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# Contents

# **Full Paper**

The properties of composites based on phenolic resins and different types of clays to be used as metal coatings is studied. It is found that the composite containing the clay without chemical modification showed the most strongly crosslinked chemical structure, the highest thermal resistance and the strongest adhesion to a metal substrate. Additionally, it was concluded that the type of modifier added to the clay strongly influences the chemical structure and the final properties of the material.



#### Influence of Clay Modification on the Properties of Resol Nanocomposites

L. B. Manfredi, D. Puglia, A. Tomasucci, J. M. Kenny, A. Vázquez\*

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# Influence of Clay Modification on the Properties of Resol Nanocomposites

Liliana B. Manfredi, Debora Puglia, Annalisa Tomasucci, José M. Kenny, Analía Vázquez\*

Two organically modified (Cloisite<sup>®</sup> 30B and 10A) and one unmodified clay (Cloisite<sup>®</sup> Na) were added to a resol-type phenolic prepolymer. The modified montmorillonites showed a better dispersion in the prepolymer. The dispersion of the clay, the chemical structure as well as the

thermal degradation behavior of the cured polymer and nanocomposites were studied. It was observed that the addition of Cloisite<sup>®</sup> Na leads to enhanced crosslinking of the cured polymer, leading to a higher activation energy for thermal degradation. The resol with Cloisite<sup>®</sup> 10A contained a higher percentage of voids, which seems to be one of the major factors that reduce hardness and adhesive strength when the nanocomposite was applied to a metal substrate.



# Introduction

Polymer nanocomposites based on layered silicates have 1 attracted considerable scientific and technological interest 2 during the recent past.<sup>[1-3]</sup> The technological interest 3 4 derived from the enhancements in barrier, thermal and mechanical properties of these materials with minimal 5 increase in density due to the low inorganic loading 6 required.<sup>[4]</sup> Then, an understanding of the changes in the 7 structure and properties of the polymers by the addition of 8

9 clay is essential to tailor nanocomposites for specific

#### L. B. Manfredi

Research Institute of Materials Science and Technology (INTEMA), National University of Mar del Plata, Juan B. Justo 4302, 7600, Mar del Plata, Argentina D. Puglia, A. Tomasucci, J. M. Kenny Materials Engineering Center, University of Perugia, Loc. Pentima Bassa 21, 05100 Terni, Italy A. Vázquez INTECIN, Facultad de Ingeniería, Universidad Nacional de Buenos Aires, Las Heras 2214, Buenos Aires, Argentina

E-mail: anvazque@fi.mdp.edu.ar

Macromol. Mater. Eng. 2008, 293, 000–000 © 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim applications. In addition, understanding the rheological 1 properties of polymer nanocomposites is crucial for 2 application development and understanding polymer 3 processability.<sup>[5]</sup> The rheological behavior of polymer/clay 4 nanocomposites is related to their microstructures show-5 ing enhanced viscoelastic properties compared to the neat 6 polymers, and exhibiting time and shear dependent 7 responses. This behavior was attributed to a percolated 8 network structure formed by clay platelets or tactoids.<sup>[6]</sup> 9

In recent years, thermosetting polymer/clay nanocom-10 posites have attracted more attention. Epoxy<sup>[7-14]</sup> poly-11 urethane,<sup>[15]</sup> unsaturated polyesters<sup>[16]</sup> and phenolic 12 resins<sup>[17-25]</sup> are the common matrices studied so far. The 13 studies about phenolic resins nanocomposites were made 14 on both novolacs and resols. The disadvantage of using 15 resols as matrix is their crosslinked structure that makes 16 the entrance of the chains into the clay galleries difficult 17 and consequently the intercalation or exfoliation of the 18 montmorillonite. In a previous work,<sup>[25]</sup> we obtained resol-19 layered silicate nanocomposites curing by means of acid 20 addition. It was found that the composites made by the 21 addition of organically modified montmorillonite showed 22



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a better dispersion of the clay in the polymer matrix than

2 those with unmodified montmorillonite. However, the

first one showed a less crosslinked structure than the neat
resol in the same conditions due to the interaction
between the modifier and the prepolymer.

