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Curing characteristics of resol-layered silicate nanocomposites

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Abstract

The influence of the presence of montmorillonite (unmodified and modified) within a resol resin on curing of nanocomposites was studied by differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FT-IR). The acid nature of the clay seems to accelerate primary oxidation processes of resol resin at used temperatures. The nature and amount of clay-modifiers show a strong influence on oxidation reactions and on the rate of curing. In the case of phenylalanine modified montmorillonite (PheMMT), phenylalanine could act in a similar way to formaldehyde due to its reactive groups, leading to an increase of formaldehyde/phenol molar ratio and promoting oxidation at the used temperatures. In the case of a commercial organically modified clay, the presence of long alkyl chains avoids the acceleration of oxidation reactions. The contribution of montmorillonite ions to the oxidation seems to be larger than that of phenylalanine chains. Temperature of curing and state of dispersion of the clay also affect oxidation reactions.

Keywords: Resols; Nanocomposites; Montmorillonite; Phenylalanine; Curing

1. Introduction

Nanocomposites based on organic polymers and inorganic clay minerals consisting of silicate layers such as montmorillonite (MMT) have attracted great interest due to unexpected property improvements including mechanical, thermal, barrier and clarity properties without a significant increase in density, what is not possible with conventional fillers [1–8]. 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 multilayer silicate mineral that naturally possesses inorganic cations within its galleries to balance the charge of the oxide layers in a hydrophilic environment. The ion exchange of these cations with organic ammonium ions improves the compatibility of the modified montmorillonite with polymers and the dispersion of the layers into the matrix. Moreover the modified clay can react or interact with the monomer or the polymer to improve the interfacial strength between clay nanolayers and the polymer matrix.

Phenolic resins are synthesized by the reaction of phenol with aldehydes, especially formaldehyde, and are classified as resoles and novolacs depending on synthetic conditions and curing mechanism. Phenolic resins have been widely used due to their high temperature resistance, high char yield, solvent resistance and moderate flame resistance in many areas, especially in thermal insulation materials, coating applications, adhesives, molding compounds, abrasives, laminates and in other composite materials [9–13].

On the other hand, only a few studies have been performed on nanocomposites based on phenolic resin due to their three-dimensional molecular structure even prior to cure that may avoid the exfoliation of the clay [14–22]. In addition, formation of water as a by-product of cross-linking is also another problem of this kind of resins.

In a previous study [23], resol type phenolic resin-layered silicate nanocomposites were synthesized by monomer intercalation to overcome the structural problem of MMT dispersion and exfoliation into phenolic resins matrix. MMT was modified by using an aminoacid, phenylalanine (Phe), to induce

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condensation reactions between the carboxyl end group of the phenylalanine and the hydroxyl groups of the formaldehyde and enhance the compatibility with the phenolic resin matrix. Morphology, dispersion and thermal stability of resol–MMT nanocomposites were investigated. From X-ray diffraction (XRD) analysis and AFM images, it was shown that the silicate layers of clay had been intercalated in the resol matrix. Moreover a slight improvement in thermal stability of the resin system was also observed by the incorporation of the organically modified clay.

To produce high-performance polymer nanocomposites, selection of the best curing condition based on the polymerization kinetics is very important. Curing kinetics of phenolic resins has been previously studied [24–27] in the presence of lignin [28], tannin [29] or urea [30]. However the curing kinetics of phenolic resins during nanocomposite formation has not been still investigated. In this paper, the effects of clay content within a resol resin on process of curing have been studied by differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FT-IR).

2. Experimental

Cloisite^R-Na$^+$ (Na$^+$-MMT), an untreated Na$^+$-montmorillonite and Cloisite 30B, an organically treated MMT with methyl tallow bis-2-hydroxylethyl quaternary ammonium, were purchased from Southern Clay Products Inc. Phenylalanine was purchased from Aldrich. Phenol was supplied by Hexion Specialty Chemicals Ibérica and formaldehyde (35–40% aqueous solution) and triethylamine (TEA) were purchased from Panreac and used without further purification.

