

The relationship between thermal degradation behavior of polymer and the fire retardancy of polymer/clay nanocomposites

Bok Nam Jang, Marius Costache, Charles A. Wilkie*

Department of Chemistry, Marquette University, P.O. Box 1881, Milwaukee, WI 53201, USA

Received 11 June 2005; received in revised form 26 August 2005; accepted 31 August 2005

Available online 3 October 2005

Abstract

The change in the degradation pathway of a polymer by incorporation of clay has a significant effect on the fire retardancy of polymer/clay nanocomposites. Since the clay layers act as a barrier to mass transport and lead to superheated conditions in the condensed phase, extensive random scission of the products formed by radical recombination is an additional degradation pathway of polymers in the presence of clay. The polymers that show good fire retardancy upon nanocomposite formation exhibit significant intermolecular reactions, such as inter-chain aminolysis/acidolysis, radical recombination and hydrogen abstraction. In the case of the polymers that degrade through a radical pathway, the relative stability of the radical is the most important factor for the prediction of the effect that nanocomposite formation has on the reduction in the peak heat release rate. The more stable is the radical produced by the polymer, the better is the fire retardancy, as measured by the reduction in the peak heat release rate, of the polymer/clay nanocomposite.

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Keywords: Nanocomposites; Fire retardancy; Clay

1. Introduction

Polymer/clay nanocomposites offer the advantage of a large interfacial area, which leads to increased mechanical [1–3], gas permeability [4] and fire properties [5–8] with the addition of a small amount of clay (≤ 5 wt%) and they have attracted considerable attention because of these effects [9,10]. Among these enhanced properties, mechanical property and gas permeability are related to the types of dispersion of the clay in the polymer, while fire retardant properties of polymer/clay nanocomposites have been ascribed to the formation of a barrier which impedes mass transport of degrading polymer species and insulates the flame from the underlying polymer [11].

The fire retardancy of polymer/clay nanocomposites in terms of the reduction in peak heat release rate (PHRR) in the cone calorimeter depends on the particular polymer under investigation. For polyamide 6 (PA6), polystyrene (PS) and poly(ethylene-co-vinyl acetate) (EVA) nanocomposites, a large reduction in peak heat release rate, about 60%, is

obtained. The changes in degradation pathway of these polymers have been elucidated [12–14] and the common factor is that inter-chain reactions, such as intermolecular aminolysis/acidolysis, radical recombination and hydrogen abstraction, become significant in the presence of clay.

In the cases of poly(styrene-co-acrylonitrile) (SAN) and acrylonitrile-butadiene-styrene terpolymer (ABS), the clay nanocomposites show a moderate reduction in PHRR (around 40%), and the degradation pathway of these in the presence of clay have also been elucidated [15]. The change in the degradation pathway upon incorporation of clay is not significant and radical recombination reactions occur in relatively small amounts, compared to polystyrene/clay nanocomposite. Thus, it may be concluded that the extent of intermolecular reactions of the thermally degrading polymer in the presence of clay is an important aspect of the reduction in the peak heat release rate and, hence, in the fire retardancy.

On the other hand, poly(methyl methacrylate) (PMMA)/clay nanocomposites do not exhibit any changes in the evolved products upon incorporation of clay [16], and the fire retardancy of PMMA/clay nanocomposites is not significantly improved. It was suggested that the number of degradation pathways of the polymer is one of the factor that can affect the fire retardancy of polymer/clay nanocomposites. If the degradation occurs by only single pathway, then more thermally stable products are not produced and the fire

* Corresponding author.

E-mail address: charles.wilkie@marquette.edu (C.A. Wilkie).

retardancy is not significantly improved in the presence of clay [16].

To systematically examine and compare the effect of clay on the fire retardancy of polymer/clay nanocomposites, previous work on PS, PA6, EVA, SAN, ABS and PMMA [12–16] is reviewed and re-evaluated and additional polymer nanocomposite systems, high impact polystyrene (HIPS), polyacrylonitrile (PAN), polyethylene (PE) and polypropylene (PP), are included in this study. In this report, the changes in the degradation pathway of the polymer of interest in the presence of clay will be discussed first, and then the factors affecting the fire retardancy of polymer/clay nanocomposite will be introduced in terms of the relative stability of the radicals produced upon degradation by considering the degradation characteristics of these polymers.

2. Experimental

2.1. Materials and preparation of nanocomposite

PA6 [13], SAN [15], ABS [15], and EVA [14] nanocomposites were all prepared by literature procedures using a Brabender mixer. PS [12,17] and PMMA [18] nanocomposites were prepared by bulk polymerization, while PAN [19] nanocomposites were prepared by emulsion polymerization following published procedures.

High impact polystyrene (HIPS)/clay nanocomposite [20]; HIPS (melt flow index 6 g/10 min at 200 °C/5 kg) was obtained from the Aldrich Chemical Co. The HIPS/clay nanocomposite was prepared by melt blending in a Brabender mixer at 60 rpm and 200 °C at 4.0 wt% inorganic clay content, using an oligomerically-modified clay (COPS) [20,21].

