Synthesis and Characterization of Resol-Layered Silicate Nanocomposites

M. López,[1] M. Blanco,[1] J. A. Ramos,[1] A. Vazquez,[1] N. Gabilondo,[1] J. J. del Val,[2]
J. M. Echeverría,[3] I. Mondragon[1]

[1]Materials and Technologies' Group, Escuela Politécnica, Department of Chemical and Environmental Engineering,
Universidad País Vasco/Euskal Herriko Unibertsitatea. Pza. Europa 1, 20018 Donostia-San Sebastián, Spain
[2]Departamento de Física de Materiales, Univ. País Vasco, Apdo. 1072, 20080 Donostia-San Sebastián, Spain
[3]Hexion Specialty Chemicals Ibérica Ctra. Navarra, Epele 39, E-20120 Hernani (Gipuzkoa) Spain

ABSTRACT: Resol-layered silicate nanocomposites were synthesized by intercalative polymerization of phenol and formaldehyde using layered clays such as an aminoacid-modified montmorillonite (MMT) and a commercial modified MMT (Cloisite 30B). The composites were prepared by a sequential process in which one of the reactives of the phenolic resin was reacted with the organosilicate and subsequently cured with triethylamine. The nanocomposites were studied by means of X-ray diffraction, atomic force microscopy, and thermogravimetric analysis. Results show a strong clay composition dependence on the intercalation state. The composite of resol with 2 wt % aminoacid-modified MMT content has the best dispersion of clay layers. Thermal stability of nanocomposites was slightly increased in comparison with the neat resol. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 2800–2807, 2007

Key words: resols; nanocomposites; montmorillonite

INTRODUCTION

During decades conventional fillers, such as minerals, metals, or fibers, have been added to polymers to produce composites with the aim of improving mechanical and thermal properties. In recent years, research focusing on nanocomposites employing nanofillers, has resulted in unexpected property improvements with the addition of a small amount of filler.[1–8] Polymer layered silicate nanocomposites based on montmorillonite (MMT) have attracted a great deal of attention because of the enhanced properties in mechanical, thermal, barrier, and clarity properties without a significant increase in density, which is not possible with conventional fillers. These enhanced properties are presumably a result of the nanometer size, large aspect ratio, and large surface area of the silicate layers.

MMT is a layered silicate belonging to the smectite group of phyllosilicate minerals. MMT occurs naturally as a sequence of stacked layers of 1.0–1.5 nm thick. These layers organize themselves to form stacks with a regular van der Waals gap between them, called interlayer. Isomorphic substitution within the layers generates a negative charge defined through the cation-exchange capacity (CEC). This excess of negative charge is balanced by small and easily hydrated cations (Na^+, Ca^{2+}) that give the MMT the ability to absorb large amounts of water and other liquids. The liquid is sorbed onto, or hydrates, the layers at the interlayer cation site causing swelling. To render these hydrophilic phyllosilicates more organophilic, these hydrated cations can be exchanged with cationic surfactants such as alkylammonium or aminoacids.[9–14] The modified clay being organophilic, its surface energy is lowered thus being more compatible with polymers.

The dispersion of clay particles in a polymer can result in the formation of three kinds of composite materials: conventional composites containing clay tactoids and intercalated or exfoliated nanocomposites. The last type could be the most interesting for the improvement of properties due to the homogeneous dispersion of the clay and to the huge interfacial area between polymer and clay. The dispersion meanly depends on the interactions between the polymer and the clay.

Phenolic resins have been widely used due to their excellent ablative properties, structural integrity, thermal stability, and solvent resistance that make them appropriate for thermal insulation materials, wood products industry, coatings, molding

TABLE I
Final Characteristics of Resol-Clay Composites and Neat Resol

Designation	Dilutability in water (1g/1g)	Solid content (%)
Res	1.2	76.0
Phe-1	0.86	78.5
Phe-2	0.92	81.1
Phe-4	1.02	80.7
C1	1.01	80.0
C2	0.81	78.6
R2Na	1.12	81

compounds, foundry, and composite materials.[15–19] However, only a few studies have been performed with phenolic resins in the nanocomposite field because their three-dimensional molecular structure that may avoid the exfoliation of the clay even when they are not crosslinked.[20–28]

In this work, resol type phenolic resin/layered silicate nanocomposites have been synthesized by monomer intercalation to overcome the structural problem of MMT dispersion and exfoliation in phenolic resins. The study was focused on the modification of the MMT and the following cure reactions to improve the interactions between the modifiers and the phenolic resin. MMT has been modified by using an aminoacid, phenylalanine, (PheMMT), with the aim of inducing condensation reactions between the carboxyl end group of the phenylalanine and the hydroxyl groups of the formaldehyde for improving the compatibility with the phenolic matrix. Morphology, thermal behavior, and stability have been studied by means of atomic force microscopy (AFM), wide angle X-rays measurements (WAXS), and thermogravimetric analysis (TGA).

EXPERIMENTAL

Cloisite®-Na$^+$ (Na$^+$MMT), an untreated Na$^+$-MMT with a CEC of 96.4 mequiv/100 g and Cloisite 30B,

an organic treated MMT with methyl tallow bis-2-hydroxylethyl quaternary ammonium (90 mequiv/100 g clay), were purchased from Southern Clay Products. Phenylalanine (Phe) was purchased from Aldrich and used for modifying Na-MMT. Phenol was kindly supplied by Hexion Specialty Chemicals Ibérica and formaldehyde (35–40% aqueous solution) and triethylamine (TEA), used as catalyst, were purchased from Panreac and used without further purification.

