Synthesis and Characterization of Nanocomposites Based on a Furan Resin

Guadalupe Rivero,[1] Analía Vázquez,[2] Liliana B. Manfredi[1]

[1]Research Institute of Materials Science and Technology (INTEMA), National University of Mar del Plata, Juan B.Justo 4302, Mar del Plata 7600, Argentina
[2]Polymer and Composite Material Group-INTECIN (UBA-CONICET)- Engineering Faculty, University of Buenos Aires, Las Heras 2214, Buenos Aires 1127AAR, Argentina

ABSTRACT: Formaldehyde emissions are nowadays trying to be reduced because of its atmospheric pollutant character. Besides, it is encouraged the use of polymeric materials synthesized from biomass wastes as row materials. For this reason, furan resins would be an alternative to phenolic resins, where formaldehyde is replaced by furfural as a reactant. Regarding, the addition of nanoparticles to the furan resin should enhance their performance as metal coatings with good thermal and oxidative resistance. The aim of this article is to study the influence of the in situ addition of different type of nanoparticles on the chemical reactions involved in the synthesis of a furan resin. From the viscosity measurements it was observed that the addition of the nanoreinforcements led to a higher resin reaction rate. Differences in the final chemical structure among the materials were also observed by infrared spectroscopy analyses. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 1667–1673, 2010

Key words: clay; nanocomposites; synthesis; FTIR

INTRODUCTION

During the last years, the global trends to ambient protection as well as the new international regulations have promoted the use of biomass wastes as row materials for the development of new polymeric materials.

Even though the use of biomass products is not economically favorable nowadays because of the dominant competition represented by the petroleum's industry,[1] the agricultural waste-based policies have become very attractive.[2] Therefore, the government, business, and scientific sectors are concerned about the environmental, industrial, and financial considerations related to the nonrenewable character of petroleum derivatives.

Furfural is commercially obtained from a wide range of agricultural or forestry wastes containing pentoses[3] so that several polymeric systems based on it constitute a serious alternative to materials based on petroleum with numerous applications, such as adhesives, molding compounds, coatings, absorbing resins, abrasive surfaces, etc.

Phenol-furfural resins are similar to phenol-formaldehyde resins as formaldehyde is replaced by furfural. Given that formaldehyde is a dangerous atmospheric pollutant, its replacement in paints and coatings would decrease its potential emission.[4] For this reason, it is worth proposing furan resins as metal substrates coatings.

On the other hand, it has been reported that the addition of low quantities of nanoparticles to a polymeric matrix displays sizeable properties improvement and increases the technological interest.[5] These nanocomposites tend to exhibit better mechanical and barrier properties, as well as more thermal and oxidative stability.[6] Regarding, an enhancement of the thermal stability of polyfurfurylalcohol was achieved by employing an in situ polymerization with montmorillonite clay.[7]

The reactions involved in the synthesis of different furan resins have been reported;[8] however, nanocomposites based on furan resins were not chemically characterized yet. As coating properties will depend on their chemical structure, it is significant to understand the influence of the clay addition on the synthesis reactions of the furan resin.

Then, the purpose of this research work is to obtain a furan resin from phenol and furfural and to follow the chemical reactions involved in its synthesis. Thereafter, the variation in the chemical structure of the furan resin with the in situ addition of three types of montmorillonites was investigated.

TABLE I
Characteristic of the Cloisite® Clays

Clay	Cloisite® Na+ (CNa)	Cloisite®30B (C30B)	Cloisite®10A (C10A)
Organic modifier	None	H₂C—CH₂—OH H₃C—N⁺—T H₂C—CH₂—OH	H₃C H₃C—N⁺—CH₂—⟨ ⟩ HT
Modifier concentration	–	125 meq/100 g clay	90 meq/100 g clay
Interlayer distance (d_{001}) [Å]	11.7	18.5	19.2
pH (4 mg/mL)	9.90	8.46	8.30

EXPERIMENTAL

Materials—synthesis

Phenol (Anedra) was molten into a reactor supplied with a refrigerant, a thermometer and constant mechanical stirring. The reaction media was adjusted using an aqueous solution of K_2CO_3 40% wt/vol. After heating to 135°C, furfural (Fluka) was dropt for 30 min in 1 : 1 molar ratio respect to phenol. The temperature was maintained at 135°C for 4 h and samples were taken every 30 min to follow the reaction progress.