6 Phenolic resins are one of the most used thermosetting 7 resins and the principal applications of these resins are due to their excellent thermal and chemical resistance.<sup>[26]</sup> 8 However, the addition of layered silicates to the phenolic 9 resins could increase their thermal resistance and mechan-10 ical properties for use in critical applications such as pipe 11 coatings in the oil industry and matrices of composites for 12 structural applications. 13

14 The aim of this work is to study the behavior of the 15 resol/clay nanocomposites before and after curing in order 16 to determine the structure/properties relationships of 17 these materials.

#### **Experimental Part**

#### Materials

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18 A resol-type phenolic resin was synthesized with a formaldehyde/ 19 phenol molar ratio (F/Ph) of 1.3. Formaldehyde water solution 20 (37 wt.-%) and phenol were placed in a reactor provided with 21 reflux condenser and a mechanical stirrer. The pH was set to 9.0 22 with NaOH solution (40 wt.-%) at the beginning of the reaction 23 and the mixture was maintained for 2 h at 90 °C. Then, boric acid 24 was used to neutralize the solution reaching a pH value in the 25 range of 6.8–7.0. The resol was kept at  $-10\,^\circ\text{C}$  until it was used. 26

Three types of montmorillonites were used: purified Cloisite<sup>®</sup> Na<sup>+</sup> (CNa) and the organically modified Cloisite<sup>®</sup> 30B and Cloisite<sup>®</sup> 10A (Southern Clay Products, USA). The characteristics of the modified clays are shown in Table 1.

The composites were obtained by adding 5 wt.-% of clay to the resol resin and then sonicated for 30 min at ambient temperature. After that, the mix was dehydrated in vacuum at 75–80 °C until total extraction of water. Then, the composite was applied over an aluminium sheet and cured by temperature in an oven following the cure cycle: 1 h at 50, 80, 100, 110, 130, 150 and 190 °C, with a heating rate of  $1 \, ^\circ C \cdot \min^{-1}$  between the different temperatures.

Table 1. Characteristics of the modified clays.

#### Method

Rheological measurements were made on an ARES 2 rheometer. Frequency sweep tests were performed from 1 to 100 shear rate values at 30 °C.

X-Ray diffraction analysis (XRD) of the composites was 4 performed in a Philips PW 1710 diffractometer (45 kV and 5 30 mA) at  $2^{\circ} \cdot \min^{-1}$  using Cu K<sub>\alpha</sub> radiation ( $\lambda = 1.54$  Å). 6

Transmission electron microscopy (TEM) was performed on a7JEOL 100 CX II, using an acceleration voltage of 80 kV. The8specimens were sectioned into ultra-thin slices (100 nm) at room9temperature, using a microtome.10

Dynamic degradation measurements were carried out using a11Seiko Instruments SII Exstar 6000. Tests were performed in a12dynamic mode in a nitrogen environment. Temperature programs13were run from room temperature to 900 °C at different heating14rates: 2, 5, 10, 15, 20 and 30 °C · min<sup>-1</sup>. The sample weight in all the15tests was approximately 10 mg.16

Fourier-transform infrared (FT-IR) spectra were obtained in a 17 Jasco 32 in attenuated total reflection (ATR) mode using powder 18 samples. For comparison purposes, the spectra were normalized 19 with the intensity of the band at 1610 cm<sup>-1</sup>. This band was 20 assigned to the stretching C=C of the benzene ring and its 21 intensity was expected to remain constant for all the samples.<sup>[27]</sup> 22

The contact angle determination was performed by the sessile 23 drop method. The contact angles made by the drops of two 24 25 reference liquids on the surfaces of plaques of the specimens were measured with a camera MV-50, zoom  $6\times$  and acquired with 26 27 the software Image NIH. At least five drops per liquid type were measured. The reference solvents used were ethylene glycol 28 (Aldrich, 99.1%) and diiodomethane (Aldrich, 99%). The total 29 surface energy of the materials and their polar and dispersive 30 components were determined by means of the Owens and Went 31 equation:[28] 32

$$0.5\gamma_2(1+\cos\theta) = (\gamma_1^d \gamma_2^d)^{1/2} + (\gamma_1^p \gamma_2^p)^{1/2}$$
(1)

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where 1 and 2 refer to the solid and liquid, respectively,  $\gamma^{d}$  is the 35 dispersive and  $\gamma^{p}$  the polar component of the surface energy, and  $\theta$  36 is the contact angle. From the contact angles made by two liquids 37 of known  $\gamma^{d}$  and  $\gamma^{p}$  (Table 2), it was possible to solve Equation (1)