The preparation of MMT modified by phenylalanine was based on a method of Pucciariello et al.[29] A solution of protonated phenylalanine was prepared by adding 5.75 g of HCl (37N) in 50 mL of distilled water to 3.8 g of phenylalanine by further heating the suspension under reflux at 100°C for 3 h. The solution obtained was gradually added to 1000 mL of a Na$^+$MMT (10 g) aqueous suspension, previously stirred during 24 h at 100°C under reflux. The mixture was then stirred under reflux at 100°C for an additional 14 h. The cation-exchanged silicate was collected by filtration, suspended in hot water, and stirred for 1 h. To ensure complete removal of chloride ions, the precipitate was repeatedly washed until no further formation of AgCl was observed after addition of 0.1N AgNO$_3$ to the washing water. The product was finally filtered and dried in vacuo at 85°C during 72 h. The organically modified clay underwent then a new treatment. Depending on the weight percent of the organoclay in the composite, different amounts of Phe-MMT were sonicated in formaldehyde solution (15 mL) during 50 h to prevent layered silicates from aggregation.[2] During the process, Phe-MMT-formol dissolution was treated with sulphuric acid under reflux at 100°C during 3 h to condensate the carboxyl end group of the phenylalanine and the —OH groups of the formaldehyde in aqueous solution. The product of this treatment is named PheMMT-ac-formaldehyde.

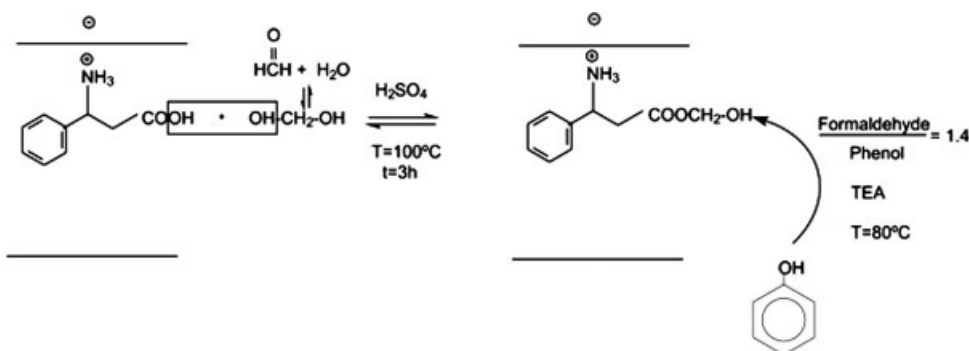For the case of Cloisite 30B, the clay underwent the same treatment but now with the aim of promoting

Figure 1 Condensation reaction of carboxyl end group of phenylalanine and —OH groups of formaldehyde in aqueous solution.
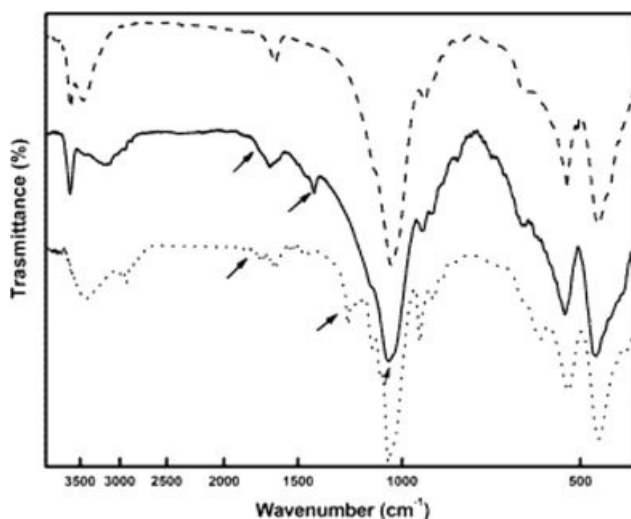
Figure 2 FTIR spectra of Na$^+$MMT (----), PheMMT (—) and PheMMT-ac-formaldehyde (·····).
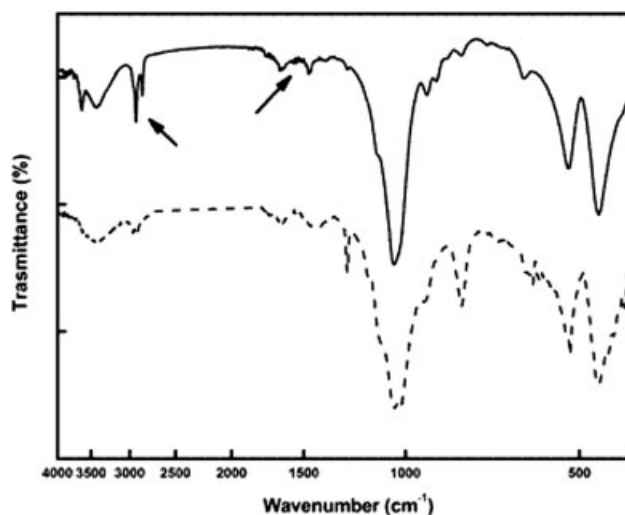

Figure 3 FTIR spectra of Cloisite 30B (—) and Cloisite 30B-ac-formaldehyde (----).

the condensation reaction between the —OH end group of the Cloisite 30B and the —OH groups of the formaldehyde solution.