Nanocomposites were synthesized following the same procedure but 2% wt/wt of clay was added *in situ* to the melt phenol, and the mixture was stirred during an hour before the addition of furfural. The montmorillonite type clays used were: a natural purified Cloisite® Na+ and the organically modified Cloisite® 30B and Cloisite® 10A (Southern Clay Products), which characteristics are shown in Table I. These were selected to promote the dispersion, because of the compatibility of their functional groups with the matrix polymer.

At last, dark viscous resins were obtained. The corresponding phenol/furfural resins were named: F (without clay), FNa (with 2% of Cloisite® Na+), F30B (with 2% of Cloisite® 30B), and F10A (with 2% of Cloisite® 10A).

Methods

Samples were collected from the synthesis reactor every 30 min and direct measurements of the viscosity were performed during the prepolymer formation reaction in a Brookfield Cone/Plate Viscometer (HBTDV – HCP) with Spindle CP-40, at 25°C. Direct measurements of the refractive index in the initial prepolymer were done using an Abbe Refractometer NAR-2T (Atago®). Temperature cycles were conducted in a stove from ambient temperature to 135°C until the mass remained constant, to determine the dissolved solid contents.

Fourier transform infrared (FTIR) spectra were obtained in a Mattson Genesis II, transmission mode. Spectra were scanned from 600 to 4000 cm⁻¹,

and the base line was manually corrected. Prepolymer samples collected every 30 min were analyzed to follow the chemical synthesis evolution. For comparison purposes, spectra were normalized with the intensity of the band at 1595 cm⁻¹ in every case. This band was assigned to the C=C benzene ring stretching and its intensity was expected to remain constant for all the samples.[9]

RESULTS AND DISCUSSION

From the viscosity measurements performed at 25°C to the different fractions obtained during the progress of polymerization reaction, it was observed that the addition of clays actually accelerates the prepolymer formation. Similar results were reported by Terenzi et al.[10] with carbon nanotubes-epoxy nanocomposites. They showed that the addition of 1% of double-walled carbon nanotubes speed up the cure process of the epoxy resin by more than 40 min. In this case, Figure 1 evidences the dramatic exponential growth of viscosity, which happens faster in the nanocomposites than in the furan resin. The materials that showed a faster increment in the viscosity are the ones with higher solid content, as shown in Figure 2. The values corresponding to the dissolved solid content as well as the refractive indexes follow a similar tendency among them. As 2% of clay was added in the composites, a similar increase in dissolved solid content among them was expected. Nevertheless, some differences arisen in the results. Then, it should indicate that a change in the chemical structure was happened due to the clay addition. The nature of the clay organic modifiers then influences the chemical reactions that take place during polymerization. So, a detailed FTIR analyses was performed to understand those changes and compare their chemical structures. FTIR spectrum was scanned for each resin, and bands were assigned to the corresponding chemical functional groups. Firstly, the variation on the chemical structure of the neat furan prepolymer with time was analyzed. Thereafter, the influence of the clay addition on the chemical structure of the furan resin was also studied.
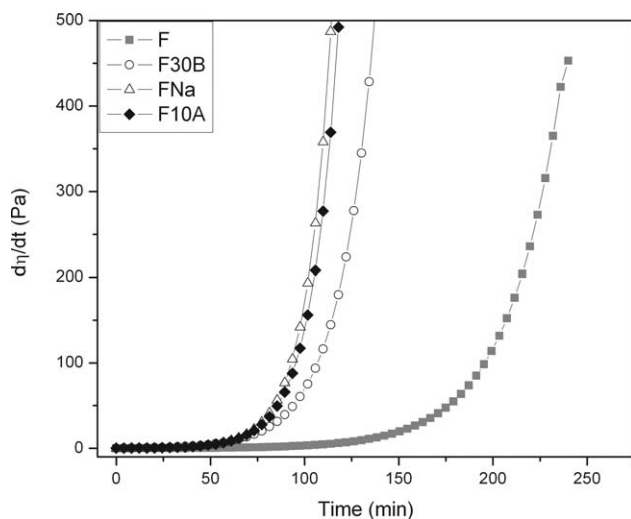
Figure 1 Time derivative of the viscosity during the progress of resins reaction.

Chemical reactions shown in Figure 3 lead to interpret the proposed possible chemical changes that take place during the synthesis[11]:

a. The initial addition of furfural to ortho and para positions of phenol causes the diminution of aldehyde functional groups (—CH=O) as well as the increment of —CH—OH groups content because of the formation of phenol-furfurylol all over the reaction.

b. These —CH—OH groups disappear when phenol-furfurylol molecules react: (i) with each other, leading to the formation of ether bridges or (ii) with the free ortho and para positions of phenol.

c. Phenol activated hydrogen atoms allow the process to keep on reacting. As a result, the degree of the crosslinking is increased, in agreement with a rise in aromatic ring substitution and bridge formation.

