Thermal decomposition behavior of clay-phenolic nanocomposite prepared by in-situ polymerization

T. Periadurai, C. T. Vijayakumar[*] and M. Balasubramanian[**]

GE India Technology Center, Plot # 122, Phase 2, EPIP, Bangalore, India, periadurai.t@ge.com
[*]Department of Polymer Technology, Kamaraj College of Engineering and Technology
Virudhunagar - 626 001, India, ctvijay22@yahoo.com
[**]Department of Metallurgical & Materials Engineering,
Indian Institute of Technology Madras, Chennai - 600 036, India, mbala@iitm.ac.in

ABSTRACT

In the present study, a clay-phenolic nanocomposite with 5 wt. % clay was synthesized through in-situ polymerization. X-ray diffraction and transmission electron microscopic studies indicate the formation of nanocomposites. Thermal stability of the phenolic resin and its nanocomposites with 5 wt. % clay has been investigated by thermogravimetric analysis. The thermal decomposition of nanocomposites occurs at a higher temperature compared to the phenolic resin due to the presence of clay layers. In this work, migration products of nanocomposites were studied by off-line pyrolysis and gas chromatographic mass spectrometry technique. The results from clay-phenolic nanocomposites are compared with those from phenolic resin to examine the influence of nanoclay on the thermal degradation behavior. Apart from the identification of the volatile products formed, the mechanism of formation of the products is proposed in accordance with the previously developed general mechanism for phenolic resin degradation. The decomposition product analysis suggests that the decomposition of phenolic resin involves hemolytic breakdown of methylene linkage to yield phenol and cresols. The clay-phenolic nanocomposite shows completely different degradation product distribution pattern, which may be attributed to the presence of Si-O-C linkages formed between clay and phenolic resin.

Keywords: phenolic resin, nanocomposite, clay, thermogravimetry, gas chromatography–mass spectrometry

1 INTRODUCTION

Polymer nanocomposites are a recent class of materials providing more impressive properties when compared to the microcomposites. The addition of small amount of nanoparticles significantly improves a variety of properties without sacrificing the light weight property of polymer matrices. Clay is a type of nanoparticle, possesses a platelet-like structure with lateral dimension ranging from several hundred nanometers to microns, while the thickness is usually less than a few nanometers. Inclusion of clay nanoparticles into the polymer matrix improves several properties which depend on the morphology of the nanocomposite and the type of interaction between the polymer and nanoparticles [1-3]. The means of interaction between the polymer and nanoparticles determines the property of nanocomposite. Pyrolysis combined with analytical gas chromatographic mass spectrometry (GC/MS) is a powerful characterization technique used to obtain information of polymer structure [4] and to evaluate the degradation in different environments [5]. Thermal decomposition of synthetic polymer in this technique can provide answers to many questions which are difficult to get from other analytical methods. It has been found that the nanoclays improved the flame retardance properties of polymers and even a small amount of clay content (ca 2%) decreases markedly the heat release rate of a number of polymers [6]. However, the mode of action of the nanocomposite structures on thermal decomposition and the migration of degradation products is not fully understood. Hence in this work, migration products of nanocomposite were studied by offline pyrolysis and GC/MS technique. This paper reports the results of isothermal offline pyrolysis followed by GC/MS investigations of clay-phenolic resin nanocomposite. The results from clay-phenolic nanocomposite were compared with those from phenolic resin to examine the effect of nanoclay on the processes and the volatile products of the thermal degradation. Apart from the identification of the volatile products formed, the mechanism of formation of the products is proposed in accordance with the previously developed [7] general mechanism for phenolic resin degradation. Thermal stability of the phenolic resin and its nanocomposite with 5 wt% clay was investigated by thermogravimertic analysis and the results were discussed in light of existing mechanisms for decomposition of phenolic resin.

2 EXPERIMENTAL

2.1 Materials

Reagent grades of natural bentonite clay, phenol, formaldehyde, hydrochloric acid, oxalic acid and sodium hydroxide were obtained from E-Merck India Limited, Mumbai and were used without further purification.