Clay	Organic modifier	Concentration	Interlayer distance <i>d</i> <sub>001</sub>
		mequiv. per 100 g clay	Å
Cloisite <sup>®</sup> 30B (C30B)	H <sub>2</sub> C — CH <sub>2</sub> — OH H <sub>3</sub> C — N <sup>+</sup> — Т H <sub>2</sub> C — CH <sub>2</sub> —OH	125	18.5
Cloisite <sup>®</sup> 10A (C10A)		90	19.2
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*Table 2*. Surface energy components of probe liquids for contact angle measurements.<sup>[29]</sup>

	Total surface energy γ	Dispersive component y <sup>d</sup>	Polar component y <sup>p</sup>	
	$mN \cdot m^{-1}$	$mN \cdot m^{-1}$	$mN \cdot m^{-1}$	
Ethylene glycol	47.7	30.1	17.6	
Diiodomethane	50.8	48.5	2.3	

1 and infer  $\gamma_1^d$  and  $\gamma_1^p$  for the material. The total surface energy is 2 then estimated using the following equation:

$$\nu_1 = \gamma_1^d + \gamma_1^p \tag{2}$$

Scanning electronic microscopy (SEM) was performed on the
lateral surfaces of the specimens to analyze their void contents.
Polished lateral surfaces were coated with a 300 Å gold layer and
observed in a scanning electron microscope (JEOL JSM-6460LV).

The strength of the aluminium/adhesive joints was measured 10 using single lap-shear specimens following ASTM D-1002-94. Test 11 was performed with an Instron 4467 machine, at ambient 12 temperature and at a crosshead speed of 1.25 mm · min<sup>-1</sup>. Six 13 specimens were tested for each composition. The aluminium 14 surfaces at the interface sides were abraded using grid 500 and 15 1000 sandpapers and cleaned with acetone prior to the resin 16 application. The resin was applied as a thin layer of 0.60 mm 17 between the aluminium arms. The assemblies were joined and 18 fastened between two glasses and the curing profile applied. 19 Spacers were used to ensure the desired bond thickness. 20

Hardness measurements were performed with a NanoTest
nanoindentation module manufactured by Micro Materials Ltd.
The specimens used for the tests were cut from 2 mm thick
plaques. The measurements were made at room temperature at
different depths from 200 to 1400 nm and five independent

indentations were carried out on each sample.

# **Results and Discussion**

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Rheometry is a powerful tool for studying the micro-27 structures of nanocomposites such as the dispersion of 28 clay in the polymer as well as the effect of silicate layers on 29 the motion of polymer chains.<sup>[30]</sup> The resol prepolymer and 30 the nanocomposites were studied in order to analyze the 31 degree of dispersion of the clay in the resin. Rheological 32 measurements on the nanocomposites of resol with C30B 33 and C10A showed a pseudoplastic behavior, the viscosity 34 diminished with increase in the shear rate, probably due to 35 the alignment of the clay sheets. The resol resin alone and 36 the composite with CNa showed a Newtonian behavior, a 37 constant viscosity at varying shear rates (Figure 1). It was 38 observed<sup>[31-33]</sup> that at low shear rates, the addition of 39 small amounts of clay to the polymer results in nonNewtonian behavior as well as a considerable enhancement in the shear viscosity. However, with increase in rate, the silicate layers exhibit the ability to align parallel to the flow field and this is reflected in the linear viscoelastic measurements after alignment comparable with those of the pure polymer.

The region at the lowest shear rates of the curves in Figure 1 was fitted to the following power law equation:

$$\eta = A \gamma^{(n-1)} \tag{3}$$

where  $\eta$  is the apparent viscosity, A a sample specific preexponential factor;  $\gamma$  the shear rate and *n* the shearthinning exponent. At low shear rates the rheological response is most representative for the unperturbed, i.e., unoriented, platelet structure in the composite. Wagener and Reisinger<sup>[34]</sup> demonstrated that the shear-thinning exponent can be used for direct comparison of the exfoliation quality of nanocomposite samples. The respective values of the exponent n are 0.35 and 0.43 for the composites with C30B and C10A. Also exfoliated samples display a lower magnitude of  $n_{i}^{[34]}$  the results obtained should indicate that the composites with the modified clays present a better dispersion of the clay than the other composite made with the unmodified montmorillonite CNa. The differences observed between the composites containing C30B and C10A could be explained by the different chemical structures of the clay modifiers and taken into account the chemical structure of the resol prepolymer. Resol type phenolic resins are obtained from the reaction between phenol and formaldehyde using a formaldehyde to phenol molar ratio higher than 1, under basic medium. In alkaline conditions, phenol and formaldehyde are present in the form of phenolate and



Figure 1. Viscosity versus shear rate for the composites.