PheMMT was prepared through the ion exchange of Cloisite^R-Na$^+$ (Na$^+$-MMT) with phenylalanine in acidic environment, as published elsewhere [23].

Different amounts of PheMMT were sonicated in formaldehyde solution and treated in presence of sulphuric acid with the aim of promoting the condensation reaction between the carboxyl end group of the phenylalanine and the –OH groups of the formaldehyde in aqueous solution [23]. Cloisite 30B, clay underwent the same treatment in order to react its –OH end groups with the –OH groups of the formaldehyde solution [23].

Prepolymers were synthesized by mixing the previously obtained formaldehyde solutions of PheMMT and Cloisite 30B with formaldehyde and phenol in order to work with a formaldehyde/phenol molar ratio 1.4. The pH of formaldehyde/phenol mixture was adjusted to 8.0 with TEA. Condensation was carried out at 80 °C until prepolymers showed 1/1 g/g solubility in water. Water extraction was performed under vacuum at 45–48 °C to a solid content of 75–80 wt.%. Samples were stored at −20 °C until they were analyzed.

Neat resol (Res), resol in presence of unmodified montmorillonite (RNa) and resol mixed with the same amount of neat aminoacid (Phe) present in the organically modified clay (Res–Phe), as measured by TGA, were synthesized following the same conditions than for the modified resins. Table 1 resumes the starting conditions of each synthesized prepolymer. Samples with montmorillonite were designed as Phe-*i*, C*i* and R*i*Na being *i* the weight content of modified montmorillonite.

Table 1
Final characteristics of clay–resol resins and neat resol before curing

Designation	Dilutability in water (1 g/1 g)	Solid content (%)	n_D
Res	1.20	76.0	1.565
Phe-1	0.86	78.5	1.579
Phe-2	0.92	81.1	1.582
Phe-4	1.02	80.7	1.580
C2	0.81	78.6	1.576
R2Na	1.12	81.0	–

Fourier transform infrared spectroscopy was used to follow the polymerization reaction. Infrared spectra on KBr pellets were performed in a Nicolet Magna-IR System 750 spectrometer using a heating chamber, Specac. The acquisition conditions were 4000–400 cm^{-1} spectral range, 20 scans, and a resolution of 2 cm^{-1}.

Differential scanning calorimetry, PerkinElmer DSC-7, was used to perform dynamic experiments. Sample weights were between 3 and 5 mg and medium pressure/Viton 120 μL pans were used. Dynamic temperature scans were conducted at five heating rates 5, 10, 15 and 25 °C/min from 30 to 280 °C. Nitrogen was used as purge gas at a flow rate of 40 mL/min.

3. Results and discussion

After the process of synthesis and curing, three kinds of different composites have been obtained. When using PheMMT as clay, at low percentages (Phe-1 and Phe-2 composites), an intercalated/exfoliated state was observed by optical microscopy and atomic force microscopy [23]. The increase of the amount of modified MMT (Phe-4 composite) results in an intercalated composite with some agglomerates of clay [23]. On the other hand, using Cloisite 30B and Na$^+$-MMT (C2 and R2Na composites), thick agglomerated clay particles are observed, indicating poor dispersion of MMT in the resol matrix [23].

Curing of composites was monitored by FT-IR at 110 °C in order to observe the influence of the clay in resol polymerization. Characteristic absorbances of resol resin are assigned in Table 2 [13,31]. Fig. 1a–f shows FT-IR spectra of curing reaction at 110 °C of neat resol, C2, R2Na, Res–Phe and Phe-2 y Phe-4 as a function of time. As can be observed, the presence of montmorillonite and its type of modification strongly affect curing of the composite. Overall, evolution of resol curing can be followed by the disappearance of the band of hydroxyphenols at 1000 cm^{-1} and the formation of the band of ether linkages at 1060 cm^{-1}. For neat resol and C2, the evolution of curing reactions is quite similar. Moreover, the presence of the band at 689 cm^{-1} of free phenol and the smaller area of the band due to the formation of ether linkages at 1060 cm^{-1} in the resin C2 could indicate lower cross-link density than for the neat resol, that it is also observed below by DSC.

