Furan resin as a replacement of phenolics: influence of the clay addition on its thermal degradation and fire behaviour

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SUMMARY

Nanocomposites based on a furan resin and different types of clays were obtained. Their thermal and fire behaviours were compared with traditional phenolic resins, which are known by their excellent flame resistance. Three types of montmorillonite clays were in situ added to the thermosetting matrix. A cone calorimeter and a smoke chamber were used to evaluate the performance of the materials against fire and their smokes generation. Global parameters were calculated for comparison purposes. Fires derived from the furan resin combustion grow faster than the phenolic ones, but they are extinguished more rapidly. This effect is enhanced by the incorporation of inorganic nanofillers. The only addition of any clay causes shorter fires but slightly speeds up the degradation process. A homogeneous nanofiller dispersion was found to be crucial to achieve good fire behaviour. Nevertheless, for materials with similar dispersion, the crosslinking degree of the polymer matrix appears as a secondary factor that determines slighter differences in the performance. Nanocomposites with organomodified clays showed a quite similar fire performance, though the composite containing the clay (Southern Clay Products, Inc., Louisville, Ky, USA) Cloisite®30B showed the best performance taking into account both the fire risk and the smoke evolution and obscuration. Copyright © 2013 John Wiley & Sons, Ltd.

1. INTRODUCTION

The high flammability and the release of toxic gases have become a critical limitation for the increasing usage of polymers. Nowadays, the fire security requirements are more rigorous, and the utilization of flame retardants is required for inhibiting the polymer combustion process. Demands concerning the polymer fire behaviour have become as important as mechanical, electrical and thermal requirements to be evaluated in the materials, given that plastics are indeed a relevant percentage of fire charge in buildings, industries and transport [1].

Flame retardants are systems capable to inhibit or to stop the combustion process by physical or chemical action. Traditionally, the incorporation of halogen- based compounds comprised an economical route for enhancing the flame retardancy of polymers without relinquishing product quality. However, regulatory concerns about the human and environmental contamination caused by the toxic compounds evolved during the combustion of halogens have pushed the market trend to halogen-free flame retardants. Some non-toxic halogen-free compounds, such as inorganic mineral fillers, require high levels of loading leading to additional costs, processing difficulties and deterioration of polymer mechanical properties. On the other hand, intumescent systems are relatively expensive to be applied

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for the large scale production of low cost combustible materials [2–5]. Consequently, the objective of developing highly effective 'green' flame retardants has prompt a rapid progress during the last decade, extending research into novel technologies [6, 7].

Recently, polymer nanocomposites emerged as one of the most promising developments in the area of flame retardancy because of their significant advantages over conventional formulations. Much attention was diverted to the use of layered silicates (clays), owing to their great potential for producing materials with improved flame retardancy along with superior physical properties [8–10]. In particular, nanoclays are the most used nanoparticles due to its wide availability and low cost. They contribute to the physical integrity of the burning material, and they are capable to migrate to the surface, acting as a barrier to mass and heat [12,14, 15]. This layer retards the flame spread but does not decrease the tendency to ignition nor the total heat release. During the last several years, a synergetic combination of nanoinorganic particles and flame retardants has been proved to improve the fire behaviour of a wide variety of systems against fire [1,11,16–19].

Regarding to thermosetting polymer matrices, it is well known that phenolics have good chemical resistance and thermal stability due to the formation a carbonaceous residue or char during their thermal degradation. Phenolic resins have been widely used for more than a century because of their excellent properties [20]. Nevertheless, the formaldehyde content in its formulation is trying to be reduced because of the damage caused to the ozone layer. In previous works [13,21–23], we have proposed a less environmental impact furan resin as an alternative to the traditional phenolic resins. Their performance has been evaluated from the structural, thermal and mechanical point of view, resulting in a highly potential replacement of phenolic resins. Nevertheless, as many of the applications of phenolic resins lay on their excellent fire behaviour, it is necessary to compare the performance of furan resins in this aspect as well.

Furthermore, three types of nanocomposites were prepared by the addition of montmorillonite clays to a furan resin. Even if the combination of these nanoclays composites with flame retardants are believed to be the optimal system expected to enter into market [1], there are still some unclear issues regarding the effect of silicates dispersion in fire behaviour. There is no theoretical background to correlate this aspect, and many results have been reported with opposite trends, depending on the type of matrix, processing or fillers compatibility. Opinions differ about the influence of the nanoparticles dispersion on the fire behaviour of polymers. Some authors reported that the type and degree of dispersion can be correlated with the fire performance of the nanocomposite [15,24, 25]. They stated that the material with the highest exfoliated structure is the most capable of reducing the peak of the heat release rate (HRR) curve, measured in a cone calorimeter. On the other hand, some authors [12,18,26–28] suggested that, although certain uniformity of the nanofillers is required, the nanomorphology (exfoliation, intercalation and presence of tactoids) does not play any significant role in the flammability of the nanocomposites.