The band intensity of the characteristic functional groups along the reaction time was evaluated in the spectra of the furan resin and then, in its composites.

The consumption of furfural was evidenced by the variation of typical bands in the furan prepolymer spectra. The decrease of the band corresponding to the *s-cis* C=O stretching at 1692 cm^{-1} is shown in Figure 4. In addition, the furfural bands related to the C=C in phase-stretching have a specific position if the double bond is conjugated to a carbonyl group (C=C=O) at 1470 cm^{-1}; or to a saturated group (C=C—CH—) at 1512 cm^{-1}.[12] As furfural reacts, is notable the increment of the last band along the progress of the reaction, in Figure 4.

The growing substitution extent on the benzene ring of phenol is evidenced. The FTIR spectra shown in Figure 5 are examples of these changes in the

furan resin. The reduction of mono-substituted rings with the advancement of reaction because of the higher substitution extent is evidenced by the intensity decrease of the corresponding band at 690 cm^{-1}. Besides, it is notable the intensity enhancement of the bands associated to di- and tri-substituted rings in positions 1,2- and 1,2,6- (736 cm^{-1}) and, 1,4- and 1,2,4- (840 cm^{-1}),[13] as shown in Figure 6. It seems, from the relative height of the bands, that the addition was more easily produced in the ortho than in the para position of the benzene ring with the advancement of the reaction.

Ether bridges formation was corroborated by the growth of the bands related to the symmetric and antisymmetric C—O stretching at 1105 and 1094 cm^{-1}, respectively, with reaction time (Fig. 6).

The bands at 1440 cm^{-1} and 1456 cm^{-1} were assigned to the para-para' and ortho–ortho' —CH$_2$— bridges between phenols in phenolic resins.[9] Similar bridges are formed during the polymerization reactions of furan resins. It was observed an increment in the intensity of these bands with reaction time (Fig. 7), and it is consistent with the reactions that are expected to take place. All the results above confirm that the synthesis reaction is being developed consistently with the chemical reactions proposed above in Figure 3.

The evolution of the functional groups was also followed for the nanocomposites to compare their behavior with the furan prepolymer without the addition of clay.

The variation on the height of the bands indicating the diminution of furfural group in the different samples is showed in Figure 8. The highest and fastest variation was observed for the nanocomposite containing CNa. The other two composites showed a slightly difference compared to the neat furan resin.
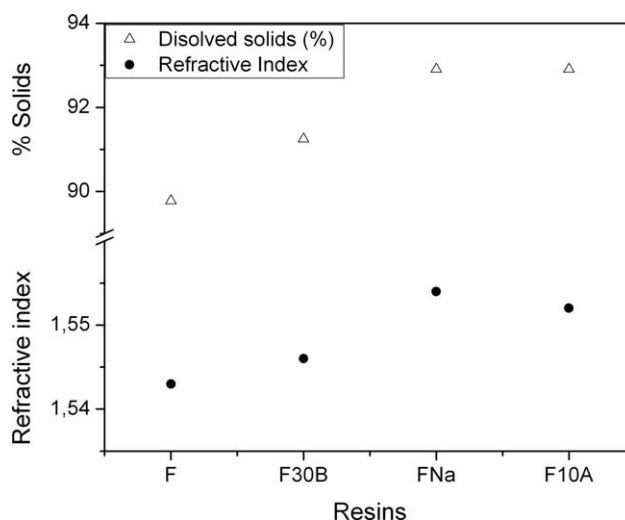