Polyethylene (PE)/clay and polypropylene (PP)/clay nanocomposites [21]; PE (melt flow index: 7 g/10 min at 230 °C/2.16 kg) and PP (melt flow index: 35 g/10 min at 230 °C/2.16 kg) were acquired from Aldrich Chemical Co. These polymers were melt-blended with an oligomerically-modified clay (COPS) in a Brabender Mixer at 60 rpm for 10 min at 190 °C [20,21]. The inorganic clay content is 4.0 wt%.

2.2. Characterization of the nanocomposites

Cone calorimetry and X-ray diffraction (XRD) were used to characterize the formation of nanocomposites. Cone calorimetry was performed on an Atlas CONE2 according to ASTM E 1354 at a heat flux of 35 kW/m², using a cone shaped heater. Exhaust flow rate was 24 L/s and the spark was continuous until the sample ignited. The specimens for cone calorimetry were prepared by the compression molding of the sample (about 30 g) into 3 × 100 × 100 mm square plaques. Typical cone calorimetry results are reproducible within ±10%. XRD patterns were obtained using a Rigaku Geiger Flex, 2-circle powder diffractometer equipped with Cu K α generator ($\lambda = 1.5404 \text{ \AA}$); generator tension was 50 kV and the current was 20 mA. Most of the XRD and cone data on these polymer/clay nanocomposites have been reported in the literature [12–21].

2.3. TGA analysis and sampling of evolved products

TGA was carried out on a Cahn TG 131 instrument at a heating rate of 20 °C/min and a nitrogen flow of 80 ml/min. The temperature reproducibility of the TGA is ±3 °C and error range of the non-volatile fraction at 700 °C is ±3%. During thermal degradation in the TGA, the evolved volatile products are collected using a cold trap through a sniffer tube that extends into the sample cup for the GC/MS analysis of the degradation products. The TGA data for the polymer/clay nanocomposites used in this study have been reported in the literature [12–21].

2.4. GC/MS analysis of the evolved condensable products

The condensable evolved products in the cold trap were dissolved in acetonitrile (cyclohexane for PE, PP and EVA) and GC/MS spectra were obtained using a Agilent 6850 series GC connected to a Agilent 5973 Series MS (70 eV ionization energy) with temperature programming from 40 to 250 °C. The identity of the evolved compounds was primarily established by co-injection with authentic compounds and/or by the analysis of mass fragmentation pattern.

3. Results and discussion

3.1. Thermal degradation of polymer/clay nanocomposites

3.1.1. Polyamide 6 and polyamide 6/clay nanocomposite [13]

Polyamide 6/clay nanocomposites can be easily prepared via melt-blending with an organically-modified clay [22,23] and typically exhibit a 60% reduction in the peak heat release rate [13,24,25]. The main degradation product of virgin polyamide 6 is ϵ -carpolactam (m/z 113), as shown in Fig. 1, which is mainly produced via end chain aminolysis or acidolysis [26,27]. The other evolved products correspond to linear structures, which are produced by chain scission and hydrolysis of amide linkage [25,26]. In the presence of clay, the GC trace of the evolved products during thermal degradation of polyamide 6 exhibits more intense peaks for the linear compounds compared to those of virgin polyamide 6 and the viscosity of degrading condensed phase was increased [13], which means that more extensive random scission and inter-chain aminolysis/acidolysis have occurred.

3.1.2. Polystyrene and polystyrene/clay nanocomposite [12]

Polystyrene/clay nanocomposites show about 60% reduction in peak heat release rate in the cone calorimeter [28,29]. This significant change in fire retardancy is caused by the introduction of the nano-dispersed clay layers in the polystyrene matrix; the clay affects the degradation behavior of polystyrene, producing a number of additional structures as shown in Fig. 2.

Virgin polystyrene evolves styrene monomer (m/z 104), dimer (m/z 208) and trimer (m/z 312) as the main degradation products during thermal degradation. Styrene monomer is produced via β -scission of a chain end formed by the initial