For R2Na, PheMMT modified resins and phenylalanine in resol matrix, the existence of the band at around 1650 cm^{-1},

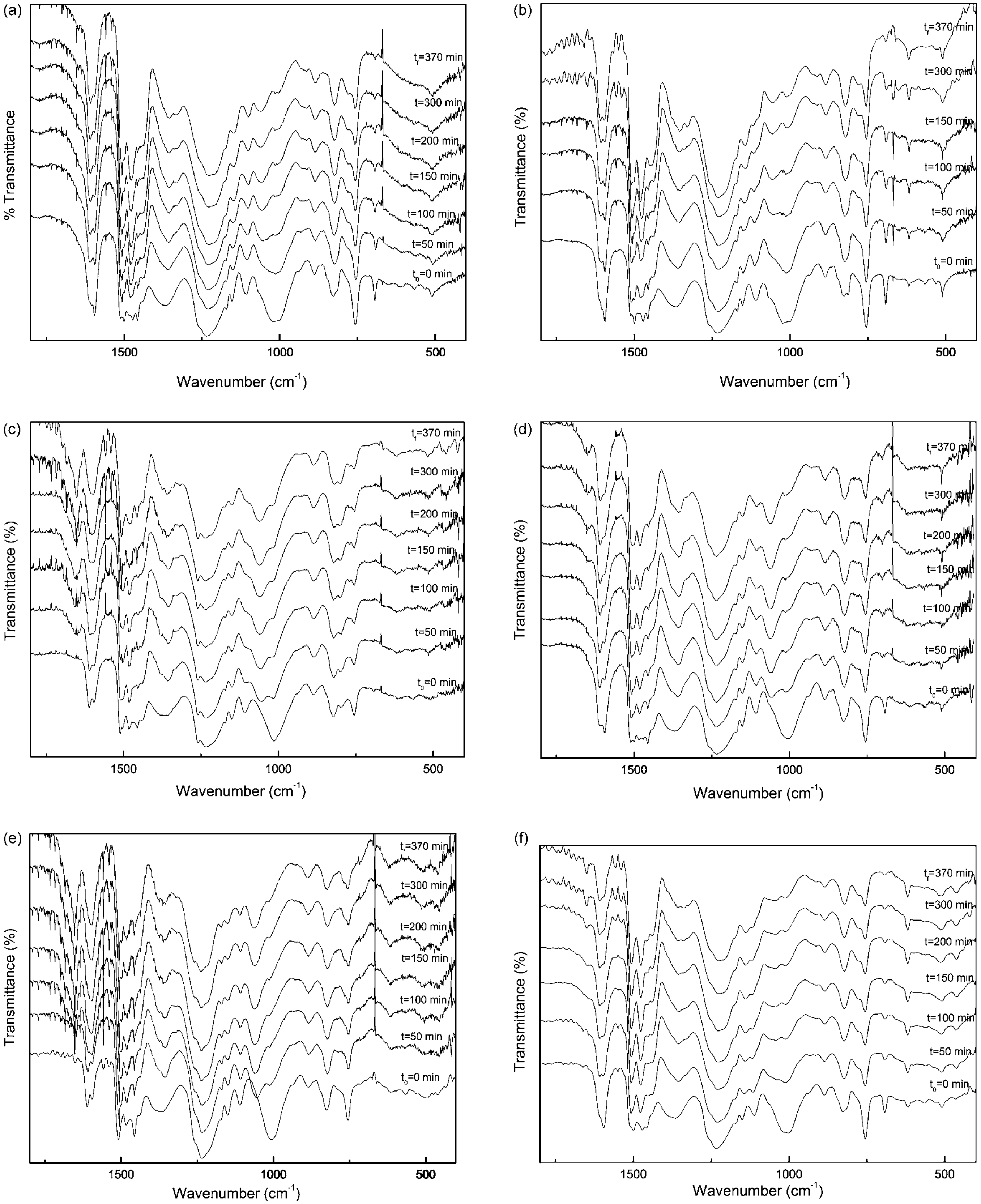

Fig. 1. FTIR spectra of the curing reaction at 110 °C as a function for time of (a) Res, (b) C2, (c) R2Na, (d) Res–Phe, (e) Phe-2 and (f) Phe-4.

Table 2
Functional groups and observed wavenumbers for phenol–formaldehyde resol resin

Wavenumber (cm^{-1})	Vibration	Functional group
3550–3450	ν (OH) free	Phenol and hydroxymethyl groups
3400–3300	ν (OH) associated	Phenol and hydroxymethyl groups
3060	ν (CH)	Aromatic ring
3010	ν (CH)	Aromatic ring
2920	ν_{ip} (CH_2)	C–H aliphatic
2860	ν_{op} (CH_2)	C–H aliphatic
1605–1595	ν (C=C)	Aromatic ring
1500	ν (C=C)	Aromatic ring
1475	d (CH_2)	C–H aliphatic methylene bridge
1450	ν (C=C)	Aromatic ring
1355	d_{ip} (OH)	Phenolic
1215	ν (C–O)	Phenolic
1140	d_{ip} (CH)	Aromatic ring
1100	d_{ip} (CH)	Aromatic ring
1060	ν (C–O)	Ether bridge
1000	ν (C–O)	Aliphatic hydroxyl
885	d_{op} (CH)	Isolated H
822	d_{op} (CH)	Para-substituted
756	d_{op} (CH)	Ortho-substituted
689	d_{op} (CH)	Adjacent 5H, phenol

attributed to carbonyl group, indicates possible oxidation reactions promoted by the presence of montmorillonite or the modifier. It has been reported [13] that increasing formaldehyde/phenol molar ratio using TEA as catalyser, oxidation reactions, which usually occur at higher temperatures, are accelerated. Different explanations about the cause of this phenomenon have been reported. Conley and Bieron [32,33] suggested that the attack of the oxygen occurs in the doubly activated methylene bridge to form benzophenone linkage. On the other hand, Lenghaus