Then, the aim of this work is to evaluate the influence of different type of clay on the fire resistance of a furan resin, taking into account the relevance of some nanocomposites properties (such as polymer crosslinking degree and dispersion of clay) on their global behaviour.

Subsequently, the system could be potentially improved for fire applications by the incorporation of flame retardants as synergetic combination, once that this aspect is clarified.

2. EXPERIMENTAL

2.1. Materials

A furan prepolymer was synthesized from phenol (Anedra) and furfural (Fluka). Phenol was molten and directly added into a stainless steel cylindrical reactor supplied with a condenser, a thermometer and constant mechanical stirring. The reaction media was adjusted using an aqueous solution of K_2CO_3 40% wt/vol. After heating up to 135°C, furfural was dropped during 30 min in a furfural to phenol molar ratio equal to 1. Each batch contained an initial volume of 750 mL. The temperature was maintained at 135°C for 4 h. The furan prepolymer was then heated up to 110°C, and 12%wt of hexamethylenetetramine was added as a catalyst.

The curing cycle intended to be slow enough to eliminate all the bubbles generated in the condensation reactions. Once the catalyst was added, the resin was poured in aluminium moulds of $10 \times 10 \times 0.5$ cm, and it was cured from 80°C to 180°C. The temperature of the mechanical convection oven was increased 10°C every 2 days, until reaching the final curing temperature. Flat plaques with no bubbles were obtained, and the material was named as F.

The nanocomposites were synthesized in the same way, but 2% wt of three different montmorillonite clays (Table I) were added in situ to the melting phenol. Mechanical stirring was applied for 30 min before dropping the furfural. Identical curing cycle was applied to the materials named as FNa, F30B and F10A.

2.2. Methods

Dynamical mechanical analyses were performed in a Perkin Elmer (Waltham, Massachusetts, USA) DMA at 10°C/min with a frequency of 1 Hz. Three points bending tests were carried out over rectangular samples from 20°C to 300°C. Results are averages of three replicas.

Thermogravimetric analyses (TGA) were carried out at 10°C/min under nitrogen using a TGA-Seiko Instrument SII Extar 6000. The tests were run from room temperature to 900°C. The mass of the sample used was close to 20 mg.

Plates of $10 \times 10 \times 0.5$ cm of the different furan materials were tested in a Cone Calorimeter Fire Testing Technology with external radiant heat flux of 50 kW/m^2 according to ISO 5660–2. An horizontal configuration was used, and the samples were placed over aluminium foil in a frame located 25 cm apart from the radiating source. The cone calorimeter is the most used instrument to assess the material properties against fire, because it records many parameters such as the time to ignition (TTI), HRR, peak of heat release rate (PHRR), effective combustion heat and total heat evolved (THE). Its measurement principle relates the oxygen consumption with the HRR during polymer combustion, through an empirical assumption.

The 'fire risk' leads to a global ranking related to the materials fire behaviour because it takes into account several parameters (THE, PHRR and TTI) [29]. It can be visualized by plotting THR versus the ratio between the PHRR and the TTI for each material. In this way, the materials with the best behaviour against fire are located close to the origin of coordinates.

Smoke related parameters such as total smoke production (TSP), specific extinction area (SEA) and CO and CO_2 evolution were also measured by the cone calorimeter.

A smoke density chamber (NBS) (Fire Testing Technology) under flaming conditions (ISO 5659) was used to measure the amounts of smoke in terms of its capacity to obscure the transmission of light. The smoke obscuration during the first 4 min of fire (VOF_4) and the maximum specific optical density (Ds_m) that measures the visible smoke intensity were recorded along with other parameters.

Table I. Characteristics of the clays incorporated to the nanocomposites.

Material	Clay	Organic modifier	Modifier concentration [meq/100g clay]	Distance between clay sheets (d_{001}) [Å]
F	-	-	-	-
FNa	Cloisite® Na$^+$ (CNa)	none	--	11.7
F30B	Cloisite®30B (C30B)	H$_2$C—CH$_2$—OH / H$_3$C—N$^+$—T / H$_2$C—CH$_2$—OH	125	18.5
F10A	Cloisite®10A (C10A)	H$_3$C / H$_3$C—N$^+$—CH$_2$— / HT	90	19.2

An opacity index (IOP) takes into account these parameters to give a global value, which is more useful for comparative proposes. It was calculated by Eq. 1, according to standard NFX 10702:

$$IOP = [(VOF_4/30) + (Ds_m/100)] \tag{1}$$

X-ray diffraction (XRD) patterns of solid monolith samples were obtained using a diffractometer Philips (Philips, Eindhoven, The Netherlands) PW 1710 (45 kV and 30 mA) at 2º/min, with a Cu Kα radiation ($\alpha = 1.54$ Å).

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.

3. RESULTS AND DISCUSSION

In previous works [22, 23, 30], we have reported that the addition of montmorillonite clays leads to different polymer crosslinking degrees, depending on the physical interactions, compatibility and processing. A similar trend was observed in the present work by comparing the rubber modulus obtained by dynamic mechanical analyzer for the different materials. In a polymer network, this property is inversely proportional to the average molecular weight between two crosslinking points. Figure 1 shows that the addition of clay favours the reticulation of the furan resin, resulting F30B the highest crosslinked material.