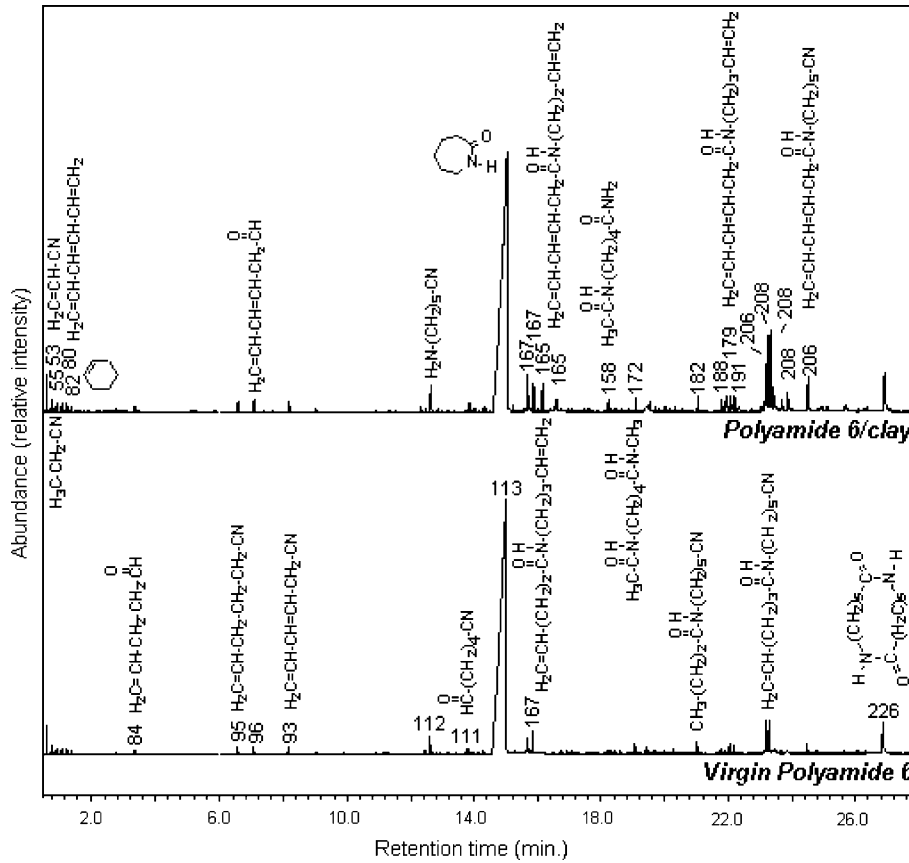


Fig. 1. GC traces of virgin polyamide 6 and its clay nanocomposite. Inset number denotes m/z in mass spectrum of each peak [13]. The inset structures correspond to each peak of GC trace.

chain scission, while dimer and trimer are evolved via radical transfer followed by β -scission [30–32].

In the presence of clay, many different evolved products are detected and these are produced via radical recombination and extensive random scission. The degraded molecules have an

opportunity to undergo radical recombination, because the degraded molecules are confined between well-dispersed clay layers. Extensive random chain scission occurs at the same time, since the degrading polymers experience superheated conditions during the thermal event. The identification of

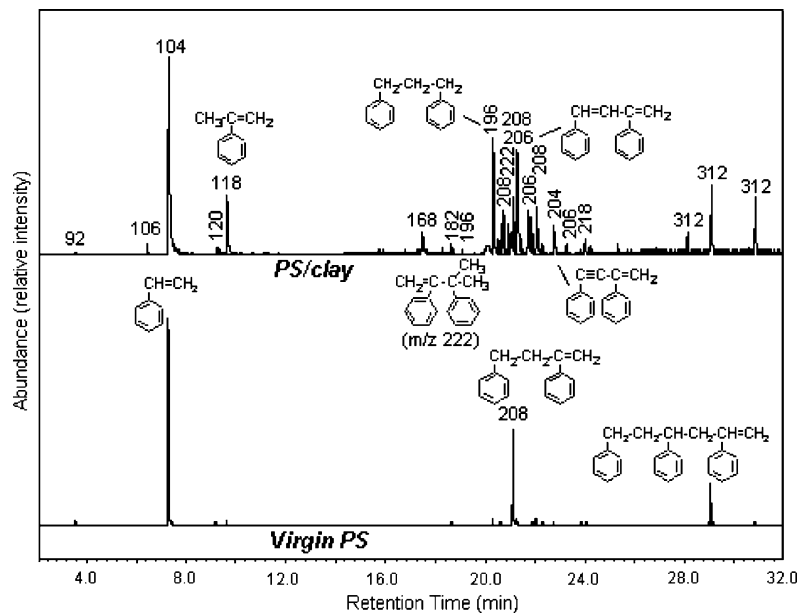


Fig. 2. GC traces of virgin PS and PS/clay nanocomposite. Inset numbers denote m/z in mass spectrum of each peak and some chemical structures are included [12].

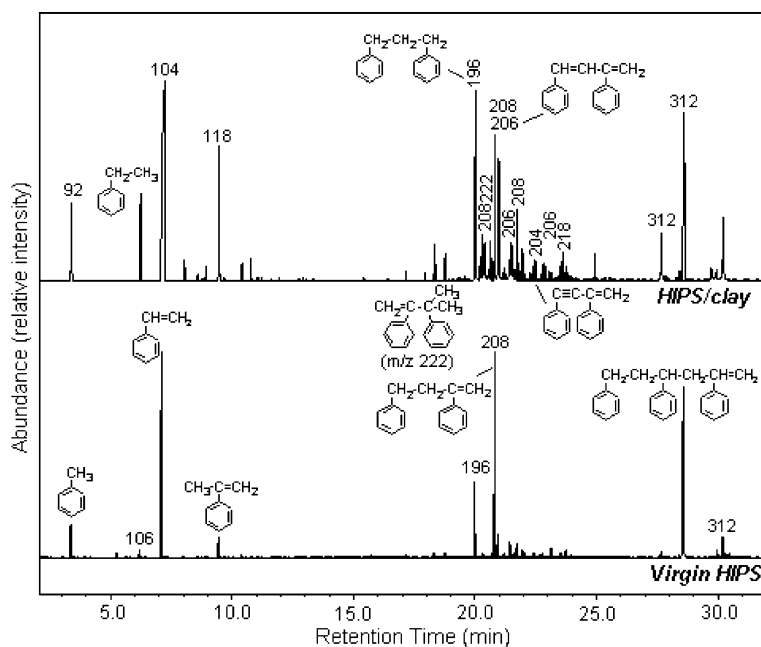


Fig. 3. GC traces of virgin HIPS and HIPS/clay nanocomposite. Inset numbers denote m/z in mass spectrum of each peak and some chemical structures are included.