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Figure 2. Reactions between phenol and formaldehyde: (a) addition and (b) condensation.

methylene glycol, respectively. The initial reaction is the 1 2 addition of formaldehyde to phenol (Figure 2a) and thereafter, condensation between the substituted phenol 3 4 rings (Figure 2b) occurs. Consequently, methylolphenols 5 are the predominant intermediate compounds in the prepolymer. They are hydrophilic compounds with reac-6 tive OH groups and they posses free reactive positions in 7 8 the benzene ring. These reactive OH groups of the resol could interact forming hydrogen bridges with the OH ends 9 present in the aliphatic chain of the C30B clay modifier, 10 explaining the better dispersion of the C30B in the 11 prepolymer. In addition, considering that the C30B has 12 an aliphatic chain with OH ends and the C10A has an 13 14 aromatic ring, it could be possible that the compound on 15 the C30B produces a lubricant effect allowing the platelets to move one over the other and then favoring more 16 17 intercalation.

18 The dispersion of the clay into the crosslinked resol (solid) was analyzed by means of X-ray diffraction. The 19 XRD patterns of the clays and the resol nanocomposites are 20 shown in Figure 3. The 001 diffraction peak of the clays 21 22 was more clearly observed in the composite containing C30B. Neither in the composite containing CNa nor in the 23 24 one containing C10A, the basal peak of the clay was 25 observed, indicating a better dispersion of the clay in the 26 cured resin. A small peak at  $2\theta = 4.8$  was observed in the

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Macromolecular Journals pattern of the composite with CNa, 1 showing a displacement to low angles 2 with respect to the basal peak of the CNa. 3 It indicates that the galleries enlarge their 4 distance without reaching complete exfo-5 liation. Additionally, a broad band at 6 lower angles was observed signifying that 7 in all the studied nanocomposites the clay 8 layers enlarged their distance but in an 9 inhomogeneous way. There is wide range 10 of different interlayer spacing between 11 the clay layers in the composites. 12

To visualize the clay layer distribution 13 in the polymer matrix, TEM microphoto-14 graphs were obtained (Figure 4). Usually, it 15 is useful to use XRD technique together 16 with TEM is useful to study the clay 17 interlayer spacing in nanocomposites 18 because TEM allows direct observation 19 of the microstructure of the material. The 20 TEM photographs (Figure 4) revealed an 21 intercalated structure of the composites in 22 accordance with the XRD spectra results. 23 Upon comparing them, the composite 24 containing C10A showed a more disor-25 dered structure of the clay sheets 26 (Figure 4a). Their arrangement is similar 27 to an exfoliated distribution in some 28

regions where the sheets are not all oriented in the same 29 direction. Inversely, the composites containing CNa and 30 C30B showed a well-ordered distribution of the clay sheets 31 forming a multilayer morphology with alternating poly-32 meric and inorganic layers (Figure 4b and c). It is the typical 33 arrangement of an intercalated structure. This distribution 34 is also observed in some regions of the composite 35 containing C10A. The clay sheets showed a curved pattern 36





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*Figure 4.* TEM photograph of the nanocomposites containing the clays: (a) C10A; (b) CNa; (c) C30B.

specially those from C30B and CNa. The flexibility of the
 layers was attributed to the large aspect ratio and very low
 thickness of the clay sheets.<sup>[20]</sup>

The chemical structure of the resol resin was studied by 4 FTIR and the influence of the addition of clay to the resol in 5 its structure was analyzed. The FTIR spectra in the range of 6 950–1950  $\text{cm}^{-1}$  are shown in Figure 5. The condensation 7 reactions from the methylolphenols compounds produce 8 ether and methylene bridges. The band at 1100 cm<sup>-1</sup> 9 corresponds to ether bridges and it is not so high, as a 10 11 consequence they are not the main bridges formed during 12 the crosslinking reactions. Some differences arisen in the

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Figure 5. FTIR spectra in the 950–1950  $\text{cm}^{-1}$  range for the resol and its composites.