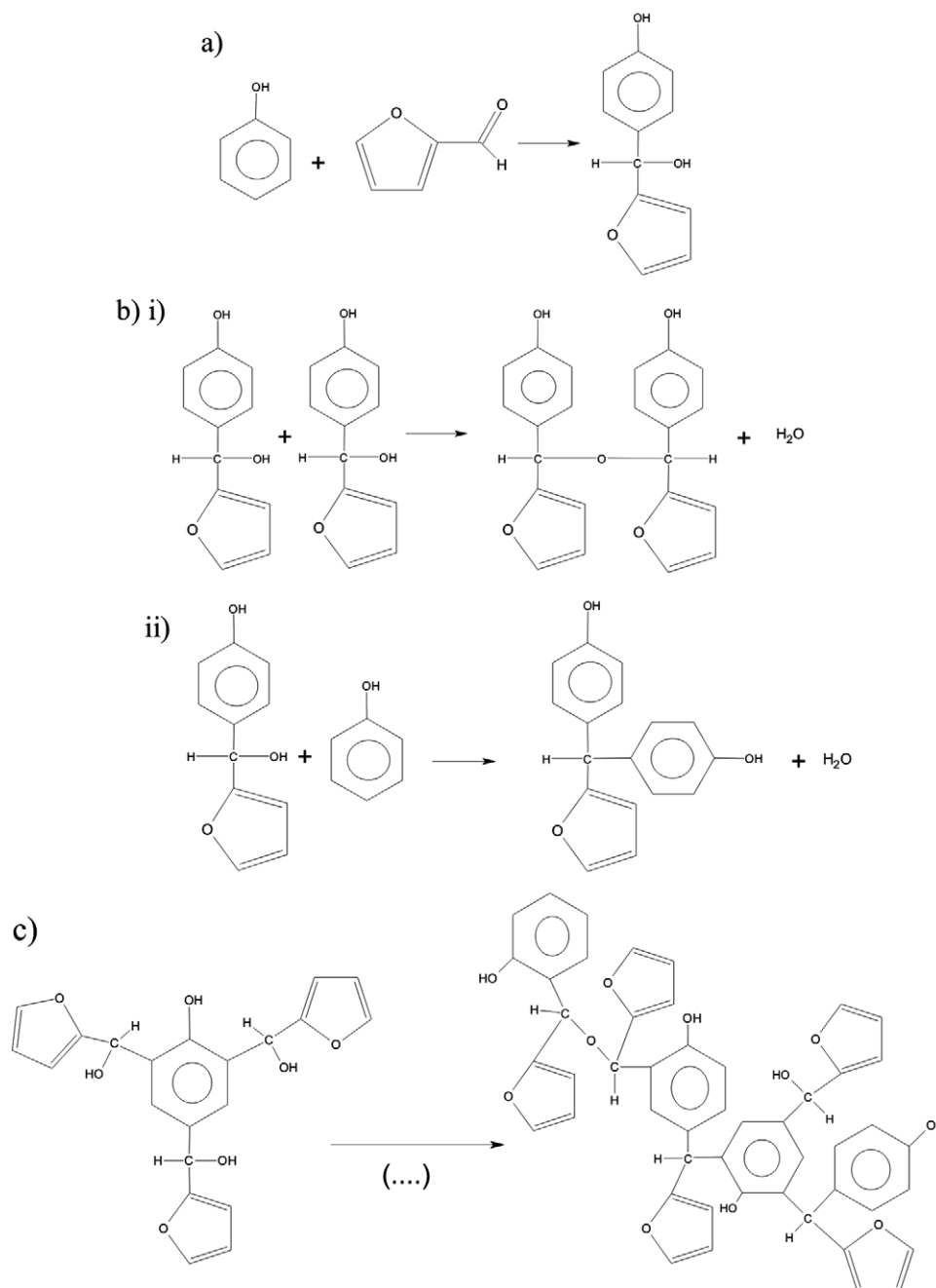**Figure 2** Dissolved solids content (△) and refractive index (●) of the resins.

Figure 3 (a) Initial addition of furfural to phenol forming phenol-furfurylol; (b) Reaction of phenol-furfurylol molecules with: (i) each other, (ii) phenol free positions; (c) Posterior crosslinking. (Idem susbstitutions occurs in the ortho position of the phenol ring).

The bands indicative of the benzene ring substitution were also compared among the samples (Figs. 9–11).

This comparison leads to deduce that the benzene rings were more easily substituted in the ortho position (736 cm^{-1}) in the presence of CNa than in the others samples due to the higher relative value all over the reaction time. Benzene ring substituted in the para position (840 cm^{-1}) grows faster at the beginning in the CNa samples but the quantity was similar at the final of the reaction in all the samples.

Similar results were obtained in phenol/formaldehyde resins where substitutions in the benzene ring were favored in the presence of Na$^+$ due to the formation of chelates.[14] It was also observed that the presence of modified clays do not modify significantly the quantity of ortho substituted rings compared to the neat resin. However, the quantity of para substituted rings was slow diminished in the presence of C10A at the early stages.