head-to-head structures and many isomers in the evolved products suggests that recombination reaction between tertiary and/or secondary radicals occurs in the presence of clay [12].

3.1.3. High impact polystyrene (HIPS) and HIPS/clay nanocomposite

Fig. 3 shows the GC/MS results for virgin HIPS and HIPS/clay nanocomposites. High impact polystyrene (HIPS) contains a butadiene rubber phase that is grafted to styrene and

the remaining phase is free polystyrene. Some changes are observed between virgin HIPS and virgin PS (bottom traces of Figs. 2 and 3), specifically the compounds of m/z 92, 118, 120, 196 are increased in the GC trace of virgin HIPS. These compounds have an odd number of carbons in their chain backbone, which means that these are produced via extensive random scission due to butadiene rubber phase, the same trend seen in SAN and ABS (Figs. 4 and 5). In the presence of clay, many other compounds are evolved and these structures are

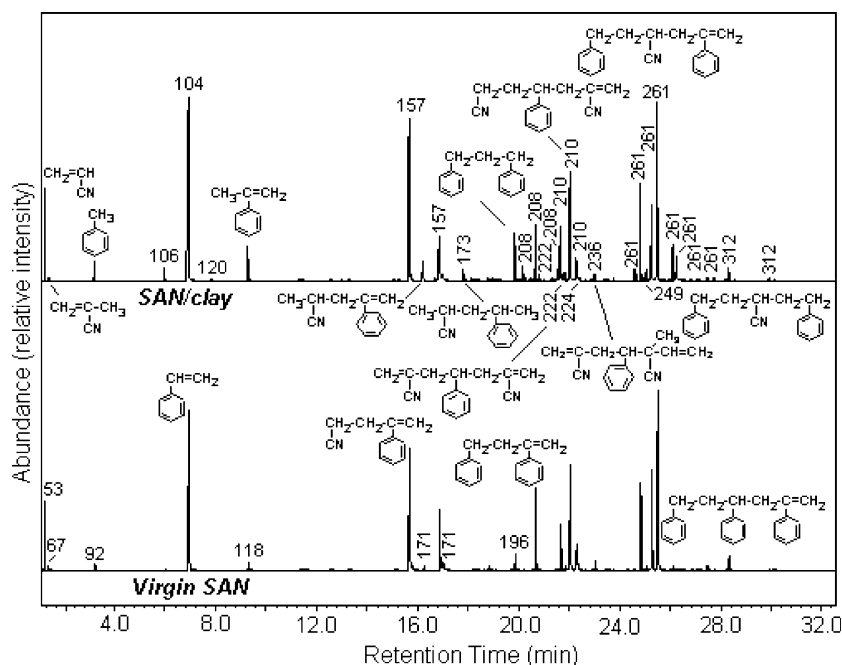


Fig. 4. GC traces of virgin SAN and SAN/clay nanocomposite. Inset numbers denote m/z in mass spectrum of each peak and some chemical structures are included [15].

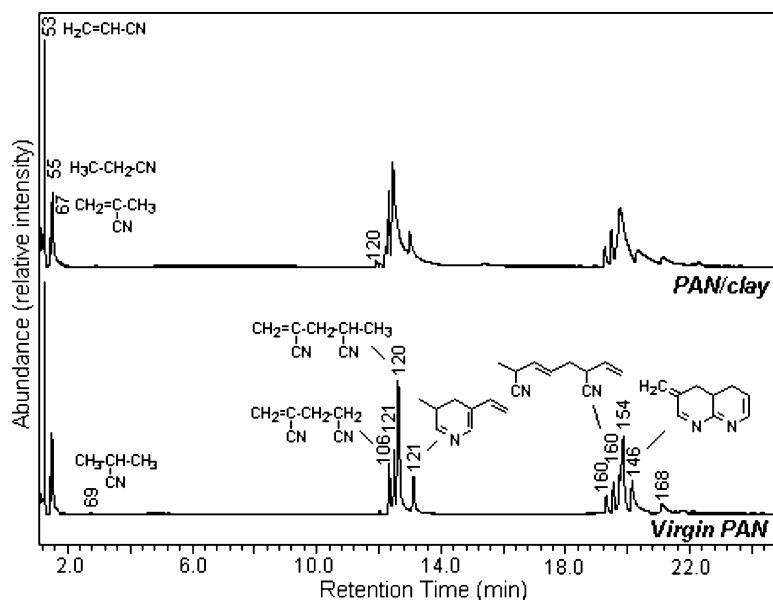


Fig. 7. GC traces of virgin PAN and virgin PAN nanocomposite. Inset numbers denote m/z in mass spectrum of each peak and some chemical structures are included.

tendency inherently through intra- and inter cyclization [38], it appears that the presence of well-dispersed clay layers does not play a role in increase of the thermal stability and the quantity of non-volatiles in the TGA, and no reduction in the peak heat release rate is observed by cone calorimetry.