2.2 Synthesis of clay-phenolic nanocomposite

Phenol (650 g, 13.8 mol), natural bentonite clay (5 wt%), water (130 g), and oxalic acid (110 g) crystals were mixed for 1 h using a high speed mechanical stirrer. About 350 g (11.45 mol) of 30% aqueous formaldehyde was added dropwise (20-30 min) into the reaction mixture. After the initial exothermic reaction subsided, the mixture was refluxed for 60 min (first condensation) with continuous stirring. Hydrochloric acid (15%, 450 g) was slowly added to this mixture. The reaction mixture was further refluxed for another 35 min (second condensation). The reason for the use of both oxalic acid and hydrochloric acid is to have slow reaction at the beginning of condensation and to complete the conversion at the end of the condensation reaction. After the completion of second stage of the condensation, 1500 mL of cold water was introduced and the reaction mixture was cooled to about 75°C. The crude resin was allowed to settle for 30 min. After the removal of the supernatant layer of water, the resin was dehydrated at 100°C. The whole mixture became clear at 100°C. Sodium hydroxide solution (36 %) was added to neutralise the resin. The concentration by evaporation of the reaction mixture was continued until the resin temperature reached 115°C. The resin was finally degassed for 10 min by applying vacuum. The resin was then cooled down, which yielded brittle solid phenolic clay nanocomposite (PFN-C5). Phenolic resin (PFN) without clay was also prepared by following the same procedure.

2.3 Characterization

The X-ray diffraction studies of unmodified bentonite clay (UBC), and clay-phenolic nanocomposite (PFN-C5) samples were performed in a SHIMADZU XD-D1 X-ray diffractometer. It was carried out at a scanning rate of 0.05 °/min using Cu-Kα radiation (λ = 1.5406Å).

The thermogravimetric studies for the phenolic resin (PFN), clay-phenolic nanocomposite (PFN-C5) were carried out in a NETZSCH (STA 409PC) thermal analyser. The materials were heated from 50 to 700°C at a heating rate of 10°C/min in nitrogen atmosphere.

The off-line isothermal degradation of the material was carried out in an all glass apparatus [8]. A Hewlet Packard (HP5890) gas chromatograph (GC) containing a 12 m capillary column coated with the cross-linked methyl silicon gum (HP 1) was used for the separation. The identification was done using a HP5970 mass selective detector (MS) coupled to the GC using a jet-separator.

Solid-state ^{13}C NMR analyses were carried out in a Bruker (DMX 300) 7.04 T widebore magnet system. It has multinuclear facilities that covers nuclei resonating between 44-121 MHz. Analysis was carried out at room temperature.

A 100 nm thick slice of sample was ultramicrotomed by using a diamond knife. Transmission electron microscopic (TEM) image was obtained using Technai™

Polara microanalyzer with an accelerating voltage of 120 kV.

3 RESULTS AND DISCUSSION

3.1 Clay dispersion studies

X-ray diffraction patterns of clay, the sheet fabricated using phenolic resin molding powder mixed with 5 wt% clay and nanocomposite are shown in Fig. 1. The clay mixed with phenolic resin molding powder has a diffraction peak at the 2θ value similar to clay. The chance of disintegration of clay is very less, when the clay is mixed with phenolic resin moulding powder.
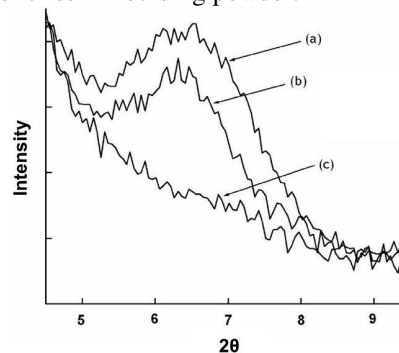

Figure 1: XRD patterns of (a) unmodified clay; (b) 5 wt% clay added phenolic resin and (c) in-situ polymerized phenolic nanocomposite with 5 wt% clay