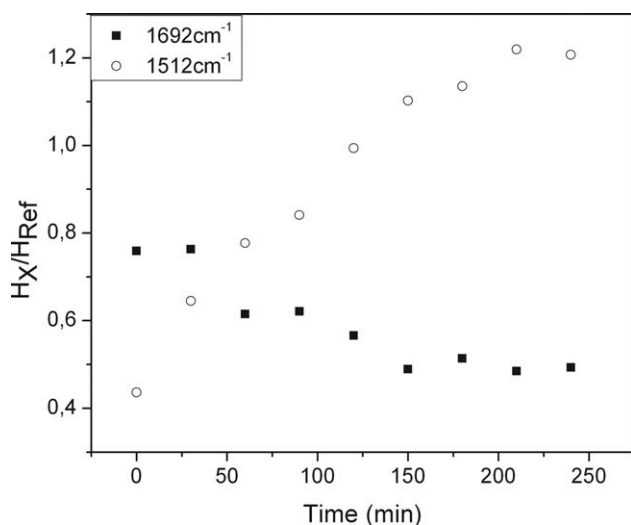Formation of bridges is indicative of the occurrence of the condensation reactions showed in

Figure 4 Relative intensity of the bands at 1692 and 1512 cm^{-1} that characterize the consumption of furfural with reaction time in the furan resin.

Figure 6 Variation of substituted benzene rings and ether bridges with time in the furan resin.

Figure 3. The relative quantity of methyl bridges in the different resins is showed in Figures 12 and 13. It was observed that the ortho–ortho' bridges formation is favored over the para–para' bridges. Additionally, the composite containing CNa showed the largest quantity of both of them from the beginning of the reaction. This result is in accord to the one obtained for the relative quantity of substituted benzene rings, because while a methyl bridge is formed, a position in the ring is substituted.

It was observed that the relative quantity of bridges with time is in accordance to the measures of viscosity performed (Fig. 1). The nanocomposites clearly showed a faster increment in the quantity of ─CH─ bridges up to ~100 min, which is the time
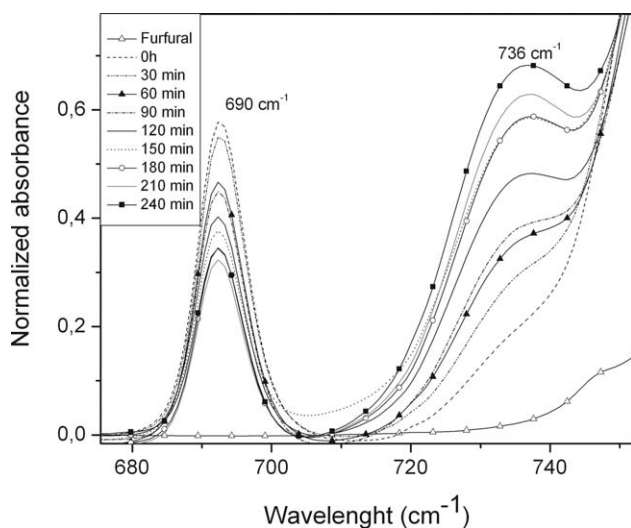
when their viscosity suddenly grows up. The furan resin showed a change in the slope of the bridges curve at ~200 min, in accordance to their later increment in the viscosity. These results would indicate that the presence of the clay favors the advancement of the reactions because the appearance of products occurs faster in the prepolymers containing the nanoreinforcements. The differences among the distinct nanocomposites could be related to the type of organic modifier that is able to interact with the chemical groups of the furan resin. This interaction may modify the phenol/furfural molar ratio outside and inside the galleries. Additionally, the pH of the clays were measured (Table I), and it would be possible that it modifies the medium conditions and then, altering the reactions and consequently the final chemical structure of the materials.

Figure 5 Relative intensity of the bands corresponding to the substituted benzene rings in the furan resin at different reaction times.