The evolved products of virgin PAN and PAN/clay nanocomposite are the same, as shown in the GC traces of Fig. 7, which means no change in the degradation pathway of PAN in the presence of clay. The monomer (m/z 53), dimer (m/z 106) and odd number carbon structures in the backbone (m/z 67, 120) are evolved, which implies that random scission occurs, along with cyclization. The structures of m/z 121 and 146 contain a ring structure, which is produced through cyclization of adjacent nitrile groups followed by chain scission. The presence of m/z 160 structures suggests that there was some elimination of hydrogen cyanide.

3.1.7. Polyethylene (PE) and PE/clay nanocomposite

The evolved condensable products of polyethylene (PE) and PE/clay nanocomposite during thermal degradation consist of C7–C31 (m/z 96–436) [39]. Molecules smaller than C7 are also evolved but these cannot be detected by GC/MS because of volatility higher than that of the solvent, cyclohexane. At each carbon number, there are three components, α,ω -diene, 1-ene and alkane. Fig. 8 shows GC traces of the structures corresponding to C17–C20; m/z 236, 250, 264 and 278 are α,ω -diene, m/z 238, 252, 266 and 280 are 1-ene structures, and m/z 240, 254, 268 and 282 correspond to linear alkane structures. These compounds are produced through disproportionation after random scission. Assuming that disproportionation is the only process for the termination of the degradation reaction, the ratio of α,ω -diene/1-alkene/alkane should be 1:2:1. Referring to the GC trace of virgin polyethylene, the intensity of α,ω -diene is small compared to alkane, which implies that, when polyethylene undergoes thermal

degradation, some hydrogen abstraction reactions must occur in the condensed phase.

In the presence of clay, some changes are observed; the peaks due to the α,ω -diene structures decrease, those of alkane structures increase and other noise-like peaks corresponding to other unsaturated structures are qualitatively increased. This result suggests two facets to the degradation in the presence of clay: the extent of the hydrogen abstraction reaction is increased qualitatively, producing more intense alkane peaks, and, more random scission occurs, which produces various unsaturated aliphatic structures having different positions for the double bond in the chain. Since the clay layers act as a barrier, the degrading molecules are

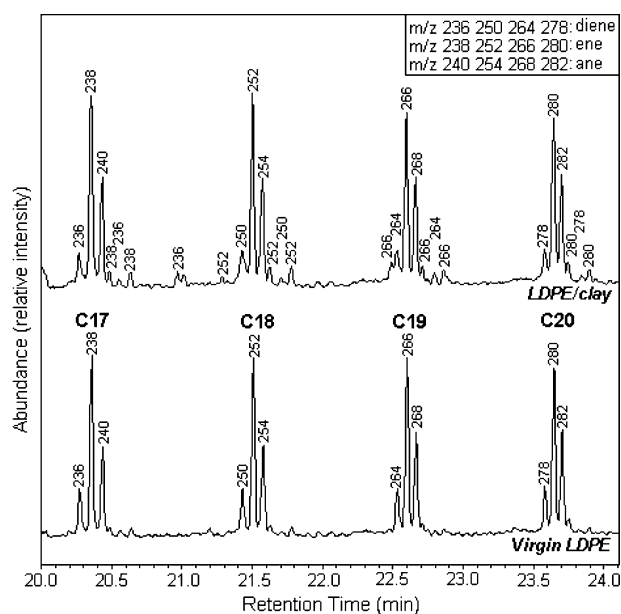


Fig. 8. Expanded GC traces of virgin LDPE and LDPE/clay nanocomposite corresponding to C17–C20. Inset numbers denote m/z in mass spectrum of each peak.

confined, which leads to more extensive random scission and hydrogen abstraction.

3.1.8. Poly(ethylene-co-vinyl acetate) (EVA) and EVA/clay nanocomposite [14]

The trend as described in the section of PE and PE/clay nanocomposite become clearer in the poly(ethylene-co-vinyl acetate) (EVA)/clay nanocomposite system. EVA first undergoes the elimination of acetic acid (chain stripping) in the temperature region of 300–350 °C, leaving a double bond in the chain backbone, hence EVA is converted into poly(ethylene-co-acetylene), which undergoes further degradation to smaller molecules at higher temperature [40,41]. Considering the molar ratio of vinyl acetate to ethylene (wt. ratio of ethylene/vinyl acetate: 81/19), one double bond is present on average for every 28 carbons in the backbones. When one compares the GC of virgin EVA with that of PE (the bottom GC traces of Figs. 8 and 9), the GC traces are the same in terms of the major components and relative intensities. The qualitative agreement in the GC traces of EVA and PE suggests that there is some common degradation pathway. This can occur if an allylic radical is formed by random scission and, after this radical either disproportionates or hydrogen abstracts, random scission occurs at the other allylic position, leaving radicals which are identical to those seen in PE and which will degrade as PE does. Since the minor peaks in the GC trace are slightly different from those seen in PE, there are probably other degradation pathways as well.