bands at 1 480 and 1 450 cm<sup>-1</sup> that corresponds to the o-p' and p-p' methylene bridges, respectively, formed during the crosslinking of the resol. Those bands are characteristic of the deformation vibrations of -CH-bonds in -CH<sub>2</sub>-groups.<sup>[27]</sup> The relative quantity of methylene bridges, obtained from the normalized spectra of each material, is shown in Figure 6. It was observed that the resol containing CNa showed the higher bridges content, than the higher crosslinking density. It could be due to the higher concentration of cations Na<sup>+</sup>. It was demonstrated that the Na<sup>+</sup> are able to form an intermediate chelate,<sup>[35]</sup>





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thus favoring the addition of formaldehyde to the phenol 1 2 ring. The effect of increase in the amount of sodium hydroxide basically affects the activation and the rate of 3 polymerization reaction.<sup>[36]</sup> On the other hand, the 4 5 nanocomposite containing C30B showed a similar bridge 6 content than the resol, while the resol + C10A showed a 7 slightly higher bridge content. The difference of crosslinking density between the CNa and the other modified 8 9 clays (C10A and C30B) is due to the long chain of the organic compounds which produces a higher free volume. 10

Figure 7 shows the relative quantity of primary OH from 11 the methylol groups, measured in the band at  $1015 \text{ cm}^{-1}$ . 12 The methylols are formed during the addition reaction of the 13 formaldehyde to the phenol, and thereafter the condensa-14 tion between the substituted phenol rings occurs.<sup>[26]</sup> The 15 relative quantity of primary OH is in agreement with the 16 crosslinking density (Figure 6). These results indicate that 17 the chemical structure of the resol is influenced by the 18 presence of the clay. Additionally, the final crosslinked 19 structure depends also on the type of organic modifiers that 20 21 the clay contains.

22 At this point, it is necessary to clarify that there are 23 different results of intercalation from the liquid to the solid state in resol/clay nanocomposites. The behavior could be 24 25 the results of three factors that should be taken into 26 account: the compatibility between resol and clay, the way 27 to measure the intercalation and the change of the intercalation due to shrinkage during curing reactions. 28 29 The results could be related to the free functional groups that are in the liquid resol after the reaction of 30 methylolation and in the solid state after the reaction of 31 32 crosslinking or condensation. In the liquid state, the resol 33 has many OH groups from the methylol phenols, and in the solid state the OH disappears to form methylene 34 35 bridges. Under this aspect, the C30B is more compatible in

the liquid state than the C10A. The rheological measure-1 ments were done using the prepolymer before curing, in 2 the liquid state and under shear. In that situation there is 3 also water in the medium affecting the dispersion of the 4 clay. The dispersion of the modified montmorillonites was 5 favored in the liquid state, which means that the oligomers 6 are allowed to enter easily into their higher galleries as 7 compared to the unmodified clay. Another explanation 8 could be the shrinkage that the C30B-resol suffered during 9 the crosslinking reaction. Wu et al.<sup>[38]</sup> proposed that the 10 organic modifiers can be partially excluded from the 11 galleries or the galleries collapse during polymerization, 12 leading to the contraction of interlayer spacing. These 13 results are in agreement with the result that the resol with 14 C10A presented a higher methylene bridge content than 15 the resol with C30B, and the last one could shrink more 16 easily during the curing reactions. 17

In addition, the thermal degradation of the composites 18 was studied by TGA. Figure 8 shows the time derivative of 19 the loss mass (DTG) curves for the resol plus and CNa at 20 different heating rates. In those curves three main peaks 21 can be distinguished. A similar pattern was obtained in a 22 previous work<sup>[39]</sup> where the thermal degradation of resol 23 of different formaldehyde/phenol molar ratios was 24 studied. The first peak was attributed to the loss of water 25 and oligomers. The other two peaks belong to the thermal 26 fragmentation zone where scission of side and main 27 polymer chains as well as further crosslinking takes place. 28 The two peaks in the region between 350 and 650 °C were 29 deconvoluted. Flynn and Wall kinetic thermal degradation 30 model<sup>[40]</sup> was applied to the experimental data obtained 31 for the resol and the composites in order to calculate the 32 activation energy of the degradation process. This method 33 allows the determination of the activation energy from 34 dynamic tests by plotting the log of the heating rate as a 35