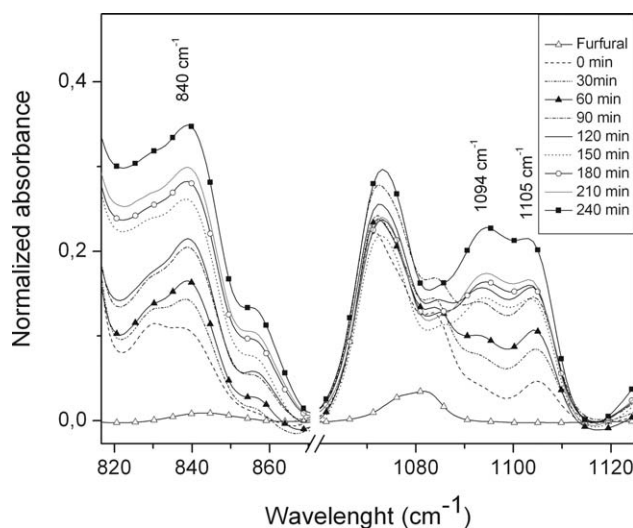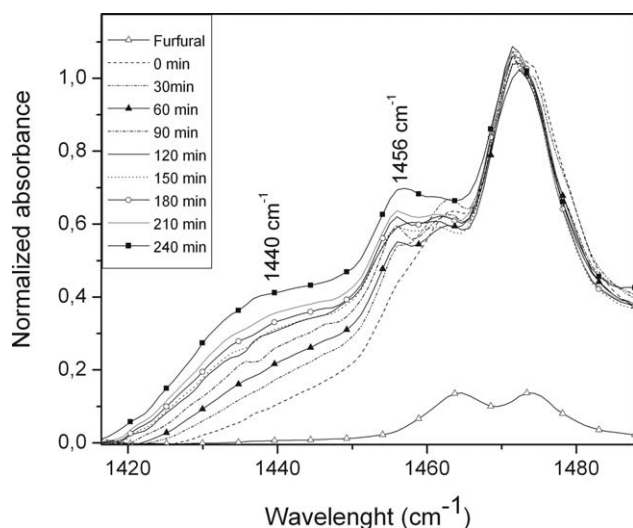**Figure 7** Relative intensity of the bands assigned to the ─CH─ bridges in the furan resin with reaction time.
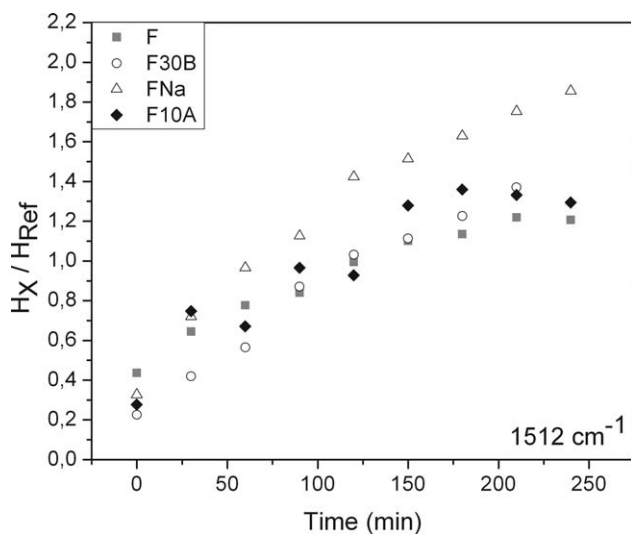
Figure 8 Variation of the relative intensity of FTIR band at 1512 cm^{-1} with time, in the different samples.

Ether bridges are the other type of functional group that appear during condensation. Figure 14 shows the relative quantity of the ether groups formed along the reaction time. It was observed that the presence of clay favors their formation compared to the neat resin. At the early stages, the bridges are easily formed in presence of C10A but at the end of the reaction, the quantity is similar among the composites. In general, the quantity of methyl bridges was more than twice of the ether bridges.

The relative quantity of —CH— and ether bridges measured in this work is similar to that previously reported for high ortho novolak resins obtained in a weakly acid medium.[15] It was stated that the quantity of ortho–ortho' —CH— bridges was ∼ 45% while that of the para–para' was only 5%. The preference for the ortho position was attributable to structural
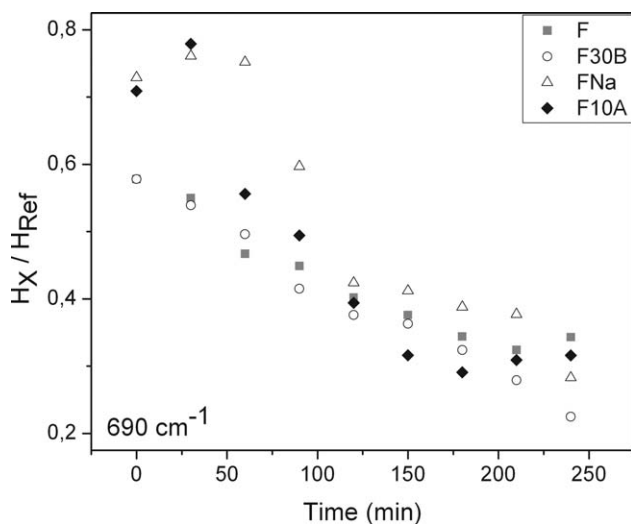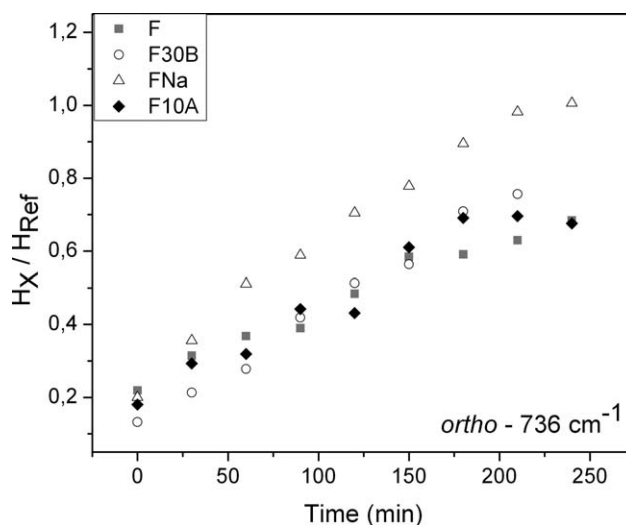