Prepolymers were synthesized by mixing the previously obtained formaldehyde solutions of Phe-MMT and Cloisite 30B with formaldehyde and phenol to work with a formaldehyde/phenol molar ratio 1.4. The mixtures were placed in a 500 mL five necked flask equipped with a thermometer, stirrer, and refrigeration column.[16–19] The pH of formaldehyde/phenol mixture was then adjusted to 8.0 with TEA while it was stirred vigorously at room temperature. The mixture was heated to 80°C and stirred during reaction. Evolution of condensation was monitored according to the change in solubility. The reaction was stopped when the resin showed a 1/1 (g/g) dilutability in water. The product was then dehydrated in vacuo in a rotational evaporator at 45°C to a solid content of 75–82 wt %.

The resin was cast in a rectangular glass mold that was pretreated with an antiadhesion agent, and preheated to the cure temperature. The resins were then cured at 95°C overnight, 2 h at 115°C, 2 h at 150°C, and 1 h at 195°C.

After postcuring, the samples were slowly cooled to room temperature and then separated from the glass. Neat resol (Res) and resol in presence of unmodified MMT (RNa) were synthesized and postcured following the same conditions that the modified resins. The final properties of the obtained resin are given in Table I.

Samples were designed as Phe-i, Ci, and RiNa being i the weight percent of modified MMT.

Fourier transform infrared spectroscopy (FTIR) was used to follow the reaction between the carboxyl (—COOH) end group of the phenylalanine and the

—OH groups of the formaldehyde in aqueous solution. Infrared spectra on KBr pellets were performed at 100°C to maintain dry samples. Spectra were carried out in a Nicolet Magna-IR System 750 spectrometer using a heating chamber. Spectra were taken with a 2 cm^{-1} resolution at a wavenumber range from 4000 to 400 cm^{-1}.

WAXS measurements were carried out with a powder difractometer Philips, equipped with a graphite monochromator and an automatic divergence slit, using Cu Kα radiation ($\lambda = 1.54$ Å).

Morphologies of the nanocomposites were investigated by transmission optical microscopy using an Olimpus BH-2 optical microscope and by AFM using a Nanoscope IIIa, Multimode ^{TM} from Digital Instruments operating in tapping mode. An integrated silicon tip/cantilever, from the same manufacturer, having a resonance frequency over 300 kHz, was used. The specimens were prepared by ultramicrotoming at room temperature.
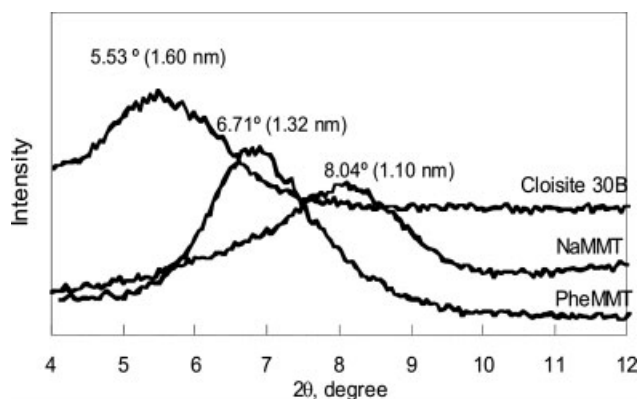

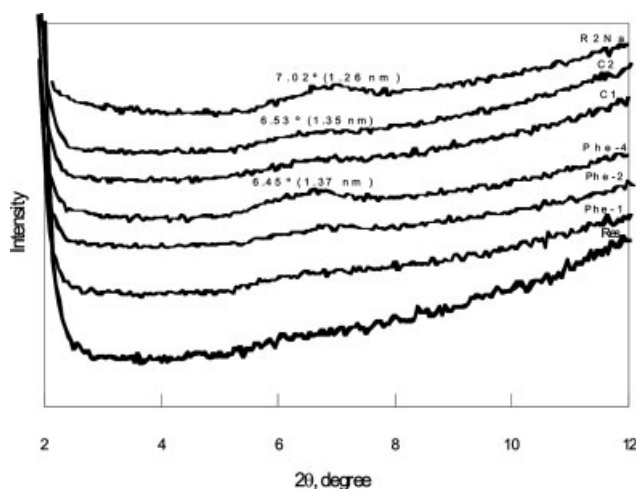**Figure 4** X-ray diffraction patterns of natural MMT and modified clays.

Figure 5 X-ray diffraction patterns of neat resol and C1, C2, R2Na, Phe-1, Phe-2, and Phe-4 composites.

TGA was carried out using a Setaram thermoanalyser (Model 92). The samples were scanned from 25°C to 1000°C at a scanning rate of 10°C/min under helium atmosphere.

RESULTS AND DISCUSSION

Because of the polyfunctionality of phenol, phenolic resins have three-dimensional structure and rigidity, even when few cross-linked, that hinders the penetration of the polymer chains inside the layers of the clay. This makes very difficult the formation of nanocomposites by simple addition of the organically modified silicate to the prepolymer of resol through it has low molecular weight.[23] So, the addition of the clay has to be performed before the creation of cross-linked structure. Different surfactants and methods have been investigated to solve this problem and to improve the interactions between the clay and the resol.[11–14,22,23,29] In this work, a specific surfactant as phenylalanine, an aminoacid with an aromatic ring having a similar structure to the phenolic resin, has been chosen to make the organophilic clay more compatible with the matrix.