Other structural differences are evidenced by analysing the percentage of residual mass as a function of temperature (Figure 2) for the furan resin and its nanocomposites, measured by thermogravimetry. No significant differences were observed up to 450°C, but then, a higher thermal resistance for the composites containing the organically modified clays was observed. No correlation between the clay content and the residual mass was observed. It seems that the residual mass was not only related to the amount or type of inorganic filler added but also to the final chemical structure of the material. In previous works [23], the addition of different types of clays led to some differences in the chemical structure of the furan resin.

The thermogravimetric studies also indicated that the degradation of the nanocomposites occurred over a similar temperature range as that of the furan resin. The time derivative of the mass loss for each material is reported in Figure 3. A similar behaviour was observed for a traditional phenolic resin [31]. The peaks at temperatures up to 350°C could be related to the evaporation of water and to the free residual monomers and the oligomers release. The region from 350°C to 600°C can be related to the overall degradation zone, where the chains scission/fragmentation and the crosslinking reactions take place. Then, the structures previously formed partially decompose, leading to the
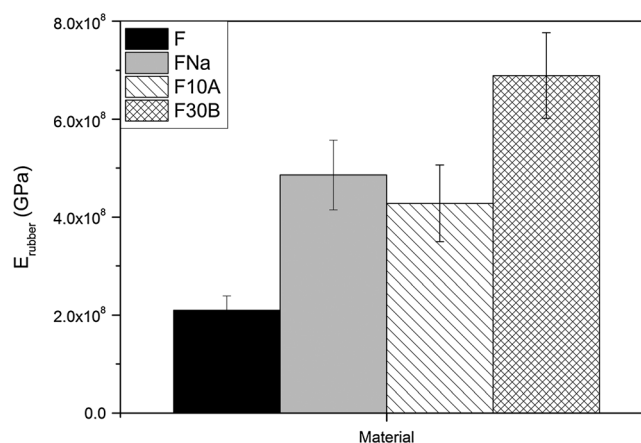

Figure 1. Rubber modulus of the materials, determined by dynamic mechanical analyzer.
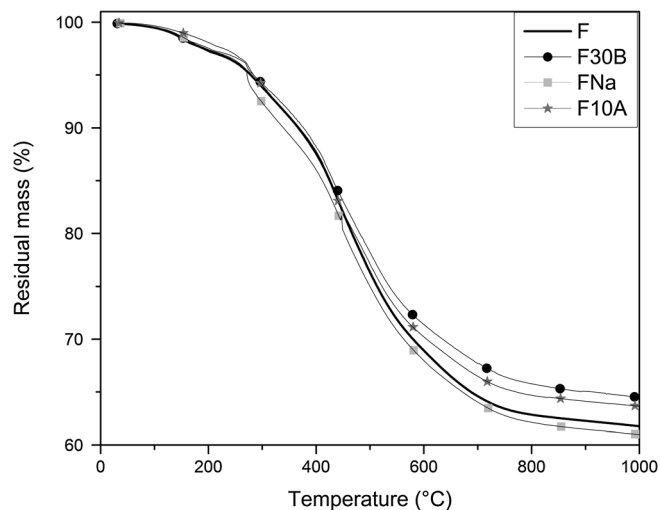
Figure 2. Percentage of residual mass versus temperature of the furan resin and its nanocomposites.
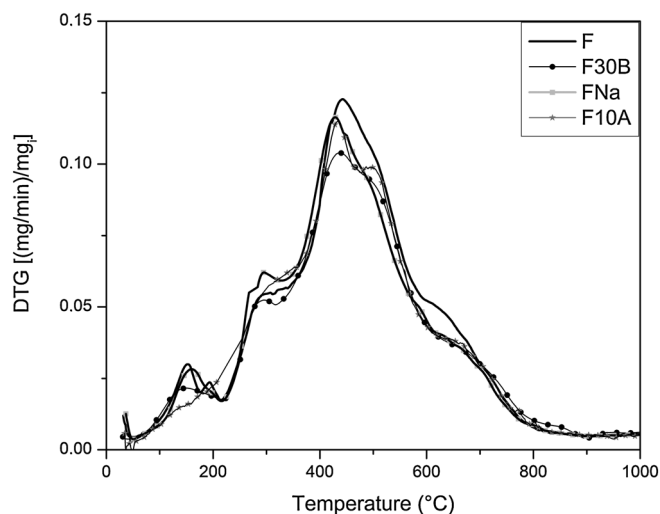

Figure 3. Derivative thermogravimetry (DTG) curves of the furan resin and the nanocomposites with the different clays.

development of the carbonaceous residue or char at temperatures higher than 600°C. All the nanocomposites showed a lower height of the peak compared with the one of the furan resin in the main region. This fact indicates that the clay addition diminishes the degradation rate of the furan resin in this condition. This behaviour could be related to the more crosslinked structure of the nanocomposites, as explained previously.