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function of the inverse of the temperature, at different 1 conversions. The calculus of the activation energy revealed 2 that it changed with the conversion, a higher conversion 3 4 leads to a higher activation energy. It is in accordance with the increase in the crosslinking density when the 5 temperature increases. In the previous work,<sup>[39]</sup> we tried 6 to understand if each peak is related with different 7 reactions that occur during the thermal degradation 8 process. We concluded that all of the products from the 9 degradation reactions proposed were present in the 10 residue obtained at 400 and 600 °C. Then, all the reactions 11 are superimposed along the thermal fragmentation zone. 12 The activation energy obtained for each material 13 applying the Flynn and Wall method is shown in 14 Figure 9 and it was observed that the resol containing 15 CNa was the one that showed the highest activation 16 energy for the second peak while the composite with C30B 17 was the one with the lowest value. These results are in 18 accordance with the crosslinking density observed by FTIR 19 (Figure 6) because the material with a more crosslinked 20 21 structure needs higher activation energy for their thermal degradation. The FTIR results of the other samples could 22 23 also be correlated with the activation energy behavior.

In order to evaluate the hydrophilic character of the 24 materials, the surface tension and their polar and dispersive 25 components were calculated by the sessile drop method. 26 The results are shown in Figure 10. It was observed that 27 the resol showed the highest polar component of the surface 28 tension among the materials studied. In addition the 29 polarity was calculated as  $x^p = \gamma^p / \gamma$ ,<sup>[29]</sup> and the results 30 are shown in Figure 11. The polarity of the nanocomposites 31 studied containing the different clays follows the order: 32 resol + can > resol + C10A > resol + C30B.33





*Figure 10.* Surface tension and their components for the resol and their composites.

The percentage of voids present in the samples was measured from the SEM micrographs by means of the software Image Pro Plus. The void content was calculated and the results are shown in Table 3. It was observed that the composite containing C10A showed the higher quantity of voids, whereas the CNa and C30B contain a lesser percentage of voids.

The single-lap shear test was used to evaluate the strength of the adhesive joints between the resins and the metal substrate. Table 3 shows the average shear stress obtained for the different materials. It can be observed that the addition of clay to the resol improves the strength of the adhesive joint up to 80%. Fogelström et al.<sup>[41]</sup> also found that the adhesion of acrylated polyester coatings to metal was enhanced by the addition of clay. It was



Figure 11. Polarity of the resol and different composites.

resol and their composites obtained by the Flynn and Wall method.

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Table 3. Percentage of voids	and shear s	tress measured	by single-
lap shear.			

Void area/ total area	Shear stress	
%	MPa	
_	$2.08 \pm 0.15$	
2.21	$3.74 \pm 0.40$	
2.34	$3.27 \pm 0.21$	
3.48	$2.56 \pm 0.31$	
	Void area/ total area % - 2.21 2.34 3.48	

1 observed that the adhesion of the polymer to the metal 2 substrate depends on the polarity and void content of the 3 coating. It was shown in Table 3 that the materials with higher quantity of voids are those that showed a lesser 4 5 adhesive strength. On the other hand, the polarity also 6 influences the adhesion because the metal has a polar 7 surface having affinity with polar polymers. The type of 8 montmorillonite present in the polymer modifies their 9 polarity in the surface. The Na/MMT has higher polarity 10 than the modified MMTs because the modifiers have the tallow containing a hydrophobic carbon chain with up to 11 18 carbon atoms. This causes the diminution of the 12 polarity in the nanocomposites containing modified clays 13 with respect to the ones containing Na/MMT. The 14 nanocomposite containing CNa showed the highest 15 polarity as well as the best adhesion to the metal. 16

The elastic modulus and the hardness of the resol and the 17 nanocomposites were measured in a nanoindenter at 18 19 different depths. It was observed that the elastic modulus of the resol and the composites with CNa and C30B was 20 similar among them at the different depths measured 21 (Figure 12). However, the nanocomposites containing C10A 22 showed a lower value and an important diminution in the 23 24 value with the increase in of depth. The elastic modulus 25 depends on the packaging density, free volume as well as volume fraction of voids. On the other hand, it was observed 26 that the composite containing C10A showed the lowest 27 hardness value at the different depths measured (Figure 13). 28 29 These results reveal an inhomogeneous distribution of the 30 clay along the coating and it seems that there is a higher concentration of clay C10A near the surface of the 31 32 composite because of the higher hardness value at lower depths. The void content could also be related to these 33 34 results because the composite containing C10A was the 35 one that showed the higher void content. It could be due to the higher viscosity of this composite compared to the 36 37 others at the beginning of the curing (Figure 1). The higher 38 initial viscosity leads to a structure with a higher void content because it is more difficult for the bubbles to move 39 40 inside the polymer. In addition, a higher concentration of 41 voids in the down region near the metal substrate was