et al. [34] proposed that the formation of carboxylic groups was due to scission of ether bridge. In our case, the presence of montmorillonite and also phenylalanine modified montmorillonite seems to accelerate the oxidation reaction during cross-linking process. The oxidation of phenol in the presence of unmodified montmorillonite has been already reported [35]. Different mechanisms have been suggested to contribute to the oxidation of phenol. Larson and Hufnal [36] proposed that structural metals of clay minerals such as Al, Fe, Zn and Cu transfer electrons to the surface-adsorbed oxygen of the clay which are then released as hydroperoxyl radicals, capable of abstracting electrons from phenols. Mortland and Halloran [37] indicated that the oxidation–reduction properties of the exchangeable cations of the clay, such as Fe(III) and Cu(II), contribute to phenol polymerization through the coupling of the radical cations with phenols. Solomon and Hawthorne [38] showed that partially coordinated Al located on the edge of the clay crystals and Al in the silica sheet resulted of isomorphous substitution are Lewis acids capable of accepting electrons from various aromatic compounds. The band at around 1650 cm^{-1} attributed to carbonyl group of benzophenone structures was reported as a consequence of primary oxidation processes [32]. Secondary oxidation can also be observed as a shoulder on the carbonyl bands growing at a frequency of 1680 cm^{-1} in composites R2Na and Phe-2. This band is due to the formation of quinone-type structures [32]. Fig. 2 shows the possible reaction pathway of oxidation of resols in presence of montmorillonite.