The cone calorimeter is the most effective-bench scale method for the evaluation of flame retardant properties. The HRR is a variable of great interest in the characterization of fires. A high HRR causes fast ignition and flame spread, whereas the PHRR represents the point in a fire where heat is likely to propagate further or ignite adjacent objects.

The characterization of the flammability properties of the furan resin and its nanocomposites, under fire-like conditions using the cone calorimeter, has been performed. Figure 4 shows the same pattern in the HRR curves of all materials. The first peak corresponds to the start of burning, and then, the HRR diminishes because of the development of the insulating char layer. After that, the second stage begins with the overall develop of the fire, represented by the second peak. Finally, the fire is extinguished at a
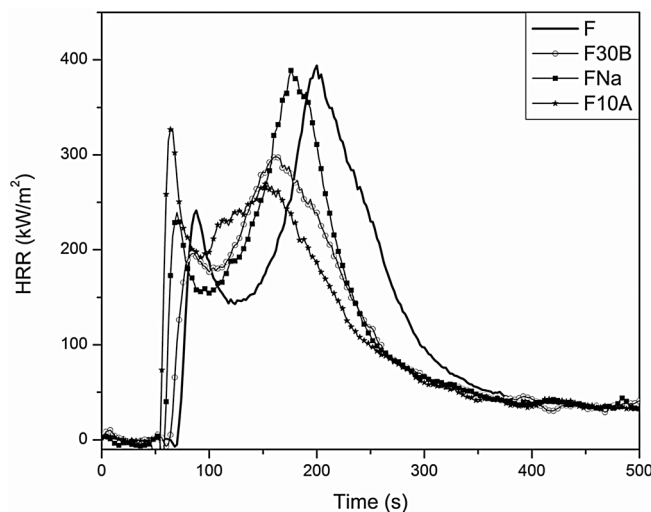
Figure 4. Heat release rate for the furan resin and the nanocomposites.

certain time, showing a strong decrease in the HRR. The presence of the decay after the first peak indicates that these materials are suitable for a fire scenario, because there is a time between the first and the second peaks that allows escaping prior to the fully developed fire.

It was observed from the HRR curves that there is no significant difference in the ignition time among the materials. This was expected because the experimental conditions applied, that is a flux of $50\,kW/m^2$, were chosen to simulate the combustion condition but not the first stages of real fires [32]. However, a decrease in the flame duration as well as in the time of the maximum of the peak of HRR with the clay addition was observed. These values were reported and compared in Figure 5.

Heat related parameters such as the height of the PHRR, THE and the effective heat of combustion were also obtained from the HRR curves and reported in Table II. No significant changes were observed in the effective heat of combustion, and a slight diminution of the THE occurred with the clay addition. These results indicate that in fact, the clays act as barrier, thus reducing the heat and mass transfer between the flame and the polymer and also slowing the escape of gases from the polymer degradation. The barrier effect was reported as the most common fire retardancy mechanism of clays in polymers. In this way, several authors reported little or no differences in the
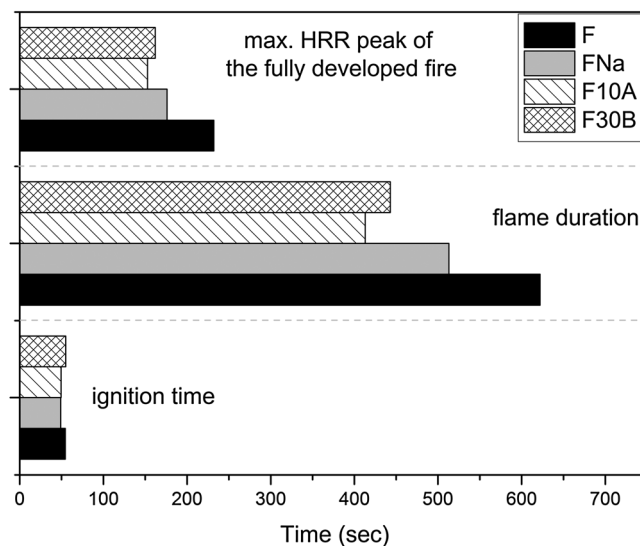

Figure 5. Characteristic times of the materials from the cone calorimeter test.

Table II. Heat and smoke related parameters for the furan resin and the nanocomposites.

Material	Height of the peak of HRR [kW/m^2]	Total heat evolved [MJ/m^2]	Effective heat of combustion [MJ/kg]	Specific extinction area [m^2/kg]
F	393	75.4	19.8	368.9
FNa	389	58.3	20.0	246.7
F10A	272	53.0	19.7	262.4
F30B	298	51.5	18.8	207.2

TTI nor in the THE when clays were added to polymers [12,15,33]. They claimed that nanoparticles influence principally the flame spread reducing the peak of heat release, so the reduction in PHRR without varying the THE is an indicative of the existence of a physical barrier that prolongs the flaming times without decreasing the amount of combustible material. Despite that the particles act as barriers to heat and mass transport, they also could produce additional effects such as changes in the thermal/thermo-oxidative decomposition (Figure 3) and the melt viscosity of the polymer. The reduction in the time of the maximum of the PHRR (Figure 5) could be associated to the products evolved because of the clay organomodifier decomposition, which can catalyze the degradation of the polymer matrix [1].