As shown in Figure 1, the presence of the aminoacid inside the MMT could induce the condensation reaction of the carboxyl (—COOH) end group of the phenylalanine and the —OH groups of the
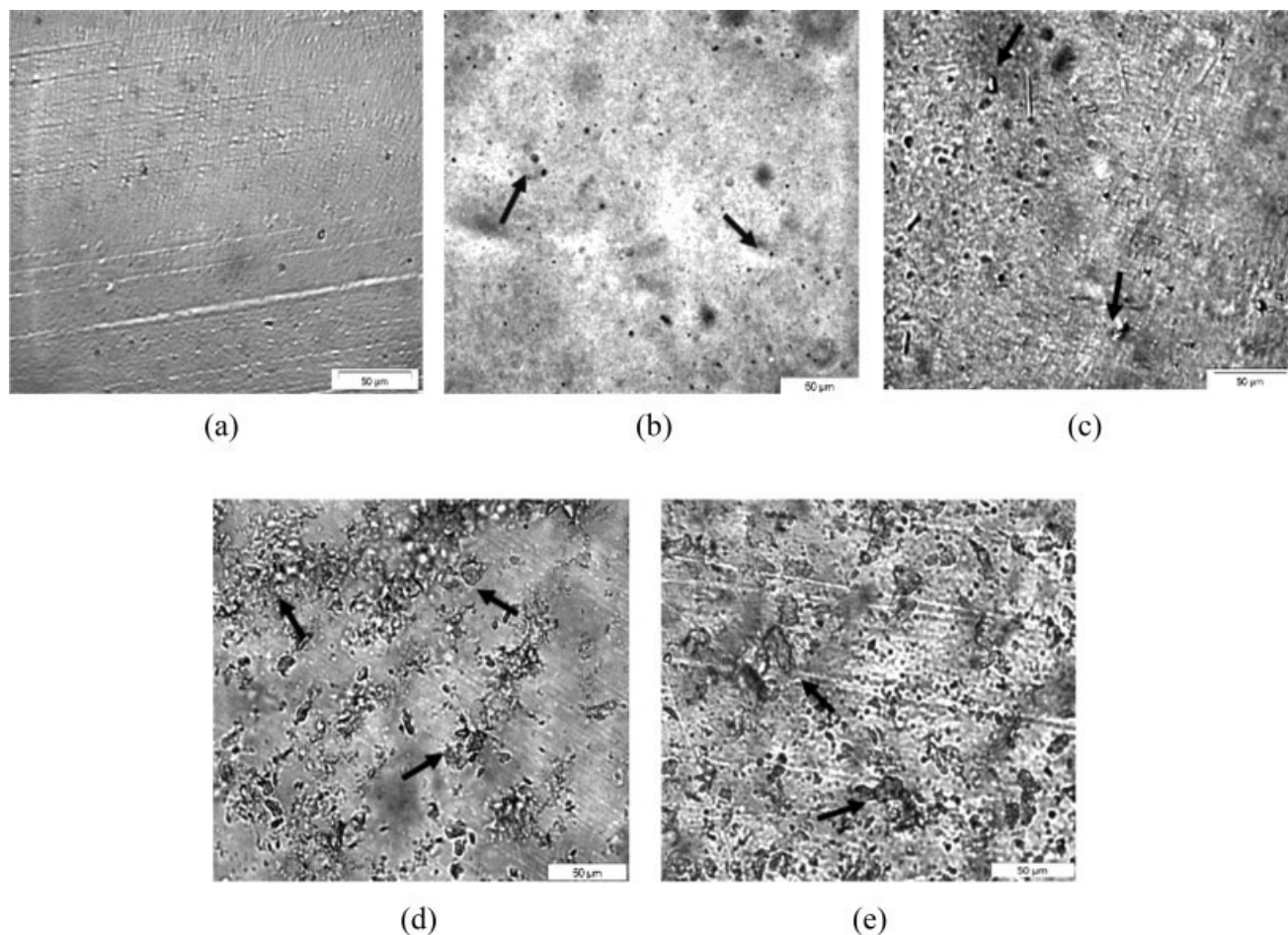

Figure 6 Optical micrographs of (a) neat resol, (b) Phe-2, (c) Phe-4, (d) C2, and (e) R2Na composites. Tactoids and aggregates are indicated by arrows.
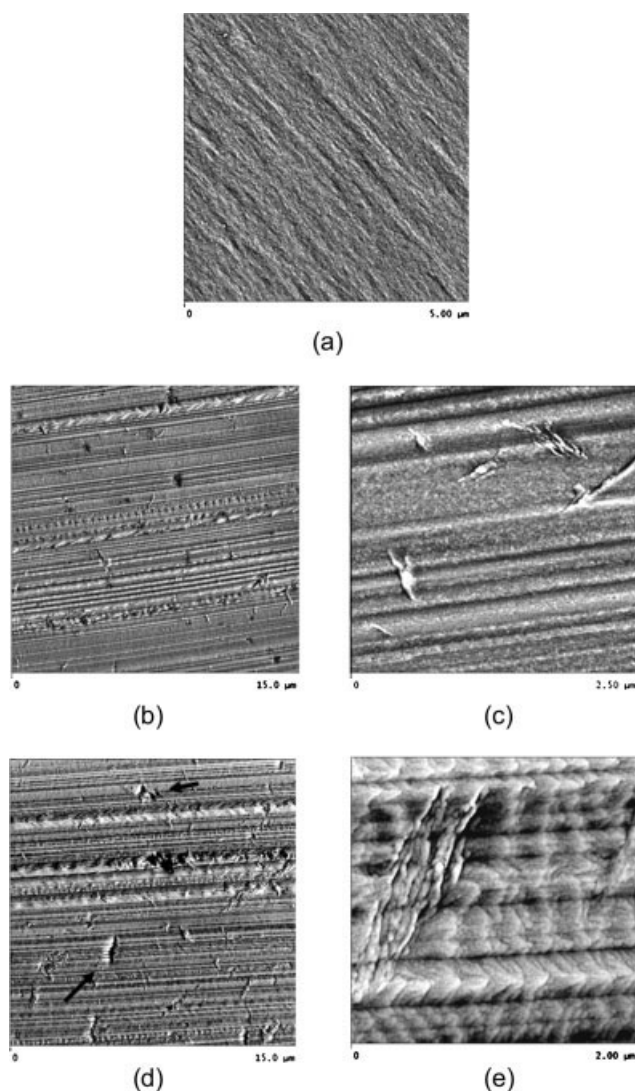
Figure 7 AFM phase images of (a) neat resol, (b, c) Phe-2 composite at two magnifications, and (d, e) Phe-4 composite at two modifications.