The contribution of montmorillonite to oxidation reactions seems to be larger than that of phenylalanine, as can be observed by the area of carbonyl signal of benzophenone structures at 1650 cm^{-1} for R2Na, Res–Phe and Phe-2 composites. This behaviour is also confirmed below by means of DSC. The acid nature of the montmorillonite seems to act as a stronger contribution to oxidation than the modifier of the clay, namely phenylalanine.

As shown in Fig. 1, the disappearance of the band of hydroxyphenols at 1000 cm^{-1} and of formation of ether linkages at 1060 cm^{-1} have also been observed, following the sequence Phe-2 > Res–Phe > Phe-4 > R2Na > Res > C2. In addition, according to the larger area of the band at 1060 cm^{-1}, the presence of phenylalanine in Res–Phe and Phe-2 composites seems to catalyse the formation of ether linkages. The reaction between phenylalanine and resol chains giving ether linkages

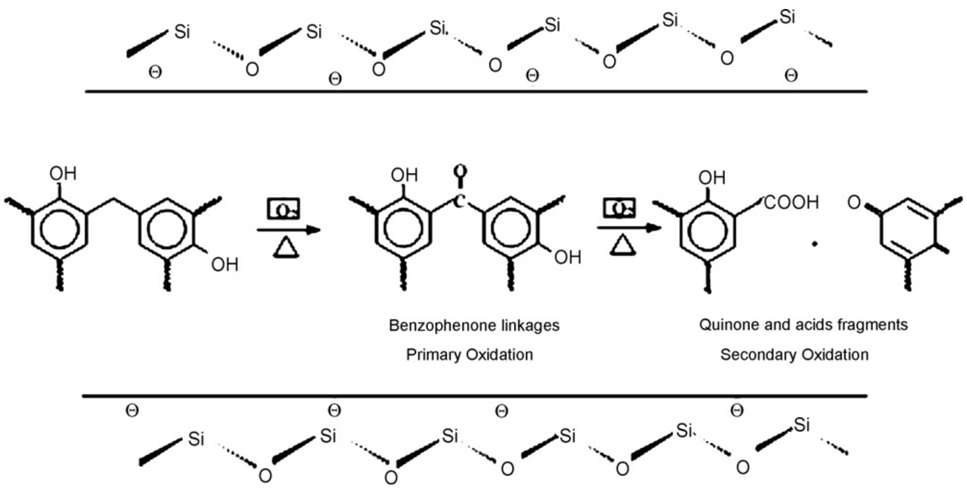

Fig. 2. Possible oxidation reaction of resol matrix in presence of montmorillonite.

could also promote further oxidation in these composites. It has been previously reported using TEA as catalyser [13] that oxidation reactions are catalysed when formaldehyde/phenol molar ratio increases. In this work, phenylalanine could act as in a similar way to formaldehyde due to its reactive groups, thus increasing formaldehyde/phenol molar ratio and inducing oxidation at the used temperatures. Thereby, for Phe-2 composite, the oxidation seems to be larger than in the other composites. In this case, the two effects that induce oxidation, the cationic nature of the montmorillonite and the fact of the increase of the reactives ratio by the presence of phenylalanine are observed. This behaviour would only occur when intercalation is achieved and the reaction between the modifier of MMT and formaldehyde is possible. On the other hand, according to the area of the band at 1650 cm^{-1}, for composite Phe-4, the oxidation reaction seems to be lower. This behaviour is also observed below by DSC. The existence of excess of non-reacted surfactant, due to poor dispersion of the clay in the matrix and the lack of reaction between the modifier and formaldehyde, could decrease the acid nature of the montmorillonite, thus leading to less oxidation. On the other hand, it is worth to note the behaviour of composite C2. In contrast with the other MMT modified composites, C2 composite has a similar behaviour to the resol matrix. This fact could be related to the nature of the organic modifier of the clay. In the case of C2 composites, the acid nature of the montmorillonite could be decreased for the presence of long alkyl chains, thus avoiding the acceleration of oxidation reactions at the used temperatures. Indeed, the presence of natural montmorillonite and its acid nature accelerates oxidation reactions, usually occurring at higher temperatures. On the other hand, modification of the clay can affect this acceleration, being this fact function of chemical composition of the modifier.