8 Elastic modulus (GPa) 6 5 reso o resol + CNa 4 resol + C30B resol + C10A з 200 400 600 800 1000 1200 1400 Depth (nm)

*Figure 12.* Elastic modulus as a function of the depth for the resol and the nanocomposites.

observed in all of the composites. The bubbles were not1able to get away during the curing of the resin in the2surface. The other two nanocomposites showed a higher3hardness than the resol, indicating that the addition of clay4enhances this property of the polymer.5

The results obtained in the present work could be 6 compared with the ones published previously<sup>[25]</sup> where 7 resol nanocomposites were also studied. The main 8 difference between both works was the way of curing 9 the polymer. While in the previous investigation an acid 10 catalyst was used, only temperature was applied for curing 11 the resol in the present one. The nanocomposite contain-12 ing the unmodified clay CNa results in the highest 13 crosslinking density network in both curing conditions 14



*Figure 13.* Hardness as a function of the depth for the resol and the nanocomposites.

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due to its effect as a catalyst. Compared with the other 1

- organically modified clay nanocomposites, the less cross-2
- linked network obtained with the addition of C30B or C10A 3
- 4 was attributed to the long chain of the chemical groups of
- 5 these compounds.

### Conclusion

- 6 Nanocomposites were obtained by the addition of
- different montmorillonites to a resol type phenolic resin. 7
- Power law equation was applied to the rheological results 8 and it was found that the modified montmorillonites were 9
- 10 better dispersed in the polymeric matrix. However, from
- the XRD patterns and TEM photographs, C10A and CNa 11
- 12 seem to be better dispersed in the cured polymer. The
- analysis of this different behavior should be done taking 13
- into account not only the type of clay, but also the free 14
- functionalities on the resol in the liquid and in the solid 15
- state. Also the effect of shrinkage during the crosslinking 16
- 17 reactions should be taken into consideration.
- Additionally, it was observed that the presence of CNa 18 19 leads to a higher crosslinked chemical structure as well as a better thermal resistance than the resol. The polarity and 20 21 the void content of the samples were also analyzed and 22 these results were related with the adhesive strength of 23 the polymer/aluminium joint. It was observed that the sample containing C10A showed a lesser shear stress, 24 measured by single-lap shear test and it was the sample 25 with a higher void content. Similarly, it showed a lower 26 hardness and an elastic modulus value compared with the 27 28 other composites. It was concluded that the type of clay added to the resol influences their chemical structures and 29 properties. Among the montmorillonites studied, CNa 30 seems to be the one more adequate because of the 31 enhancement in the thermal resistance and adhesive 32 properties compared to the resol. In addition, it showed a 33
- slight increment in the hardness value due to its higher 34
- 35 crosslinking density.
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- 42 [1] P. C. LeBaron, Z. Wang, T. J. Pinnavaia, Appl. Clay Sci. 1999, 15, 43 11.
- 44
- [2] S. S. Ray, M. Okamoto, Prog. Polym. Sci. 2003, 28, 1539.