Figure 10 Relative intensity of FTIR band at 736 cm^{-1} as function of time, in the different samples.

intramolecular interactions. The ortho intermediates form four to six-membered ring structures through intramolecular hydrogen bond interactions. In addition, the ether bridges in novolak resins were reported to be formed in a lesser quantity than the methylene bridges, as it was observed in this work.

CONCLUSIONS

Furan resin and nanocomposites were successfully obtained by the *in situ* addition of three different montmorillonite clay types. The FTIR analysis performed indicated that the proposed reactions are consistent with the structural chemical changes in the functional groups during the synthesis reactions. Indeed, the consumption of free furfural as well as the formation of bridges and the growing
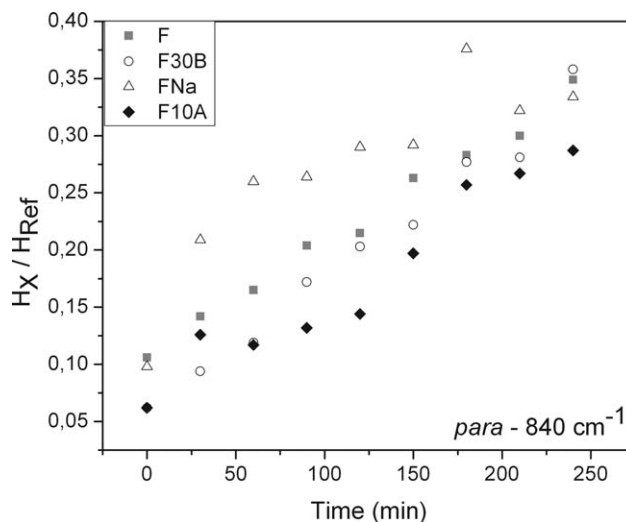

Figure 9 Diminution of monosubstituted benzene rings quantity with time, in the furan resin and their composites, at 690 cm^{-1}.

Figure 11 Relative intensity of 840 cm^{-1} FTIR band versus time, in each material.
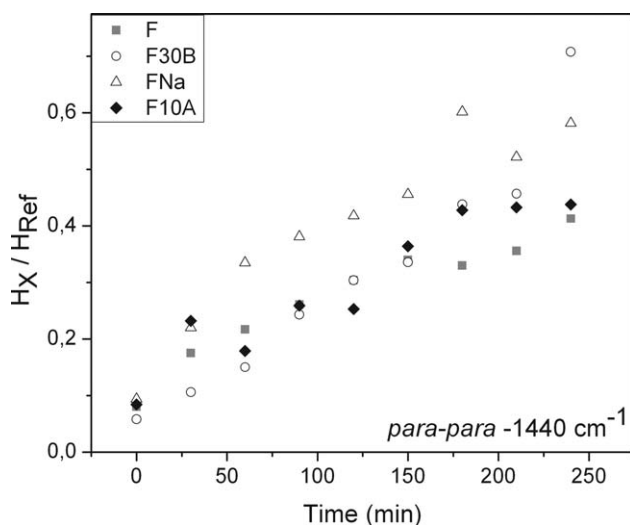
Figure 12 Relative height of the FTIR band at 1440 cm^{-1} versus time, in the resin and composites.