In Fig. 3 the overall changes produced through oxidation reactions are shown for samples cured at 110 °C. As can be observed for Phe-1 and Phe-2 composites, the formation of benzophenone structures is confirmed by the presence of the band of carbonyl group at 1650 cm^{-1}. Furthermore, it is worth to note the disappearance of OH stretching vibration band present at around 3500 cm^{-1} due to the oxidation of these groups. On the other hand, the disappearance of the CH_2 asymmetric stretching band at 2920 cm^{-1} and the increase of the area of the CH_2 symmetric stretching band at 2860 cm^{-1} are also seen. This fact along with the disappearance of the CH_2 scissor vibration band at 1475 cm^{-1} in composites that undergo oxidation could prove the tendency to form ether bridges instead of methylene bridges, as observed in FT-IR spectrum for neat resol. These changes related to oxidation reactions have been previously reported for a resol matrix at 200 °C by Conley and Bieron [32].

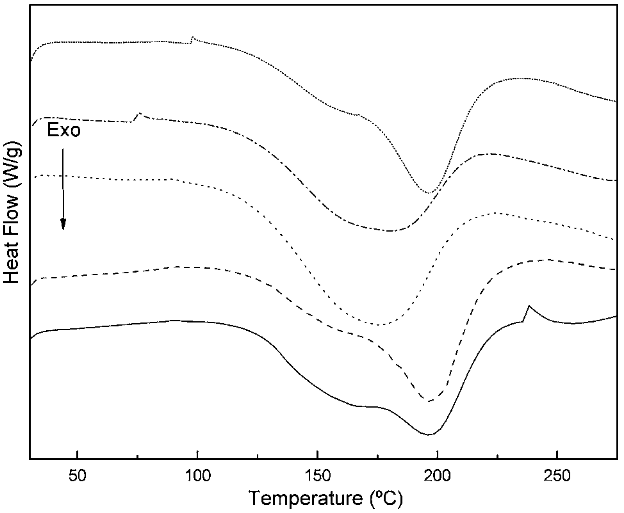

Fig. 4. DSC thermograms at 10 °C/min for neat resol (—), Phe-1 (– –), Phe-2 (- - - -), Phe-4 (– – –) and C2 (- - - -) composites.

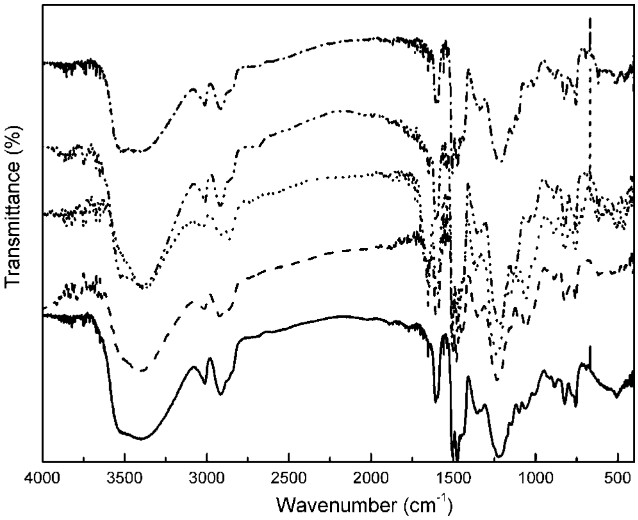

Fig. 3. FTIR spectra of neat resol (—), Phe-1 (– –), Phe-2 (- - - -), Phe-4 (– – – –) and C2 (. . .) composites at the end of curing.