- [3] F. Hussain, M. Hojjati, M. Okamoto, R. E. Gorga, J. Compos. Mater. 2006, 40, 1511.
- [4] J. Ren, A. S. Silva, R. Krishnamoorti, *Macromolecules* 2000, 33, 3739
- [5] J. Zhao, A. B. Morgan, J. D. Harris, Polymer 2005, 46, 8641.
- [6] J. A. Lee, M. Kontopoulou, J. S. Parent, Polymer 2004, 45, 6595.
- [7] X. Kornmann, H. Lindberg, L. A. Berglund, Polymer 2001, 42, 1303
- [8] J. Park, S. C. Jana, Macromolecules 2003, 36, 8391.
- [9] J. Park, S. Jana, Polymer 2004, 45, 7673.
- [10] W. Liu, S. V. Hoa, M. Pugh, Compos. Sci. Tech. 2005, 65, 307.
- [11] M. Zammarano, M. Franceschi, S. Bellayer, J. W. Gilman, S. Meriani, Polymer 2005, 46, 9314.
- [12] G. Camino, G. Tartaglione, A. Frache, C. Manferti, G. Costa, Polym. Degrad. Stab. 2005, 90, 354.
- [13] B. Qi, Q. X. Zhang, M. Bannister, Y.-W. Mai, Compos. Struct. 2006. 75. 514.
- [14] C. K. Lam, K. T. Lau, Mater. Lett. 2007, 61, 3863.
- [15] C. H. Dan, M. H. Lee, Y. D. Kim, B. H. Min, J. H. Kim, Polymer 2006, 47, 6718.
- [16] D. J. Suh, Y. T. Lim, O. O. Park, Polymer 2000, 41, 8557.
- [17] M. H. Choi, I. J. Chung, J. D. Lee, Chem. Mater. 2000, 12, 2977.
- [18] H. Y. Byun, M. H. Choi, I. J. Chung, Chem. Mater. 2001, 13, 4221.
- [19] Z. Wu, C. Zhou, R. Qi, Polym. Compos. 2002, 23, 634.
- [20] H. Wang, T. Zhao, L. Zhi, Y. Yan, Y. Yu, Macromol. Rapid Commun. 2002, 23, 44.
- [21] M. H. Choi, I. J. Chung, J. Appl. Polym. Sci. 2003, 90, 2316.
- [22] H. Wang, T. Zhao, L. Zhi, Y. Yan, Y. Yu, J. Appl. Polym. Sci. 2004, 92, 791.
- [23] M. Kato, A. Tsukigase, A. Usuki, T. Shimo, H. Yazawa, J. Appl. Polym. Sci. 2006, 99, 3236.
- [24] M. López, M. Blanco, J. A. Ramos, A. Vazquez, N. Gabilondo, J. J. del Val, J. M. Echeverría, I. Mondragón, J. Appl. Polym. Sci. 2007. 106. 2800.
- [25] L. B. Manfredi, D. Puglia, J. M. Kenny, A. Vázquez, J. Appl. Polym. Sci. 2007, 104, 3082.
- [26] A. Gardziella, L. A. Pilato, A. Knop, "Phenolic Resins", Springer-Verlag, Berlín, Heidelberg 2000.
- [27] C. Rockniak, T. Biernacka, M. Skarzynski, J. Appl. Polym. Sci. 1983, 28, 531.
- [28] W. Gutowski, in: "Fundamentals of Adhesion", L.-H. Lee, Ed., Plenum Press, New York 1991, Chapter 2, p. 130.
- [29] R. N. Shimizu, N. R. Demarquette, J. Appl. Polym. Sci. 2000, 76, 1831.
- [30] D. Wu, C. Zhou, X. Fan, D. Mao, Z. Bian, Polym. Degrad. Stab. 2005, 87, 511.
- [31] P. F. Luckham, S. Rossi, Adv. Colloid Interface Sci. 1999, 82, 43.
- [32] Y. H. Hyun, S. T. Lim, H. J. Choi, M. S. Jhon, Macromolecules 2001. 34. 8084.
- [33] R. Krishnamoorti, K. Yurekli, Colloid Interface Sci. 2001, 6, 464.
- [34] R. Wagener, T. J. C. Reisinger, Polymer 2003, 44, 7513.
- [35] M. F. Grenier-Loustalot, S. Larroque, D. Grande, P. Grenier, D. Bedel, Polymer 1996, 37, 1363.
- [36] M. F. Grenier-Loustalot, S. Larroque, P. Grenier, Polymer 1996, 37. 639.
- [37] T. Holopainen, L. Alvila, J. Rainio, T. Pakkanen, J. Appl. Polym. Sci. 1998, 69, 2175.
- [38] Z. Wu, C. Zhou, R. Qi, Polym. Compos. 2002, 23, 634.
- [39] D. Puglia, J. M. Kenny, L. B. Manfredi, A. Vázquez, Mater. Eng. 2001, 12, 55.
- [40] J. H. Flynn, L. A. Wall, Poly. Lett. 1966, 4, 323.
- [41] L. Fogelström, P. Antoni, E. Malmström, A. Hult, Prog. Org. Coat. 2006, 55, 284.

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