomposites.

typical groups of the phenolic resin such as methylene bridges between phenolic rings and primary hydroxyls were studied. Those methylene bridges are formed during the crosslinking reactions that involve two methylolphenols or a methylolphenol with a free *ortho* or *para* position in the benzene ring [Fig. 5(b)]. The methylolphenols were formed from the addition of formaldehyde to phenol in a first step [Fig. 5(a)]. The addition occurs in the activated *para* and *ortho* position of the benzene ring.[1] The bands corresponding to the methylene bridges are those that appeared at 1450 and 1480 cm^{-1}, for the *para-para'* and *ortho-para'* bridges, respectively.[17] The relative quantity of those bridges measured from the FTIR spectra is shown in Figure 4. It was observed that the methylene bridges content is higher for the composite containing CNa, corresponding to a higher crosslink network. The composites with modified clays reached a lower crosslinking density than the resol resin and the composite with CNa.

The primary OH groups content was measured in the peak at 1015 cm^{-1}.[23] These OH groups are from the methylols that are formed during the addition of formaldehyde to phenol [Fig. 5(a)], but thereafter they are condensed forming more substituted species, water, and formaldehyde [Fig. 5(b)]. As it was expected, the composites showing a higher crosslinking density are the ones that showed the lower quantity of free OH groups (Fig. 6). Similar results about the higher crosslinking density of the composites containing CNa were obtained in previous works when resol nanocomposites were synthesized by mixing the prepolymer with the clays and then cured by temperature[15] as well as cured by the addition of an acid catalyst.[14] It was attributed to the presence of Na$^+$ ions in the medium that are able to

form intermediate chelates favoring the addition reactions between phenol and formaldehyde, increasing the activation, and the rate of polymerization.[24] The lower crosslinking density with the modified MMTs could be attributed to the presence of the long carbon chains of the surfactants producing more free volume. Because of the contraction observed, it seems that the organic modifiers are expulsed from the galleries and then they are able to interact with the polymer affecting the reactions.

As these materials could be used as metal coatings, the strength of the adhesive joint between the resin and aluminium was measured by the Single Lap-Shear test. An increment in the shear stress of the nanocomposites when compared with the neat resin was observed (Table III). The best result was obtained with the CNa reaching a 34% of increment in the shear stress. In addition, the void content was measured in the samples, as the voids area/total area (Table III). The composites containing lesser quantity of voids were the ones that showed the better strength of the adhesive joint between the metal and the polymer. Also, the ones that presented a higher quantity of voids contained a bigger voids (Table III), resulting in detriment of the adhesive behavior. The presence of voids in the polymer layer affects the bond strength because of the lower contact area and the diminution in the polymer mechanical properties. The crack surfaces from the Lap-Shear test showed both adhesive and cohesive failures. Niklaus et al.[25] investigated the influence of different bonding parameters on void formation in a bond. They reported an increment in the bond strength when using void-free polymer coatings on a silicon substrate.
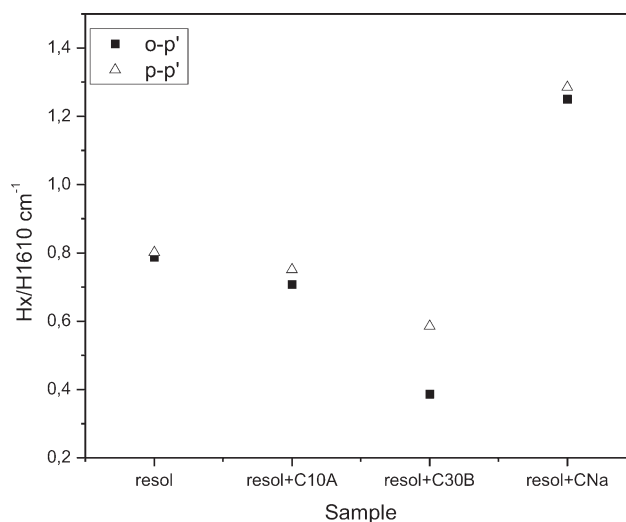