A reduction in the height of the PHRR was observed for the furan nanocomposites containing the organically modified clays (Table 2). However, no influence in this parameter was observed when the unmodified CNa was added. This result could be related to the clay dispersion in polymeric matrix, as follows.

The morphology of the nanocomposites was studied by XRD and TEM. It is useful to use these two techniques together to better determine the nanoparticles dispersion in a polymeric matrix. The XRD technique provides the distance between the clay layers from the basal peak while the TEM images allow a direct visualization of the platelets distribution in the sample. From the XRD patterns (Figure 6), it was observed that the clay has a similar interlayer length in all the nanocomposites, given that all the curves showed a peak at approximately $2\theta = 6°$ corresponding to an interlayer distance of 14.7 Å. In spite of this, the gallery distance of the CNa was expanded when it was added to the polymer, evidenced by a displacement of its basal peak (Table I) to smaller angles. This indicates that the polymer chains enter into the galleries due to the interaction between the −OH groups of the clay layers and the polymer. Inversely, a contraction of the interlayer region of both modified montmorillonites (Table I) occurred when they were added to the furan resin. This behaviour was also reported for epoxy and phenolic based nanocomposites [30,34–36]. It could be
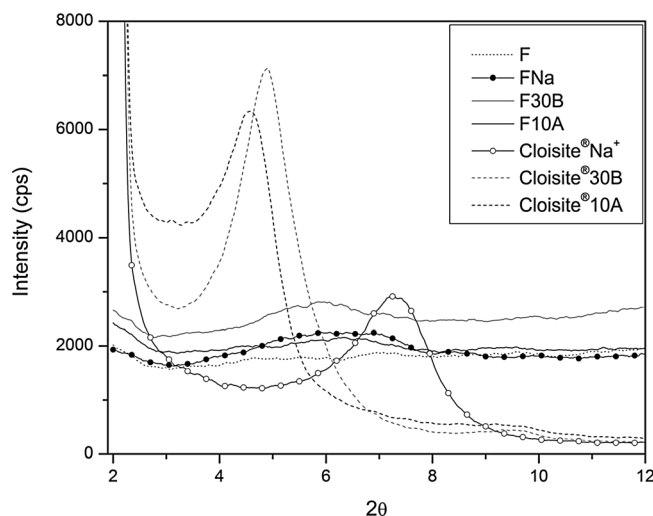

Figure 6. X-ray diffraction patterns of different clays and furan nanocomposites.

due to the loss of clay surfactants during curing and/or to a different rate of polymerization inside and outside the interlayer region. TEM micrographs of the material revealed the homogeneity of the clay distribution in the materials (Figure 7). Regions with large agglomerations were detected in FNa, while a better dispersion and distribution of the modified clays was observed in the furan resin.

Due to the different tendencies of the results obtained from the cone calorimeter test, the 'fire risk' was calculated to better evaluate the global fire performance of the materials. The y-axis indicates the propensity to cause a fire of long duration, and the x-axis illustrates the propensity to cause a quickly growing fire. Figure 8 shows the results obtained for the furan resin and its nanocomposites, as well as the values corresponding to traditional phenolic resins reported in a previous work [37]. It was observed that the furan resin causes a faster growing fire with slightly shorter duration in comparison with the one generated by the phenolic resins. On the other hand, the duration of the fire markedly diminished with the clay addition to the furan resin independently of the clay type. As it was previously explained, the clay contributes to the carbonaceous char that was produced during combustion acting as a physical barrier limiting not only the oxygen flow to the material but also the escape of volatiles from polymer degradation [1]. Thus, the difficulty for releasing flammable volatiles could explain that the flame was extinguished faster in the nanocomposites than in the resin alone. The worst behaviour against fire was obtained for the FNa. Although the clay causes a shorter duration fire in this material than in the furan resin, FNa produces the fastest growing fire and the highest PHRR (Table II). This behaviour could be related to the poor clay dispersion in the polymer as it was observed in the TEM micrographs (Figure 7).

The fire hazard is also strongly related to the smoke evolution. Indeed, the loss of visibility that avoids the escape is one of the most common causes of death in a fire scenario together with the carbon monoxide inhalation.