formaldehyde in aqueous acidic solution, thus acting like an anchor between the layers and the resin.[23,30]

Figure 2 displays FTIR spectra of natural MMT (Na$^+$MMT), PheMMT, and PheMMT-ac-formaldehyde. For Na$^+$MMT, in the range from 3700 to 3200 cm^{-1} the typical O—H stretching vibration bands are present, which are due to different types of water molecules in the clay structure, adsorbed or coordinated, and to the presence of OH groups coordinated to the metallic cation Al^{3+} in the octahedral sheets. At 1640 cm^{-1} a band because of the OH water bending vibrational modes is present. A broad and intense band is observed, centred at around 1045 cm^{-1}, attributed to the Si—O—Si in-plane-vibration, and also a shoulder at 1115 cm^{-1} because of Si—O bond stretching vibration modes. Low intensity bands can be observed in the region centered

close to 920 cm^{-1} that can be attributed to Al—OH—Al deformation bands. Weak bands at around 800 cm^{-1} can be attributed to other OH deformation bands of free silica that can be present as impurities in the sample.[29] At around 620 cm^{-1}, the O—H bending vibration band can be seen and at around 530 and 460 cm^{-1} the Si—O—Si and Si—O—Al in-plane-vibrations, respectively, are observed.

For PheMMT, the band at around 3200 cm^{-1} can be attributed to the N—H stretching superimposed to the carboxylic OH stretching. As expected, in the range from 3000 to 2800 cm^{-1}, the typical bands of the CH$_2$ stretching occur. A broad band attributed to the nonhydrogen-bonded and hydrogen-bonded C=O stretching in carboxyl groups[22] appears about 1665 cm^{-1} superimposed to the OH water bending vibrational mode. In the 1700–1400 cm^{-1} range, weak bands that could be attributed to NH$_3^+$ bending,[29] likely superimposed to the OH bending of the clay adsorbed water, can be seen. At around 1050 cm^{-1} the broad, intense band that corresponds to the clay Si—O—Si in-plane vibration, is slightly shifted toward higher wavenumbers with respect to the same band in Na$^+$MMT due to the increasing ionicity of the Si—O bond. Such an increase in polarity is because of the electronattracting/electrondonor effects of the NH$_3^+$ and COOH groups of the protonated form of phenylalanine.

For the product of the condensation reaction of carboxyl end group of phenylalanine and —OH groups of formaldehyde in acidic solution, in the range from 3700 to 3200 cm^{-1}, the typical O—H stretching vibration bands are present due to the different types of water molecules in the clay structure, adsorbed or coordinated, and to the presence of OH groups of the aqueous formaldehyde. The C=O stretching band is observed at around 1740 cm^{-1} as a result of the esterification reaction.[22] In the 1700–1450 cm^{-1} range, a combination of weak bands can be detected that can be attributed to NH$_3^+$ bending and OH bending of the clay absorbed water and formaldehyde. Centred at 1240 cm^{-1}, the formation of ester groups is also proved by the presence of the C—O—C asymmetric stretching band also proves.