In the presence of clay, some definite differences are observed compared to those in the PE/clay system: the saturated alkane peaks (m/z 240, 254, 268 and 282) increase, while the α,ω -diene peaks (m/z 236, 250, 264 and 278) decrease or disappear, and noise-like peaks, assigned to other unsaturated structures, increase. This trend is basically

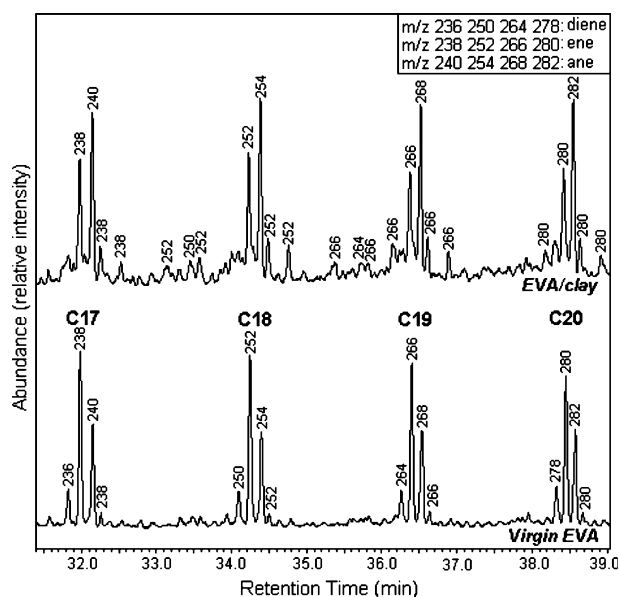


Fig. 9. Expanded GC traces of virgin EVA and EVA/clay nanocomposite corresponding to C17–C20. Inset numbers denote m/z in mass spectrum of each peak.

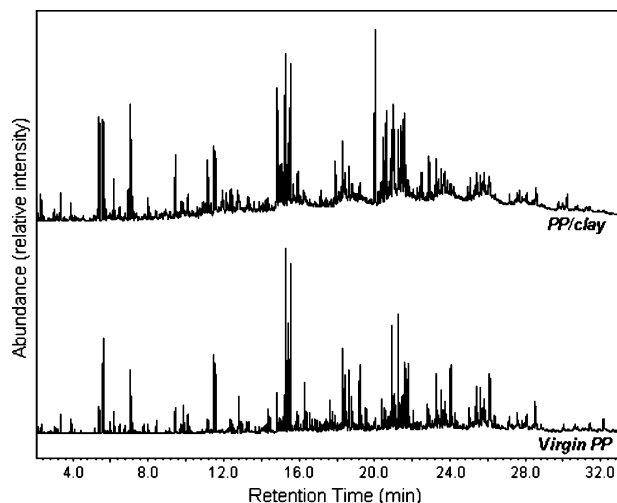


Fig. 10. GC traces of virgin PP and PP nanocomposite.

the same as seen in polyethylene–clay nanocomposites, but the extent is much greater, which suggests that the effect of the well-dispersed clay layers is more significant in the EVA/clay system. The increase in the saturated compounds and the decreased evolution of α,ω -diene mean that hydrogen abstraction becomes more important due to the presence of the clay. The increase in intensity of the other unsaturated structure implies that extensive random scission also occurs to a greater extent.

3.1.9. Polypropylene (PP) and PP/clay nanocomposite

Fig. 10 shows the GC traces of the evolved products of polypropylene (PP) and PP/clay nanocomposites. In the case of polypropylene, because the number of degraded evolved products is very large and it is difficult to distinguish linear, branched and cyclic compounds, only a qualitative comparison between the virgin polymer and its nanocomposite can be made. The number of the evolved products in the presence of clay is larger than that in the virgin PP, which supports extensive random scission due to the barrier effect of the clay.

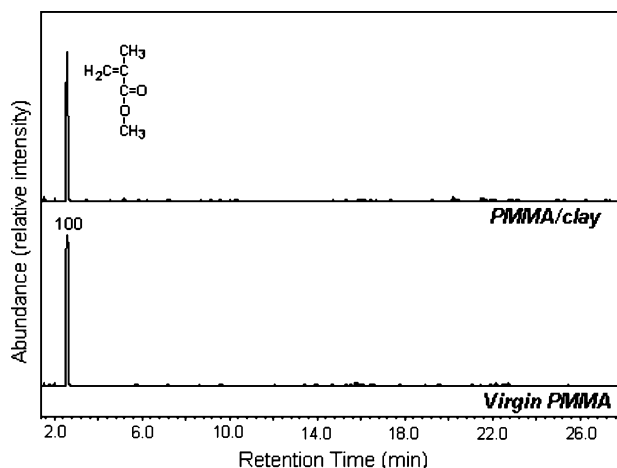


Fig. 11. GC traces of virgin PMMA and PMMA nanocomposite. Inset number denotes m/z in mass spectrum.