The presence of peak corresponding to clay indicates that if the clay layers are intact, it will show a diffraction peak in this resin system. Clay added during in-situ polymerization can disintegrate into separate layers. The peak corresponding to clay is absent in the clay-phenolic nanocomposite and this confirms the disintegration of clay layers and formation of exfoliated nanocomposite during in-situ polymerization of phenol and formaldehyde in the presence of bentonite clay. The TEM micrograph (Fig. 2) also shows the formation of exfoliated nanocomposite.
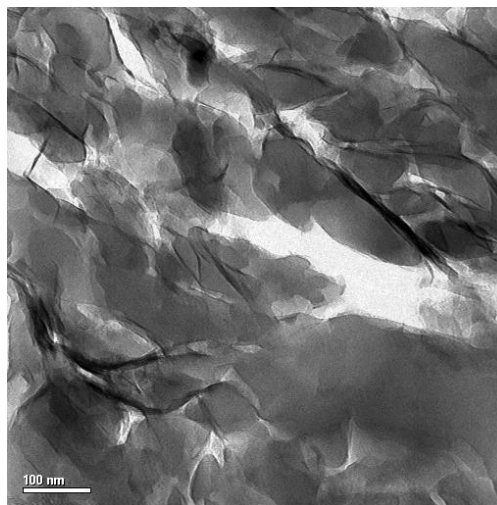

Figure 2: TEM micrograph of in-situ polymerized phenolic nanocomposite slices.

3.2 Interaction between clay and phenolic resin

Solid state ^{13}C CP/MAS NMR spectra were taken for phenolic resin and nanocomposite and are shown in Fig. 3. The chemical shift value of the C-OH in the phenol ring is 153 ppm, methylene bridge is 59 ppm and ortho-substitution of phenol ring is 117 ppm.
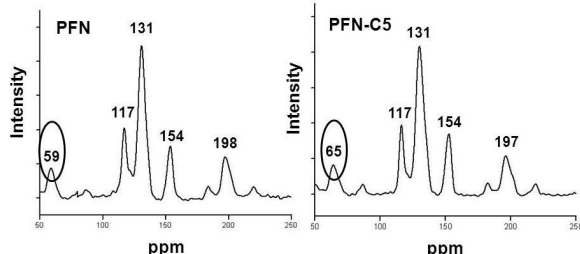

Figure 3: ^{13}C CP/MAS NMR spectra of phenolic resin (PFN) and 5 wt% clay-phenolic nanocomposite

The presence of major chemical shifts corresponding to phenolic resin and the silicate linkage confirms the formation of novolac type of phenolic resin and clay-phenolic nanocomposite. The methylol group adjacent to the phenolic group can react with silicate layers of clay, thus forming a covalent bond between the organic and inorganic components [9]. Even though this type of bonding is covalent, Si-O-C bonds are sensitive towards hydrolysis and the bonding is less stable than the Si-C bonding. The chemical shift value changes from 59 to 65 ppm when 5 wt.% of clay is introduced in the phenolic resin. In concordance with the existing literature [10-11], the chemical shift change from 59 ppm in phenolic resin to 65 ppm in phenolic nanocomposites suggests the formation of chemical linkage between the organic and inorganic components.