On the other hand, Cloisite 30B used for the synthesis of C1 and C2 underwent the same acid treatment in the presence of formaldehyde. The mixture was called Cloisite 30B-ac-formaldehyde. As can be observed in Figure 3, both spectra are very similar showing the lack of reaction between the chains ended in hydroxyl groups of the modifier of Cloisite 30B and the resol resin. Reaction between chains ended in hydroxyl groups of the modifier of Cloisite 30B and resol resin seems to be less favorable at the used temperature conditions. The presence of long
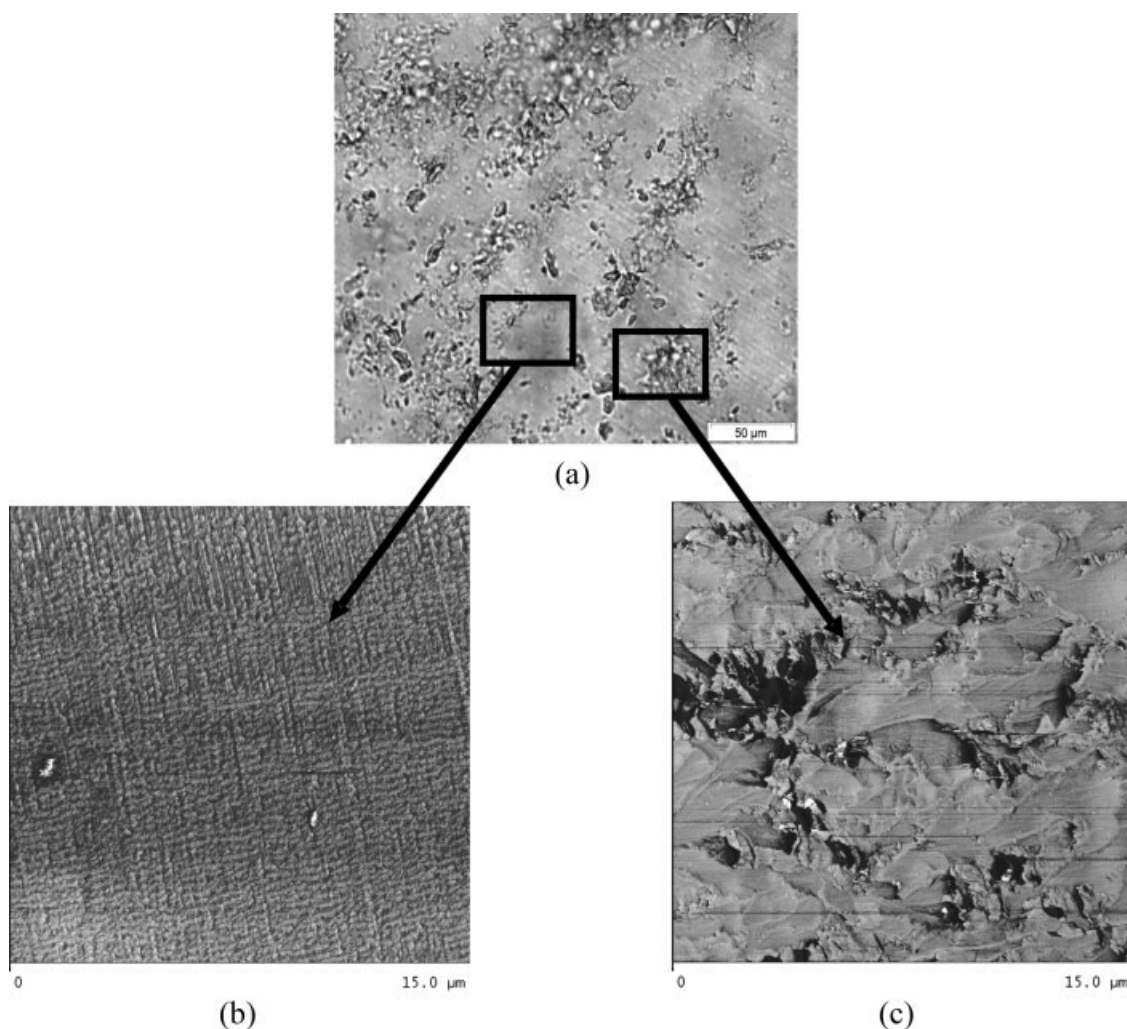
Figure 8 Optical micrograph of (a) C2 composite and AFM phase images of (b, c) C2 composite in two regions of the optical image.

alkyl chains of the surfactant is observed in the 2800–3000 cm^{-1} range due to the $(CH_2)_n$ asymmetric (2967 cm^{-1}) and symmetric (2855 cm^{-1}) vibration. In the region of 1700–1450 cm^{-1}, weak bands can be observed attributed to NH_3^+ bending and the OH bending of the clay absorbed water inside the clay. Impurities are also seen at 800 cm^{-1} in Cloisite 30B-ac-formaldehyde spectra.[29]

Figure 4 shows the X-ray diffraction patterns of natural Na$^+$MMT and modified clays. The basal spacings of Na$^+$MMT, PheMMT, and Cloisite 30B are 1.10, 1.32, and 1.60 nm, respectively. The basal spacing of PheMMT appears at a higher angle range than Cloisite 30B because of the small dimensions of the modifier (Phe), 0.53 nm in width, and 0.79 nm in length.[13] Usuki et al.[1] suggested that the carboxyl (—COOH) end group of the α-aminoacid should combine with the oxygen (—O—) group of the silicate surface through hydrogen bonding, that could explain the low d_{001} spacing.

Figure 5 show the X-ray diffraction patterns of resol composites as a function of clay content and the type of organic surfactant used. X-ray diffraction pattern of 2 wt % Na$^+$MMT modified resol (R2Na) is displayed. As can be observed, the interlayer spacing increases from 1.10 to 1.26 nm. This behavior means that part of the reactive process can occur inside the layers. However, as shown later by means of OM, this increase is not enough to achieve a complete intercalation.

On the other hand, the basal spacing for C1 and C2 composites is around 1.35 nm while the basal spacing of the Cloisite 30B is at 1.60 nm. This behavior may be caused because the galleries of the clay collapse during polymerization, leading to the contraction of interlayer spacing.[23] In this work, for the synthesis of Resol-MMT composites, TEA was used as catalyst. Extragallery reactions catalyzed by TEA and the intragallery reactions catalysed by —OH of the Cloisite 30B should have proceeded simultane-

ously. Intragallery reactions are important for the intercalation of the clay.[21] In the case of C1 and C2, intragallery reactions seem to be unfavorable maybe due to the steric hindrance of the surfactant or the weak interaction between the surfactant and the resol chains leading to the contraction of interlayer spacing.[21] X-ray diffraction patterns of the PheMMT modified composites are also shown in Figure 5. As the silicate content increases, the (001) reflection peak situated in the $2\theta = 5–10°$ region is more distinctive, which indicates that the amount of stacked clay increases.[20,22,31] However, the (001) reflection peak for Phe-4 appears at a lower angle ($2\theta = 6.45°$) than for PheMMT ($2\theta = 6.71°$). Thereby, initially, extragallery and intragallery reactions catalysed by COOH of Phenylalanine could be parallel processes.[21] It seems that the small shear forces exerted on the PheMMT tactoids during polymerization are able to overcome the attraction forces between the most superficial layers due to the weak forces that stack them together.[9,32] and surviving the larger stacks. So increasing PheMMT content, the amount of tactoids is higher, as confirmed below by means of OM.