3.1.10. Poly(methyl methacrylate) (PMMA) and PMMA/clay nanocomposite

Fig. 11 shows the GC traces of poly(methyl methacrylate) (PMMA) and the PMMA/clay nanocomposite. In this case, no differences are observed between virgin PMMA and PMMA/clay nanocomposite. PMMA undergoes thermal degradation through β -scission at the chain ends (unzipping) [42,43] to produce the monomer, methyl methacrylate. The fact that the degradation product of PMMA in the presence of clay is also monomer implies that neither a radical transfer, which is the pathway for the evolution of dimer and trimer, nor intermolecular reaction occur, due to the stability of the radicals that are produced, as will be explained in the next section.

3.2. Relationship between the degradation pathway and fire retardancy of polymer/clay nanocomposite

Table 1 summarizes the changes in the degradation pathway of the polymer and the reduction in peak heat release rate (PHRR) brought about by the incorporation of clay. To compare the effect of clay on the reduction in PHRR, the polymers are classified in terms of the reduction of PHRR; polymers showing large reduction in PHRR, those showing moderate reduction in PHRR and the polymers having little or no reduction in PHRR. As shown in Table 1, it appears that the reduction in PHRR is closely related to the changes in the degradation pathway brought about by the presence of the clay.

PA6, EVA and PS show a large reduction (typically around 60%) in PHRR. Considering the changes of degradation pathway of polymers in the presence of clay (Figs. 1, 2 and 9), these polymers exhibit a significant increase in the intermolecular reactions; inter-chain aminolysis/acidolysis for PA6, hydrogen abstraction for EVA and radical recombination for

PS, while the polymers, SAN, ABS, PE and PP, showing moderate reduction in PHRR have a decreased amount of intermolecular reactions. Regarding the polymers (PAN, PMMA) showing little or no reduction in PHRR, no change in degradation pathway is observed in the presence of clay.

The current thinking on the role of nanocomposite in bringing about a reduction in the peak heat release rate is the formation of a barrier which impedes mass transport and insulates the underlying polymer from the heat source [11]. This barrier confines the polymer chains and the degradation is performed in a superheated environment, which leads to radical recombination reaction followed by extensive random scission for any polymer/clay nanocomposite. However, PAN and PMMA do not show any evidence for other products in the presence of clay, which may be related to the degradation characteristics of these two polymers. PAN produces a large amount of non-volatile rigid char (60%) in the TGA [37] due to the cyclization reaction of adjacent nitrile groups. Thus the addition of clay does not affect the degradation pathway of PAN, even though the clay provides the nano-dispersed layer in the polymer substrate, because PAN itself produces a large amount of char upon heating. In the case of PMMA, more extensive random chain scission may occur due to the presence of clay, but the evolved products are the same product, methyl methacrylate, owing to the relative radical stability.

With the exceptions of the degradation of PA6 and PAN whose main degradation pathways are cyclization for both polymers, a non-radical pathway, the other polymers used in this study degrade primarily through a radical pathway. When heat is applied to a polymeric substrate, chain scission occurs and radicals are produced. Table 2 shows the bond-dissociation energies of each bond and stabilization energies of produced radicals. The stabilization energy of radical (SE) was calculated through the subtraction of carbon–hydrogen bond dissociation energy (C–H BDE) of each radical from that of methane (439 kJ/mol) [44]. The higher is the stabilization energy, the more stable is the radical [45,46].

The polymeric radicals that are produced may undergo several secondary reactions, disproportionation, β -scission, hydrogen abstraction, radical transfer and radical recombination. Considering both Tables 1 and 2, the allylic radical in EVA and the styryl radical in styrene-containing polymers are the most stable, and PS and EVA exhibit a large reduction in PHRR in the presence of clay. If a radical is relatively stable, it has more opportunity to undergo various secondary reactions. In the presence of clay, the clay acts as a barrier to keep the degrading compounds from evolving, hence the radicals have more opportunity to undergo additional reactions. Thus, more stable radicals may undergo intermolecular reactions, such as hydrogen abstraction and radical combination, which lead to the reduction of heat release rate in cone calorimetry.