Figure 4   Relative methylene bridges (*o-p'* and *p-p'*) in the resol and nanocomposites, measured by FTIR.
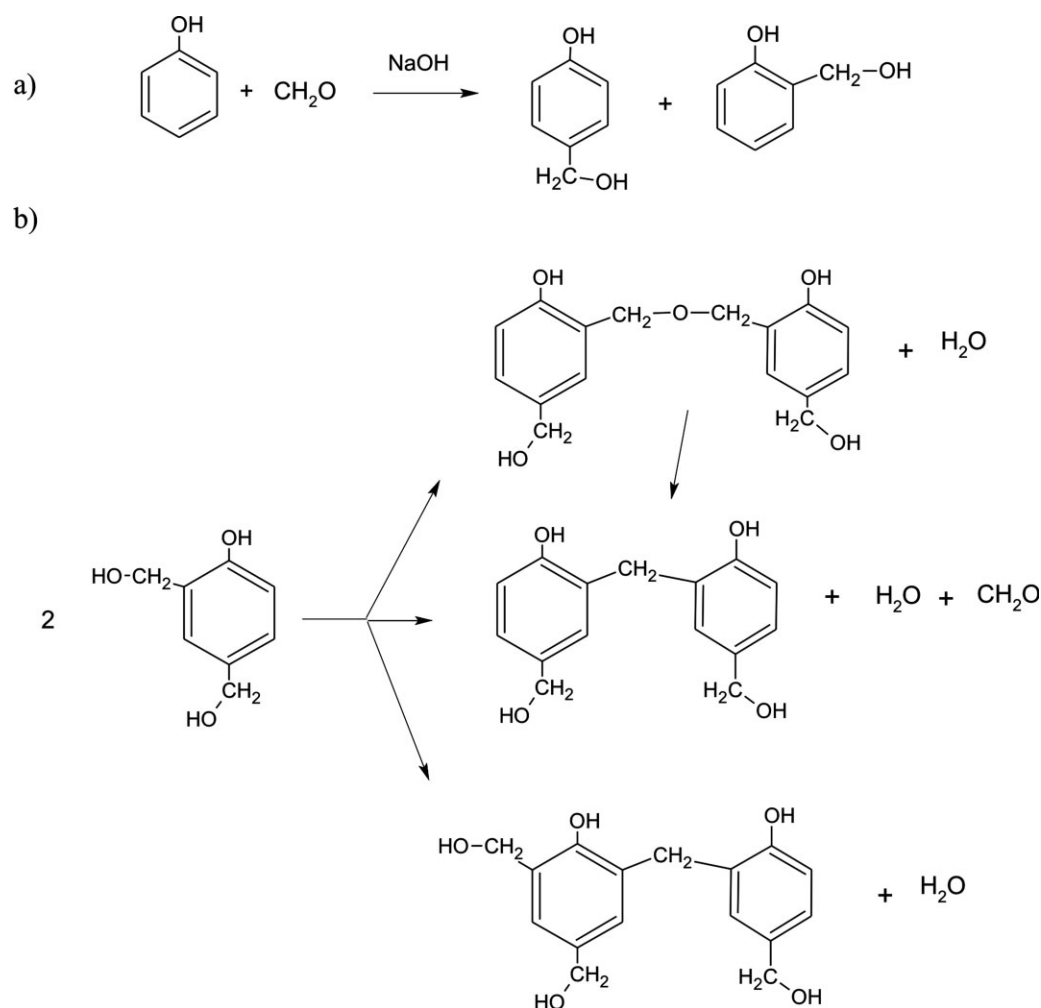
Figure 5 Reactions of addition (a) and condensation (b) between formaldehyde and phenol.

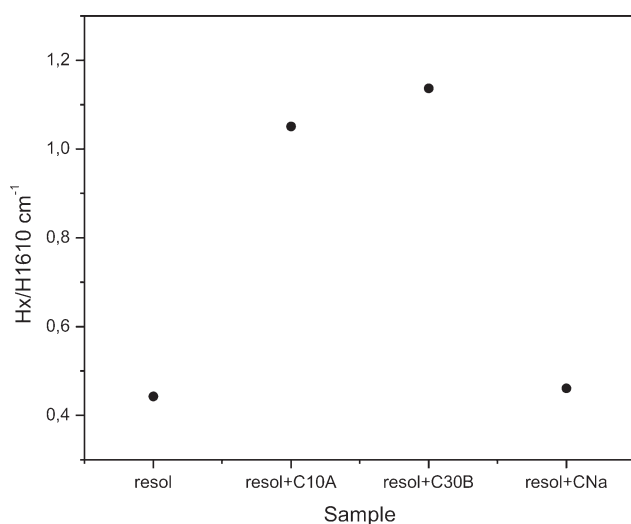Influence of void content on the adhesive strength was also observed in the previous work, where the composites were synthesized by intercalation of the prepolymer.[15] Under both conditions, the composites containing the modified MMTs showed higher quantity of voids than the composite containing the unmodified clay. It seems that part of the bubbles that are trapped during the crosslinking reactions could be due to the water evolved from the clay and in a lesser quantity to the decomposition of the surfactants. There were published several works where the thermal degradation of different clays was studied. It was reported[26] that the Na^+ montmorillonite loss mass in the temperature range between 100 and 300°C due to the evolution of free water and water

Figure 6 Relative quantity of OH groups in the samples, measured by FTIR.