The TSP and the SEA are important parameters to evaluate the smoke production of a material by a cone calorimeter analysis. The SEA is reported as the rate of smoke production because it is a measure
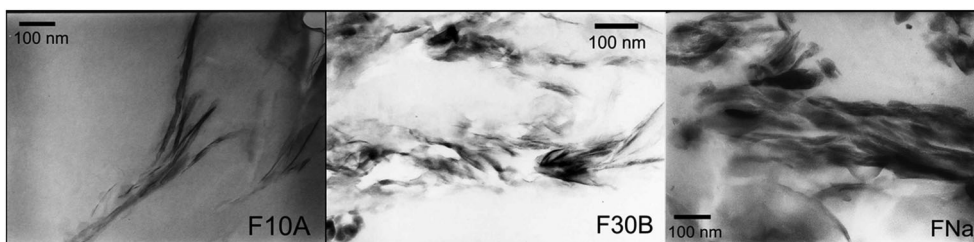

Figure 7. Transmission electron microscopy micrograph of furan nanocomposites.
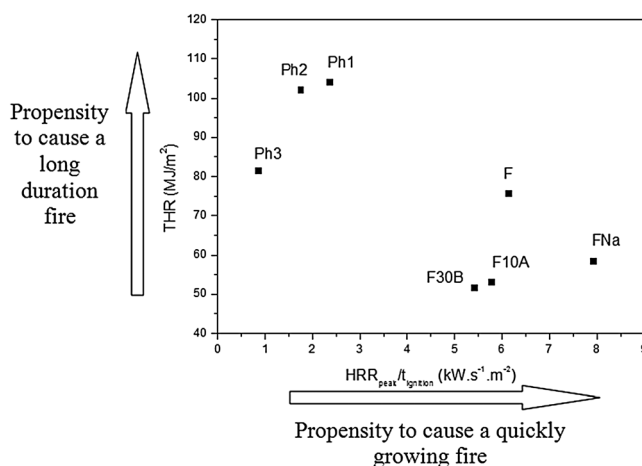

Figure 8. Fire risk of the furan resin, its nanocomposites and diverse traditional phenolic resins.

of the extinction area of the smoke produced when a unit mass of volatile fuel burns. This intensive property is often thought as a conversion factor because it quantifies the conversion of volatile fuel into smoke when the combustible burns [38]. The SEA values for the materials studied are reported in Table II, showing the F30B the lowest value. Concerning the TSP (Figure 9), it was observed that the appearance of the smoke is slightly faster in the case of the composites, in accordance with the HRR results (Figure 4). Nevertheless, a clear effect of the clays is achieved when the char is already formed. Once the flame is extinguished at around 200 s, the smoke production reaches a quite constant value. However, the smoke production curve of the neat resin continues to increase leading to the highest value, while the composites show no further increments. This may be due to a better effectiveness of the char barrier when any type of clay is present. From these results, it was observed that the F30B showed the lowest TSP and SEA values and produced the least amount of smokes, in comparison with the others materials studied.

In general, the amount of toxic carbon monoxide (CO) produced by the materials during the first 6 min is quite similar, but the nanocomposites generated lower final amounts than the neat resin (Figure 10).
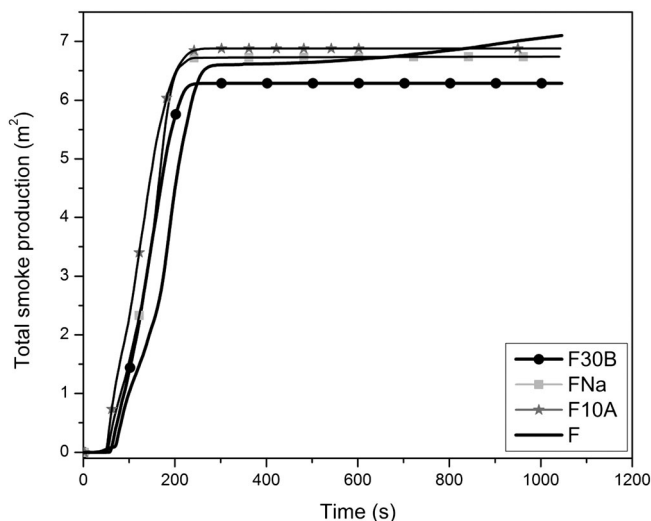

Figure 9. Total smoke production of each material with time.
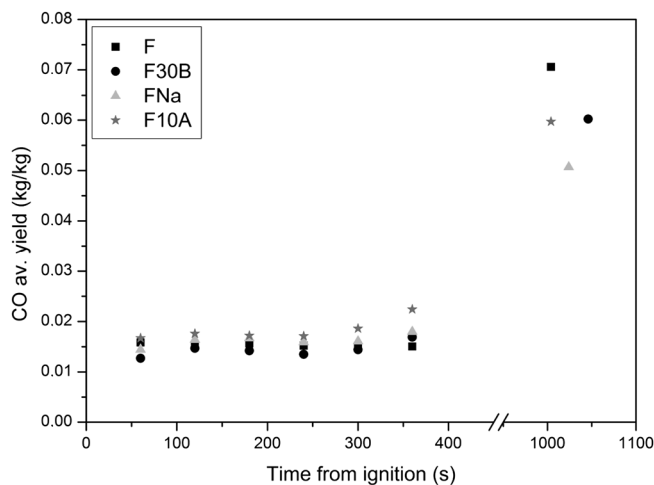