EVA degrades via two step degradation pathways, elimination of acetic acid (chain stripping), leaving a double bond in the chain backbone (one per 28 carbons), then the degradation of the aliphatic chain, which is similar to the degradation of polyethylene. In the presence of clay, the acetic acid evolution may help to form an efficient intumescent layer,

Table 1
Thermal degradation of some polymer and polymer clay nanocomposite and resulting reduction in peak heat release rate

Polymer	Degradation pathway of virgin polymer	Degradation change (increase) in the presence of clay	Reduction, in PHRR (%)	Ref.
PA6	Intra-aminolysis/acidolysis, random scission	Inter-aminolysis/acidolysis, random scission	50–70	[13,24, 25]
PS, HIPS	β -Scission, (chain end and middle)	Recombination, random scission	40–70	[12,18, 29]
EVA	Chain stripping, disproportionation	Hydrogen abstraction, random scission	50–70	[14,40]
SAN, ABS	β -Scission, (chain end and middle)	Random scission, recombination	20–50	[15,18, 36]
PE	Disproportionation	Hydrogen abstraction	20–40	[20]
PP	β -Scission, disproportionation	Random scission	20–50	[20]
PAN	Cyclization, random scission	No change	<10	This work
PMMA	β -Scission	No change	10–30	[16,21]

Table 2
Listing of the polymer, radical produced from the polymer, bond dissociation energies (kJ/mol) and stabilization energies of the radicals [43]

Polymer	Radical	C–C BDE ^a	C–H BDE ^a	SE ^a
PE	$\sim\text{H}_2\text{C}-\dot{\text{C}}\text{H}_2$	377	415	24
PMMA	$\sim\text{H}_2\text{C}-\dot{\text{C}}(\text{CH}_3)-\text{C}(=\text{O})\text{O}-\text{CH}_3$	350	400	39
PP	$\sim\text{H}_2\text{C}-\dot{\text{C}}\text{H}(\text{CH}_3)$	372	396	43
SAN, ABS	$\sim\text{H}_2\text{C}-\dot{\text{C}}\text{H}(\text{CN})$	348	393	46
EVA	$\sim\text{H}_2\text{C}-\dot{\text{C}}\text{H}=\text{CH}-\text{CH}_2$	320	357	82
PS, HIPS, SAN, ABS	$\sim\text{H}_2\text{C}-\dot{\text{C}}\text{H}(\text{C}_6\text{H}_5)$	312	357	82

^a C–C BDE is carbon–carbon bond dissociation energy, C–H BDE is carbon–hydrogen bond dissociation energy and SE is stabilization energy of radical.

which may provide an insulating barrier before the degradation of aliphatic chain can occur and may make a contribution to the reduction in PHRR. Then, as the temperature increases, the remaining aliphatic chain degrades to smaller molecules. The allylic radical is the most stable radical; it is either the first formed radical or else radical transfer occurs to form this species. This radical can undergo radical recombination reactions, followed by additional random scission to give the observed products. Alternatively, after the loss of the double bond containing species occurs, the PE radical can hydrogen abstract.

For PS/clay nanocomposites, the secondary styryl radical is as stable as the allylic radical and there are many potential tertiary styryl radical sites available. The hydrogen in the β -position to the benzene ring may be the source of hydrogen abstraction, hence, in the presence of clay, radical transfer (intra- and inter-) to this position is very probable and the possibility to undergo radical recombination becomes high, along with hydrogen abstraction because of the high stability of the styryl radicals. Thus many head-to-head structures are detected in GC/MS analysis and these significant changes may be the reason for the large reduction in PHRR.

On the other hand, SAN and ABS include the acrylonitrile radical which is much less stable than the styryl radical. Thus the probability of the acrylonitrile radical to undergo additional inter-molecular reactions is low. Since only one-half of the radicals produced may be stabilized, the reduction in PHRR is not as significant as that of polystyrene. The same explanation can be offered for polyethylene and polypropylene by comparing the stability of radical produced from these polymers with those from EVA. In the case of PMMA, the methacrylate radical is the most stable radical, but it is not as stable when compared to the radicals from other polymers that show a good reduction in PHRR and there is no available hydrogen to form tertiary radicals, thus radical transfer reaction does not occur but β -scission does, evolving only monomer.

Therefore, it can be stated that the stability of the radical produced upon degradation of a polymer is proportional to fire retardancy in terms of the reduction in

PHRR. The more stable radical a polymer produces, the better is the reduction in peak heat release rate upon nanocomposite formation.

4. Conclusion

In polymer/clay nanocomposite system, the well dispersed clay layers provide a barrier effect which causes the confinement of the degrading polymers. Since the evolution of small molecules is delayed by the clay layers, it appears that this confinement allows the degrading polymer to undergo additional degradation pathways. Extensive random scission of the products formed by radical recombination is a common additional degradation pathway for most polymer/clay nanocomposites due to the barrier effect of the clay layers. If intermolecular reactions become significant, as shown in the nanocomposites of PA6, PS and EVA, then the fire retardancy of polymer/clay nanocomposites improves remarkably. In the case of polymers that degrade through a radical pathway, whether the degrading polymer undergoes further degradation pathways depends on the stability of the radicals. The radicals from PS and EVA are the most stable and the clay nanocomposites of these polymers show a large reduction in the peak heat release rate. These radicals may undergo radical transfer to a more stable radical, if available hydrogen is present, and recombination reactions. Thus, it can be concluded that the stability of radical produced upon degradation closely relates to the fire retardancy of polymer/clay nanocomposites.

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