Figure 14 Relative intensity of 1105 cm^{-1} FTIR band as function of time, in the resin and composites.

substitution extent of the benzene rings are the most significant evidences that the reaction was in fact developed by the described path.

It can be concluded that the clay addition to the furan resin accelerates the reaction of prepolymer formation. Regarding to this, the viscosity exponential growth during the synthesis correlates with relative quantity of the characteristic functional groups analyzed by FTIR. Anyway, differences between each nanocomposite were detected in relation to the final chemical structure of each material. For instance, FNa showed the most advanced reaction rate evidenced by the most rapid disappearance of free reagents as well as the earliest increase of functional groups characteristic of the reaction products and a major rate of benzene substitution. So, it seems that the CNa is the reinforcement that leads
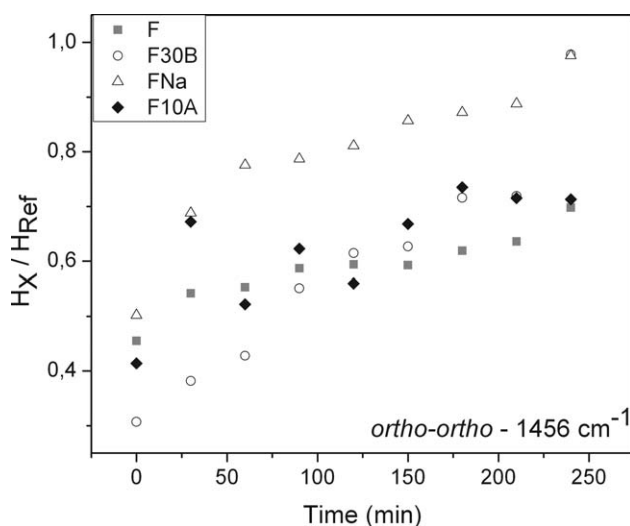
to the more reacted material. The differences on the rate and extent of reaction between the materials may be due to the chemical nature of the clay organic modifier as well as the pH of the medium. The chemical functional groups of the modifiers are compatible with the furan resin, so the clay type added has a notable influence in the polymeric chemical structure obtained.

References

1. Yu, L.; Dean, K. Prog Polym Sci 2006, 31, 576.
2. Tromp, O.-S. In UNEP-GW-SPD, Research Programme RA1 Report, United Nations Environment Programme, Working Group on Sustainable Product Development, New York, 1999.
3. Gandini, A. In Encyclopedia of Polymer Science and Technology, 2nd ed.; Mark, H., Bikales, N., Overberger, C. G., Menges, G., Kroschwitz, J. I., Eds.; Wiley: New York, 1986; Vol. 7, p 454.
4. Pizzi, A.; Pasch, H.; Simon, C.; Rode, K. J Appl Polym Sci 2004, 92, 2665.
5. Alexandre, M.; Dubois, P. Mater Sci Eng 2000, 28, 1.
6. Hussain, F.; Hojjati, M.; Okamoto, M.; Gorga, R. E. J Compos Mater 2006, 40, 1511.
7. Pranger, L.; Tannenbaum, R. Macromolecules 2008, 41, 8682.
8. Gandini, A.; Belgacem, M. Prog Polym Sci 1997, 22, 1203.
9. Rockniak, C.; Biernacka, T.; Skarzynski, M. J. J Appl Polym Sci 1983, 28, 531.
10. Terenzi, A.; Vedova, C.; Lelli, G.; Mijovic, J.; Torre, L.; Valentini, L.; Kenny, J. M. Compos Sci Tecnol 2008, 68, 1862.
11. Zeitsch, K. J. The Chemistry and Technology of Furfural and Its Many By-Products; 1st ed.; Elsevier: Amsterdam, The Netherlands, 2000; p 214.
12. Lin-Vien, D.; Colthup, N.; Fateley, W.; Grasselli, J. The Handbook of Infrared and Raman: Characteristic Frequencies of Organic Molecules, Academic Press: London, 1991; p 302.
13. Manfredi, L. B.; De La Osa, O.; Galego Fernández, N.; Vázquez, A. Polymer 1999, 40, 3867.
14. Grenier-Loustalot, M. F.; Larroque, S.; Grande, D.; Grenier, P.; Bedel, D. Polymer 1996, 37, 1363.
15. Gardziella, A.; Pilato, L. A.; Knop, A. Phenolic Resins, 2nd ed.; Springer-Verlag: Berlín, Heidelberg, 2000; p 45.

Figure 13 Relative intensity of 1456 cm^{-1} FTIR band versus time, in the different samples.