Dynamic DSC scans from the first run for neat resol, PheMMT and C2 composites are shown in Fig. 4. As can be observed, neat resol exhibits two major exothermic peaks. The first one, in the temperature range of 150–170 °C, is related to condensation reaction of resols giving as a result methylene and ether bridges [13,25]. The second exothermic peak centred around 200 °C is related to different reactions, such as the break of ether bridges to methylene bridges or/and oxidation reactions at higher temperatures [13,25]. This behaviour changes for composites with PheMMT. Increasing PheMMT content, both peaks merge in only one. The presence of modified montmorillonite confirms the acceleration of reactions that usually occur in a second step, namely oxidation reactions. Thus, the presence in DSC thermogram of an only peak for Phe-2 and Phe-4 composites could be explained by the presence of the montmorillonite and its acid nature. On the other hand, the existence of two peaks in the C2 composite is consistent with above shown FT-IR results.

To verify the origin of this change in curing behaviour of the resins, DSC scans at 10 °C/min for Res–Phe and R2Na composite were also carried out (Fig. 5). DSC results for R2Na composite seem to have the same behaviour that Phe-2 composite as only one broad peak was observed. That behaviour is in contrast with the two peaks that Res sample shows. In the case of Res–Phe the tendency to one peak also appears. Thereby oxidation is also observed by DSC for composites that contain MMT or its modifier. As shown above by FT-IR, montmorillonite and

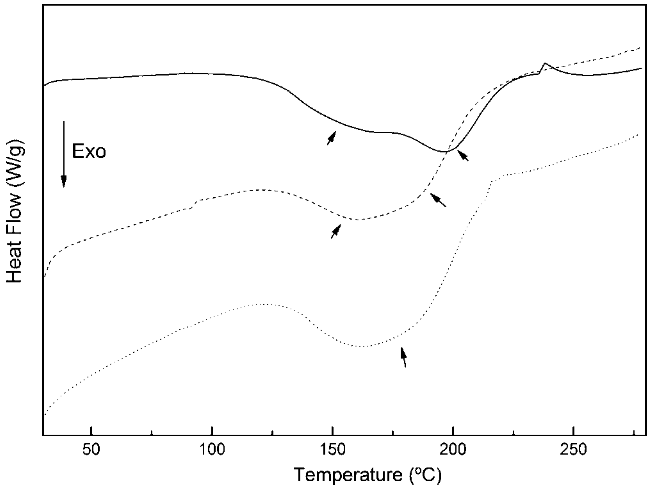

Fig. 5. DSC thermograms at 10 °C/min for neat resol (—), Res–Phe (– –) and R2Na (- - - -) composites.

phenylalanine seems to induce oxidation reactions of the resol matrix. As it has been stated above, according to the area of the carbonyl signal of benzophenone structures at 1650 cm^{-1}, the contribution of montmorillonite to oxidation reactions seems to be larger than that of phenylalanine. In the case of Res–Phe composite, the smaller area observed by DSC under the exothermic peak in comparison with that of the R2Na, also seems to confirm this behaviour.

Table 3 shows the area under exothermic peak obtained at different heating rates. As can be observed, cure enthalpy for Res–Phe (253 J/g) is slightly larger than for Res (239 J/g). Phenylalanine reacts with the chains of Res increasing the area under the exothermic peak. In the case of R2Na, the area of the exothermic peak is clearly larger than for the two previously mentioned composites. As it has been stated above, the influence of phenylalanine in the oxidation process seems to be smaller than the cationic nature of montmorillonite. On the other hand, increasing PheMMT content up to 2 wt.%, the area under exothermic peak also increases with respect to neat resol. The presence of phenylalanine-modified clay induces oxidation reactions on resol matrix, thus increasing the area of the peaks. It is worth to note that for Phe-4 and C2 composites, the area is smaller than that for Res as a result of less oxidation reactions. These results are in agreement with FT-IR results. In the case of Phe-4 composite, as the dispersion of the modified clay is poor, the reaction between modifier and resol chain is not so favourable and oxidation reactions tend to occur in a smaller account. For C2 composite, oxidation reactions are not catalysed. As explained above, the reason seems to be the presence of long alkyl chains of the surfactant that decreases the acid nature of the montmorillonite and avoids the acceleration of oxidation reactions at the used temperatures.