TABLE III
Shear Stress and Void Content Measured in the Samples

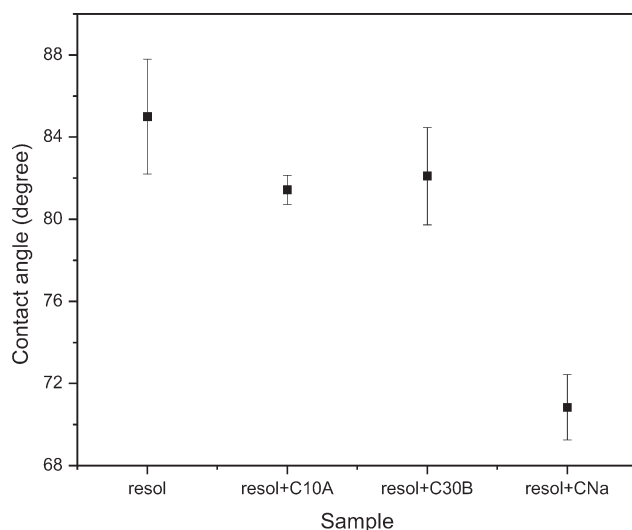| Sample	Shear stress (MPa)	Voids [%] (voids area/ total area)	Voids diameter mean (nm)
Resol	2.08 ± 0.15	–	–
Resol + CNa	2.79 ± 0.40	0.17	1.07 ± 0.51
Resol + C10A	2.27 ± 0.51	0.95	6.02 ± 1.53
Resol + C30B	2.12 ± 0.36	1.15	20.30 ± 7.61

Figure 7 Contact angle measured in the samples, using water as reference liquid.

from the interlayer region and then, the dehydroxylation of bounded hydroxyl groups of structural water occurs in the temperature range 500–1000°C. However, the onset decomposition temperature of the organically modified silicates was approximately 200°C. It has been proposed that the organic modifiers (quaternary ammonium salts) start decomposing releasing first the low molecular weight molecules, whereas the relatively high molecular weight may still exist between the interlayers until the temperature is high enough to lead to their further decomposition. Cui et al.[27] published a detailed study of the surfactant degradation analyzing the influence of the quantity and type of modifier on the nanocomposite thermal degradation. They concluded that several factors such as surfactant type and surfactant excess in the organoclay affect the thermal stability of the organoclays. The substituents on the ammonium cations may also influence their thermal stability. The degradation temperature increase with the addition of groups such as benzyl to the alkylammonium salts. The resol composites used in this work were cured at temperatures up to 190°C to be sure to obtain a totally cured material. Then, at the cure temperature the degradation of the surfactants should be low. However, the presence of more quantity of bubbles in the nanocomposites containing the OMS could be due to the water eliminated from the clay that was lost at lower temperatures, as explained earlier.

Polarity also influences the shear strength. The angles formed by a drop of water on the surface of the materials were measured (Fig. 7). The lower angle was obtained with the composite containing CNa indicating their higher affinity for water, then their higher polarity compared with the others speci-

mens. This could be due to the OH groups present in the surface of the clay layers. The composites with modified clays showed similar results among them, showing lesser polarity. The more polar material would have higher affinity with the polar metal surface.

CONCLUSIONS

Nanocomposites based on resol resin and different clays were obtained by in situ polymerization. Prepolymers were characterized and it was observed an increment in free formaldehyde content and in the viscosity with the addition of clay to the polymer. It was attributed to the entrance of part of phenol into the clay galleries both allowing the separation of the clay sheets and changing the formaldehyde to phenol molar ratio inside and outside the galleries.

The dispersion of montmorillonite in the cured composites was analyzed by XRD and TEM. It was observed that the better dispersed in the polymer was the unmodified clay CNa, whereas the modified clays showed a diminution in the width of the clay galleries compared with the pristine montmorillonites. This contraction was attributed to the loss of modifiers from the galleries or to the different rate of curing reactions inside and outside the interlayer space. In addition, a difference in the crosslinking density among the composites was observed. The composite containing CNa showed the higher crosslinked network, whereas the composites with C10A and C30B showed an even lesser crosslinked density than the pristine resol. It was attributed to the increasing in the rate of polymerization when the Na$^+$ is in the medium due to the formation of chelates. A similar behavior was obtained in a previous work when the nanocomposites were synthesized by mixing the clay with the prepolymer. The lesser crosslinking density observed in the nanocomposites containing the modified clays was attributed to the presence of the long carbon chains that increment the free volume of the system.

An increment in the polymer/aluminium joint adhesive strength was observed when clay was added to the polymeric matrix. It was related to the void content and the polarity of the samples. A higher void content and a low polarity produced a detriment in the shear stress. The composites containing CNa as nanoreinforcement showed the best adhesive behavior. Similar results were observed in a previous work using another way of synthesis.

As conclusion of the comparison of the two works, it could be stated that independently of the way of synthesis, the type of clay added to the polymer greatly influence the chemical structure and the final properties of the resol resin. Particularly, similar results were observed in the crosslinking density

and in the shear stress increment of the composites containing CNa synthesized by both methods. However, a poor dispersion of the modified clays was observed when the composites were obtained by in situ polymerization. Then, it seems that the best way to obtain the composites with modified clays is by mixing the MMTs with the prepolymer. However, similar results were obtained when the unmodified clay was added to the polymer both by mixing the clay with the prepolymer or by in situ polymerization.

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