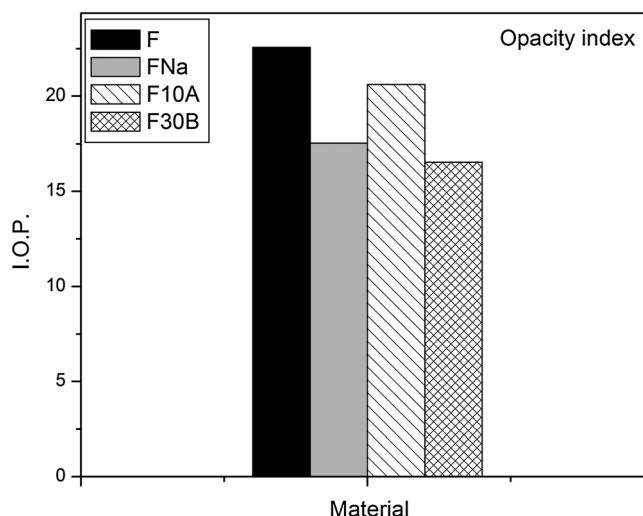Figure 10. Carbon monoxide average yield with time for all materials.

Figure 11. Opacity index of the materials.

The smoke density chamber was also used to characterize the smoke production of the furan resin and its nanocomposites. It was observed in Figure 11 that all nanocomposites showed a lower opacity index than the furan resin. As mentioned before, this global parameter is related to the density and obscuration of the smokes, and it represents a critical feature to be evaluated in case of real fires. Among them, the F30B showed the best performance.

Correlating these results with the ones obtained by the cone calorimeter, it can be concluded that the F30B was the material that showed the best performance against fire. It showed the lowest fire risk and smoke emission among the studied materials.

4. CONCLUSIONS

The proposed furan resin and their nanocomposites were ranked according to their global fire performance in terms of fire risk and then compared with a traditional phenolic resin. It was observed that furan resin has a better THR/fire growth rate than the phenolic ones. The addition of clay does not significantly modify the HRR peak of the furan resin. Nevertheless, the THR peak certainly decreased in the composites, thus further lowering the fire risk of these resins. Additionally, the parameters related to smoke release resulted greatly improved with the incorporation of inorganic fillers to the furan resin studied. Finally, F30B was considered the best of the evaluated materials, because of its best overall performance against fire and smokes.

In a further step, the incorporation of another flame retardant is suggested for the final use of this kind of resins together with the C30B clay.

REFERENCES

1. Kiliaris P, Papaspyrides CD. Polymer/layered silicate (clay) nanocomposites: an overview of flame retardancy. *Progress in Polymer Science* 2010; **35**(7):902–58.
2. Chen Y, Wang Q, Yan W, Tang H. Preparation of flame retardant polyamide 6 composite with melamine cyanurate nanoparticles in situ formed in extrusion process. *Polymer Degradation and Stability* 2006; **91**(11):2632–43.
3. Crummett W. *Decades of Dioxin. Princeton*, Xlibris Corp: NJ, 2002.
4. Irvine DJ, McCluskey JA, Robinson IM. Fire hazards and some common polymers. *Polymer Degradation and Stability* 2000; **67**(3):383–96.

5. Lomakin S, Haslam E. *Ecological Aspects of Polymer Flame Retardancy (new Concepts in Polymer Science)*. Brill Academic Publishers: Leiden, The Netherlands, 1999.

6. Bourbigot S, Le Bras M. Fundamentals: flame retardant plastics. In: J T, editor. Plastics flammability handbook: principles, regulation, testing and approval. Munich, Germany/Cincinnati, OH: Hanser Publishers/Hanser Gardner Publications Inc.; 2004. p. 134–48.

7. Lewin M. Physical and chemical mechanisms of flame retarding of polymers. In *Fire Retardancy of Plastics, the Use of Intumescence*, Le Bras M, Camino G, Bourbigot SRD, (eds). The Royal Society of Chemistry, Oxford, UK, 1998; 3–32.

8. Giannelis. Polymer-layered silicate nanocomposites: synthesis, properties and applications. *Applied Organometallic Chemistry* 1998; **12**:675–80.

9. Kandola BK. Nanocomposites. In: materials Fr, editor. Fire retardant materials. Cambridge, UK: Woodhead Publishing Ltd; 2001. p. 214–19.

10. Zanetti M. Flammability and thermal stability of polymer/layered silicate nanocomposites. In *Polymer Nanocomposites*, Mai YWYZ, (ed). Woodhead Publishing Ltd: Cambridge, UK, 2006; 256–72.

11. Laoutid F, Bonnaud L, Alexandre M, Lopez-Cuesta JM, Dubois P. New prospects in flame retardant polymer materials: from fundamentals to nanocomposites. *Materials Science and Engineering: R: Reports* 2009; **63**(3): 100–25.

12. Pavlidou S, Papaspyrides CD. A review on polymer–layered silicate nanocomposites. *Progress in Polymer Science* 2008; **33**(12):1119–98.

13. 2002/95/EC D. Restriction of hazardous substances (RoHS). European parliament 2000.

14. Toldy A, Anna P, Csontos I, Szabó A, Marosi G. Intrinsically flame retardant epoxy resin – fire performance and background – part I. *Polymer Degradation and Stability* 2007; **92**(12):2223–30.