3.3 Thermal stability of clay-phenolic nanocomposite

The thermal decomposition of phenolic resin and nanocomposite samples was investigated using thermogravimetry and the thermograms are shown in Fig. 4. The first stage of decomposition for the phenolic resin starts at 245°C and ends at 325°C, whereas the first stage of decomposition for the clay-phenolic nanocomposite starts at 260°C and ends at 365°C. The second stage of decomposition ends at 440°C for the phenolic resin and ends at 480°C for the nanocomposite. After that there is gradual loss in both the cases. The incorporation of clay in the phenolic resin shifts the degradation to higher temperature region. Decomposition of phenolic resin appears to be entirely due to breaking of methylene links catalysed by non-volatile acids or oxidising agents. A mechanism was proposed by Sinha et al., [12] for the initial decomposition, in which the methylene carbon is first oxidised to carbonyl, aldehyde and acid derivatives before chain scission.
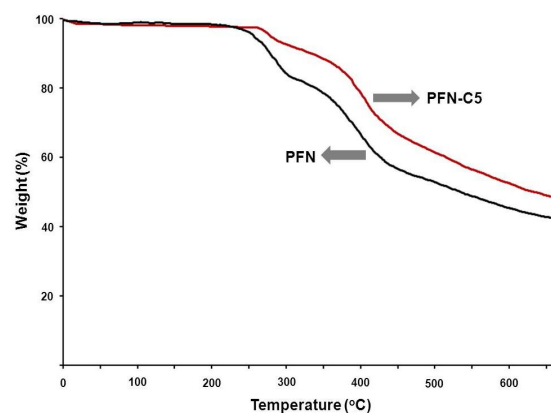

Figure 4: Thermogravimetric curves of phenolic resin and 5 wt% clay-phenolic nanocomposite

The initial decomposition of alkyl side chain at lower temperature is due to the flexibility of the long alkyl side chain in the crosslinked state of the resin. Hence in phenolic resin, the decomposition is due to the homolytic breakdown of methylene linkage to yield phenol and cresols. The decomposition pattern for nanocomposites is different, since the methylene group is covalently bonded with the silicates. Decomposition of nanocomposites is due to the cleavage of the Si-O-C linkage (due to incorporation of clay) at the methylene bridge.

3.4 Decomposition behaviour of clay-phenolic nanocomposite

The thermal decomposition of the phenolic resin has been studied extensively by Jackson and Conley [13]. In their study, pyrolysis-GC was used for analysing volatile gases evolved from the polymer sample. Detailed mechanism for the thermal decomposition was postulated based on the infrared spectral analysis of the thermally degraded polymer. The total ion chromatograms (TIC) of the volatile products formed during decomposition of phenolic resin and the clay-phenolic nanocomposite (5 wt% clay) are shown in Fig. 5.
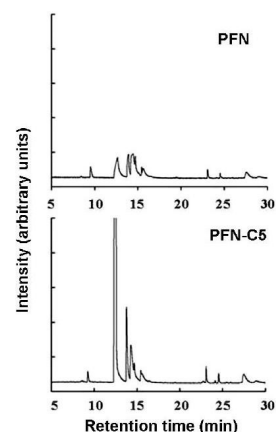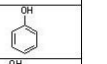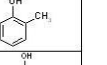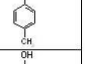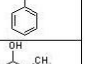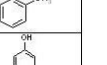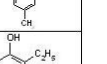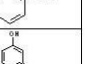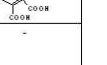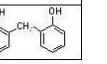

Figure 5: Total ion chromatogram of the degradation products from phenolic resin and nanocomposite

The mass spectra for the decomposition products of phenolic resin and nanocomposite samples at different retention times were recorded. The two major decomposition products identified are phenol and cresol in the case of phenolic resin. The previous study on the thermal decomposition of phenolic resin [14] showed that the major decomposition product is phenol. All the decomposition products identified are listed in Table 1. Apart from phenol and cresols, other products like 2-ethyl phenol, 4-hydroxy-1,2- dicarboxylic acid and 2,2'-methylene bisphenol are also identified among the decomposition products obtained from clay-phenolic nanocomposite. Although the mechanism is not much altered due to the presence of clay in phenolic resin, the product distribution pattern is altered indicating the subtle influence of the incorporated clay on the decomposition behavior of the phenolic resin. Fig. 6 gives a clear picture regarding the possibility of the formation of various decomposition products from an idealised clay-phenolic nanocomposite structure.