The morphology of the composites has also been studied by microscopic techniques to analyze the dispersion of the organoclay in the matrix. OM results are shown in Figure 6(a–e). As Figure 6(a) shows for neat resol, small holes can be observed due to the condensation reaction produced during postcure. In Phe-2 sample [Fig. 6(b)], besides the holes, a good dispersion of the clay in the matrix is seen. In contrast, in Phe-4 image [Fig. 6(c)], small tactoids of 1–2 μm can be observed. As explained earlier, reactive molecules can only introduce inside the most superficial layers, remaining unreacted stacked layers forming aggregates. On the other hand, in C2 and R2Na, thick agglomerated clay particles are observed indicating a poorer dispersion of clays [Fig. 6(d,e)].

The microstructure has also been investigated by AFM. Phase images are shown in Figure 7(a–e). Because of the fragility of the resols, specimens were not perfectly cut by ultramicrotomy. For that reason, lines or scratches appear in their surfaces that makes difficult the observation of individual layers. Figure 7(a) shows the neat matrix where its globular structure can be observed. Figure 7(b,c) show Phe-2 composite at different magnifications where some individual layers can be observed. Layers forming small aggregates with lateral size around 20–100 nm are shown in Figure 7(c). On the other hand, Figure 7(d,e) show Phe-4 composite where more tactoids and thicker appear.[33] Figure 7(e) shows an aggregate of stacked layers with lateral size less than 500 nm. It is composed by intercalated layers oriented perpendicular to the sample surface with very small
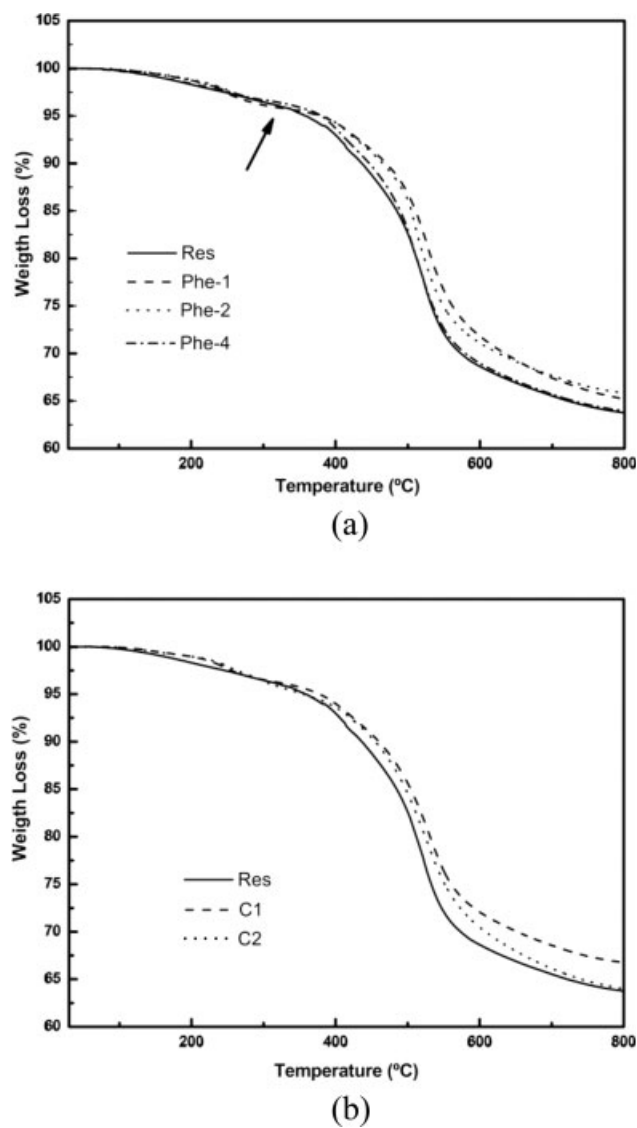

(a)

(b)

Figure 9 TGA thermograms of (a) neat resol (—), Phe-1 (---), Phe-2 (·····), and Phe-4 (·-··-·) composites and (b) neat resol (—), C1 (---), and C2 (·····) composites.

thickness. The resol matrix seems to be inserted between the layers but exfoliation is not achieved.

Figure 8(a,b) display C2 composite surface. A weak dispersion of Cloisite 30B in the resol matrix makes that two different morphologies can be found. Thus, the neat matrix of resol without clay is seen in Figure 8(a). In Figure 8(b), thick agglomerated clay tactoids are predominant.[33]

Figure 9(a,b) show the thermal decomposition behavior of neat resol and clay-filled resins. TGA curves for the composites containing PheMMT and Cloisite 30B have a very similar behavior. Different stages of degradation can be observed in the TGA thermogram: in the first stage, from 30 to 350°C, the release of formaldehyde due to the break of ether bridges, and the presence of phenol, water, and

organic modifiers of the clay are observed. In the second stage, in the temperature range of 350–700°C, two zones can be distinguished: about 450°C, the oxidation of the network and at 550°C the formation of the *char* structure.[19] In the second stage of thermal decomposition, all the composites display higher thermal resistance than the neat matrix. Composite Phe-1 seems to be more thermally stable because its thermal degradation starts at higher temperatures. The presence of the thermally stable MMT can act as a barrier to hinder heat diffusion and migration of degraded volatiles, thus retarding the decomposition rate.[34]