15. Schartel B, Bartholmai M, Knoll U. Some comments on the main fire retardancy mechanisms in polymer nanocomposites. *Polymers for Advanced Technologies* 2006; **17**(9–10):772–7.

16. Xu YY, Guo ZH, Fang ZP, Wu Y. Flame retardancy and mechanical property of bi-layer polypropylene sheets with flame retardant selective distribution. *Advanced Materials Research* 2012; **396-398**(3):2145–8.

17. Morgan AB. Flame retarded polymer layered silicate nanocomposites a review of commercial and open literature systems. *Polymers for Advanced Technologies* 2006; **17**:206–217.

18. Morgan AB, Wilkie CA. (eds). *Flame Retardant Polymer Nanocomposites*. John Wiley & Sons: Hoboken, NJ, 2007.

19. Bourbigot S, Samyn F, Turf T, Duquesne S. Nanomorphology and reaction to fire of polyurethane and polyamide nanocomposites containing flame retardants. *Polymer Degradation and Stability* 2010; **95**(3):320–6.

20. Pilato L. *Phenolic Resins: A Century of Progress*. Springer Berlin Heidelberg: Berlin, 2010.

21. Rivero G, Fasce LA, Ceré SM, Manfredi LB. Anticorrosive behaviour of metal furan coatings. *X Simposio Argentino de Polímeros* (SAP 2013). Buenos Aires, Argentina.

22. Rivero G, Pettarin V, Vázquez A, Manfredi LB. Curing kinetics of a furan resin and its nanocomposites. *Thermochimica Acta*. 2011; **516**(1–2):79–87.

23. Rivero G, Vázquez A, Manfredi LB. Synthesis and characterization of nanocomposites based on a furan resin. *Journal of Applied Polymer Science* 2010; **117**(3):1667–73.

24. Bartholmai M, Schartel B. Layered silicate polymer nanocomposites: new approach or illusion for fire retardancy? Investigations of the potentials and the tasks using a model system. *Polymers for Advanced Technologies* 2004; **15**(7):355–64.

25. Duquesne S, Jama C, Le Bras M, Delobel R, Recourt P, Gloaguen JM. Elaboration of EVA–nanoclay systems—characterization, thermal behaviour and fire performance. *Composites Science and Technology* 2003; **63**(8):1141–8.

26. Pandey JK, Raghunatha Reddy K, Pratheep Kumar A, Singh RP. An overview on the degradability of polymer nanocomposites. *Polymer Degradation and Stability* 2005; **88**(2):234–50.

27. Ray SS, Okamoto M. Polymer/layered silicate nanocomposites a review from preparation to processing. *Progress in Polymer Science* 2003; **28**(11):1539–641.

28. Samyn F, Bourbigot S, Jama C, Bellayer S. Fire retardancy of polymer clay nanocomposites: is there an influence of the nanomorphology? *Polymer Degradation and Stability* 2008; **93**(11):2019–24.

29. Schartel B, Braun U, Schwarz U, Reinemann S. Fire retardancy of polypropylene/flax blends. *Polymer* 2003; **44**(20): 6241–50.

30. Rivero G, Vázquez A, Manfredi LB. Resol/montmorillonite nanocomposites obtained by in situ polymerization. *Journal of Applied Polymer Science* 2009; **114**(1):32–9.

31. Puglia D, Kenny JM, Manfredi LB, Vázquez A. Influence of the chemical composition on the thermal degradation and fire resistance of resol type phenolic resins. *Materials engineering* 2001; **12**(1):55–72.

32. Schartel B, Hull TR. Development of fire-retarded materials—interpretation of cone calorimeter data. *Fire and Materials* 2007; **31**(5):327–54.

33. Katsoulis C, Kandare E, Kandola BK. The effect of nanoparticles on structural morphology, thermal and flammability properties of two epoxy resins with different functionalities. *Polymer Degradation and Stability* 2011; **96**(4):529–40.

34. Becker O, Varley R, Simon G. Morphology, thermal relaxations and mechanical properties of layered silicate nanocomposites based upon high-functionality epoxy resins. *Polymer* 2002; **43**(16):4365–73.

35. Kornmann X, Lindberg H, Berglund LA. Synthesis of epoxy–clay nanocomposites: influence of the nature of the clay on structure. *Polymer* 2001; **42**(4):1303–10.

36. Wu Z, Zhou C, Qi R. The preparation of phenolic resin/montmorillonite nanocomposites by suspension condensation polymerization and their morphology. *Polymer Composites* 2002; **23**(4):634–46.
37. Manfredi LB, Rodríguez ES, Wladyka-Przybylak M, Vázquez A. Thermal degradation and fire resistance of unsaturated polyester, modified acrylic resins and their composites with natural fibres. *Polymer Degradation and Stability* 2006; **91**(2):255–61.
38. Whiteley RH. Short communication: some comments concerning the measurement of smoke. *Fire and Materials* 1994; **18**(1):57–9.