Table 1: Gas Chromatograph-Mass Spectrometry analysis of decomposition products from phenolic resin and its nanocomposite

Sample	Retention Time	Molecular Formula	m/z	Structure
PFN	12.524 min	C_6H_6O	94.04	
	13.794 min	C_7H_8O	108.06	
	14.266 min	C_7H_8O	108.06	
PFN-C5	12.514 min	C_6H_6O	94.04	
	13.795 min	C_7H_8O	108.06	
	14.290 min	C_7H_8O	108.06	
	14.694 min	$C_8H_{10}O$	122.00	
	23.089 min	$C_8H_6O_5$	182.02	
	24.550 min	$C_{14}H_{12}O$	196.09	-
	27.540 min	$C_{13}H_{12}O_2$	200.08	

4 CONCLUSIONS

In-situ polymerization of phenol-formaldehyde with natural bentonite clay led to the formation of clay-phenolic nanocomposite having exfoliated structure. Phenolic resin and the nanocomposite showed two major thermal degradation stages. The nanocomposite degraded at a higher temperature compared to the pure resin. Isothermal degradation of phenolic resin and its nanocomposite counter part showed a vast difference in the product distribution pattern, which may be attributed to the chemical incorporation of the nanoclay in the phenolic resin.
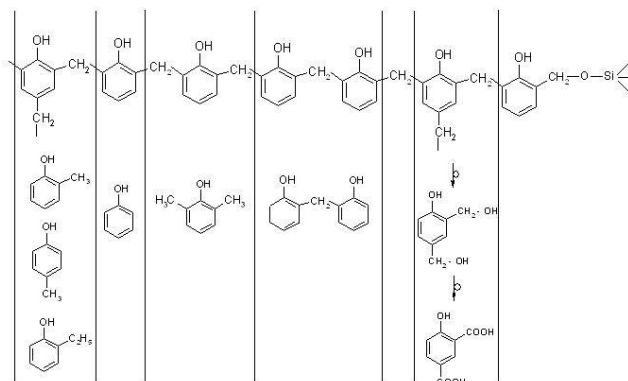

Figure 6: Typical reactions proposed for phenolic nanocomposite decomposition at elevated temperatures

REFERENCES

[1] P. Kiliarisa and C.D. Papaspyrides, Prog Polym Sci, 35, 902, 2010.
[2] L. Minkovaa, Y. Penevaa, E. Tasheva, S. Filippib, M. Pracellac and P. Magagninib, Polym Test, 28, 528, 2009.
[3] A. Orala, M. A. Tasdelenb, A. L. Demirelc and Y. Yagci, Polymer, 50, 3905, 2009.
[4] S. Tsuge, H. Ohtani, Pyrolysis-gas chromatographic studies on the micro-structures of stereospecific polypropylenes, Analytical Pyrolysis, Butterworth, 407, 1984.
[5] A. Alajbeg, B. Stipak, J Anal Appl Pyrol, 7, 283, 1985.
[6] M. Lewin, Fire Mater, 27, 1, 2003.
[7] S. S. Schwartz and Goodman, S. H. Plastics Materials and Processes, Van Nostrand Reinhold Company, New York, p. 298, 1982.
[8] C.T. Vijayakumar, Doktor Der Montanistatischen Wissenschaften Dissertation, Montanuniversität Leoben, A-8700 Leoben, Austria, 18, 1987.
[9] A.Y.C. Hung, F. Wang, C.M. Ma, and H. Wu, Eur Polym J, 39, 225, 2003.
[10] R. N. Kalfat, H. Gharbi, Zarrouk, and F. Babonneau, J Chem Soc Tunisia, 3, 533, 1994.
[11] B. M. Novak, M.W. Ellsworth, and C. Verrier, ACS Symposium Series 585, American Chemical Society, Washington, DC, pp.86-96, 1995.
[12] R. Sinha, F.D. Blum, and D.J. O'connor, J Appl Polym Sci, 38, 163, 1989.
[13] W. M. Jackson, and R.T. Conley, J Appl Polym Sci, 8, 2163. 1964.
[14] S. S. Schwartz, and S.H. Goodman Plastics Materials and Processes, Van Nostrand Reinhold Company, New York, 1982.