Table 3
Area (J/g) under the exothermic peak for the different composites at different heating rates from the first run DSC result

Designation	Heating rates (°C/min)			
	5	10	15	25
Res	266	239	194	224
Phe-1	304	269	212	218
Phe-2	306	280	222	296
Phe-4	212	203	197	210
C2	237	230	219	215
R2Na	–	290	–	–
Res–Phe	–	253	–	–

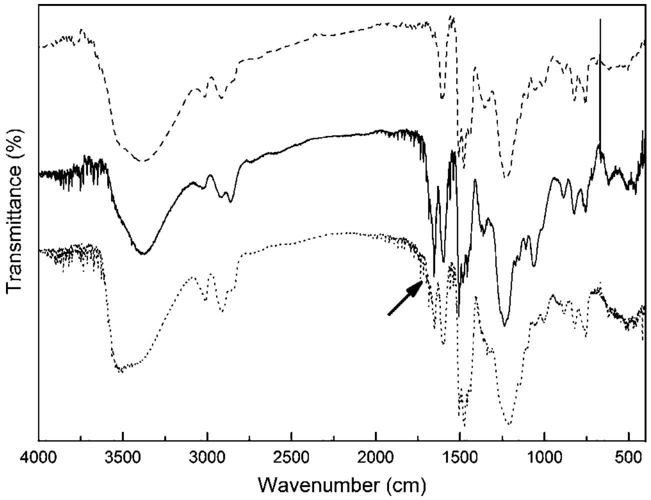

Fig. 6. FTIR spectra of the curing reaction after curing of Phe-2 at: (– –) 90 °C, (—) 110 °C and (- - - -) 130 °C.

Furthermore, for these formulations, an increased number density of non-reactive nanolayers could effectively slice through the network structure, thus disrupting a plane of cross-links [39] and decreasing reaction heat. This behaviour seems more remarkable for the composite Phe-4 where the amount of clay is higher than in composite C2. By increasing the heating rate, a similar tendency is seen but with lower values.

In Fig. 6, the influence of cure temperature in the oxidation of Phe-2 system during curing is shown by FT-IR. As can be observed, the resol does not undergo oxidation at 90 °C. On the other hand, in a similar way to that shown by Gabilondo for resols catalysed by TEA [13], the break of ether bridges and further oxidation could be accelerated depending on the conditions. As temperature increased, oxidation reactions seem to occur in a higher amount and a new peak around 1680 cm^{-1} is observed. As explained above, this band is due to the formation of quinone-type structures [32] that appear as a consequence of secondary oxidation processes. According to Fig. 2, the formation of carboxylic acids is another product due to chain scission in secondary oxidation. The presence of this group is verified for the band of O–H stretching vibration band at 3550 cm^{-1}. Thereby at higher temperatures, secondary oxidation processes seem to be accelerated.

4. Conclusions

The effect of clay content and phenylalanine modification on curing of resol matrix nanocomposites was studied by differential scanning calorimetry and Fourier transform infrared spectroscopy. The acid nature of MMT leads to oxidation of resol matrix at lower temperatures than for the neat matrix.

The presence of benzophenone structures detected by the band at around 1650 cm^{-1}, attributed to carbonyl group confirmed this behaviour. On the other hand, modification of the clay also affects curing reactions. Phenylalanine could act in a similar way to formaldehyde due to its reactive groups, leading to an increase of formaldehyde/phenol molar ratio, thus promoting oxidation at the used temperatures. In the case of Cloisite 30B, the presence of long alkyl chains seems to avoid the acceleration of oxidation reactions. The largest oxidation is seen for composite Phe-2 where both, acid nature of MMT and phenylalanine, favour oxidation reactions. In the case of phenylalanine modification, at higher cure temperatures, secondary oxidation processes also appear to be accelerated.

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