CONCLUSIONS

Resol-layered silicate composites were synthesized by intercalative polymerization of phenol and formaldehyde in presence of PheMMT and Cloisite 30B. The appropriate choice of Phenylalanine as modifier of the MMT and the interaction between the modifier and the phenolic resin resulted, at low concentration of PheMMT, an adequate method to obtain intercalated nanostructures. X-ray diffraction and AFM images confirm the presence of intercalated nanostructures, being Phe-2 the composite with the best dispersion of clay layers. On the other hand, for C1 and C2 composites, no reactions between MMT modifier and resol matrix resulted in poorer dispersion of the clay in the matrix. Thermal stability of nanocomposites was slightly increased in comparison with the neat resol.

References

1. Usuki, A.; Kawasumi, M.; Kojima, Y. J Mater Res 1993, 8, 1174.
2. Lee, S. M.; Hwang, T. R.; Lee, J. W. Polym Eng Sci 2004, 44, 1170.
3. Chen, B.; Evans, J. R. G. Polym Int 2005, 54, 807.
4. García-López, D.; Gobernado-Mitre, I.; Fernández, J. F.; Pastor, J. M. Polymer 2005, 46, 2758.
5. Tortora, M.; Gorrasi, G.; Vittoria, V.; Chiellini, E. Polymer 2002, 43, 6147.
6. Becker, O.; Varley, R.; Simon, G. Polymer 2002, 43, 4365.
7. Liu, T. X.; Liu, Z. H.; Ma, K. X.; He, C. B. Compos Sci Technol 2003, 63, 331.
8. McNally, T.; Murphy, W. R.; Lew, C. Y.; Brennan, G. P. Polymer 2003, 44, 2761.
9. Lee, Y.; Kim, S. J. Colloids Surf 2002, 211, 19.
10. Kim, Y.; White, J. L. J Appl Polym Sci 2005, 96, 1888.
11. Lepluart, L.; Duchet, J.; Gérard, J. F. Macromol Symp 2003, 194, 155.
12. Lepluart, L.; Duchet, J.; Gérard, J. F. J Adhes 2002, 78, 645.
13. Fudala, Á.; Pálinkó, I.; Kiricsi, I. Inorg Chem 1999, 38, 4653.
14. Kollár, T.; Pálinkó, I.; Kónya, Z.; Kiricsi, I. J Mol Struct 2003, 335, 651.
15. Gardziella, A.; Pilato, L. A.; Knop, A. Phenolic Resins, 2nd ed.; Springer-Verlag: Berlin, 2000; Preface, p 29.
16. Astarloa-Aierbe, G.; Echeverría, J. M.; Martín, M. D.; Etxeberria, A. M.; Mondragon, I. Polymer 2002, 43, 2239.
17. Astarloa-Aierbe, G.; Echeverría, J. M.; Martín, M. D.; Etxeberria, A. M.; Mondragon, I. Polymer 2000, 41, 3311.
18. Riccardi, C. C.; Astarloa-Aierbe, G.; Echeverría, J. M.; Mondragon, I. Polymer 2002, 43, 1631.
19. Gabilondo, N. 'Diseño de la conducta final de matrices fenólicas de tipo resol, en función de los productos de partida y de las características reocinéticas del curado'. Ph.D. Thesis, Euskal Herriko Unibertsitatea/Universidad del País Vasco, Donostia-San Sebastián, España, 2004.
20. Wang, H.; Zhao, T.; Zhi, L.; Yan, Y. Macromol Rapid Commun 2002, 23, 44.
21. Wang, H.; Zhao, T.; Yan, Y. J Appl Polym Sci 2004, 92, 791.
22. Byun, H. Y.; Choi, M. H.; Chung, I. J. Chem Mater 2001, 13, 4221.
23. Zenggang, W.; Rongrong, Q. Polym Compos 2002, 23, 634.
24. Choi, M. H.; Chung, I. J.; Lee, J. D. Chem Mater 2000, 12, 2977.
25. Choi, M. H.; Chung, I. J. J Appl Polym Sci 2003, 90, 2316.
26. Wang, H.; Zhao, T.; Yu, Y. J Appl Polym Sci 2005, 96, 466.
27. Pappas, J.; Patel, K.; Nauman, E. B. J Appl Polym Sci 2005, 95, 1169.
28. Manfredi, L. B.; Puglia, D.; Kenny, J. M.; Vázquez, A. J Appl Polym Sci 2007, 104, 3082.
29. Pucciariello, R.; Villani, V.; Langerame, F.; Gorrasi, G.; Vittoria, V. J Polym Sci Part B: Polym Phys 2004, 42, 3907.
30. Choi, M. H.; Byun, H. Y.; Chung, I. J. Polymer 2002, 43, 4437.
31. Xu, W.; Bao, S.; He, P. J Appl Polym Sci 2002, 84, 842.
32. Liu, H.; Zhang, W.; Zheng, S. Polymer 2005, 46, 157.
33. Dan, C. H.; Lee, M. H.; Kim, Y. D.; Kim, J. H. Polymer 2006, 47, 6718.
34. Chaoying, W.; Guohua, T.; Ning, C.; Yinxi, Z.; Yong, Z. J Appl Polym Sci 2004, 92, 1521.