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Studies on the thermal stabilization enhancement of ABS; synergistic effect of triphenyl phosphate nanocomposite, epoxy resin, and silane coupling agent mixtures

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Abstract

TPP nanocomposites (Nano TPP) were synthesized by intercalating triphenyl phosphate (TPP) into the galleries of organically modified mica-type silicate (OMTS) and any retarding effect of nanocomposites on the evaporation of TPP was investigated. It was found that Nano TPP has higher evaporation temperature compared to TPP and the thermal stability is slightly enhanced by adding Nano TPP to acrylonitrile–butadiene–styrene copolymer (ABS). Next, epoxy resin and silane coupling agent were incorporated as flame co-retardants. A very large increase in the limiting oxygen index (LOI) value was observed with epoxy addition and further enhancement in thermal stability was obtained for the ABS compound containing small amount of coupling agent. It was also found that the enhancement is closely related to the morphologies of the chars formed after combustion. A synergistic effect of using the flame retardant nanocomposites and addition of epoxy resin and coupling agent as flame co-retardants was also confirmed for the compounds based on DMP–RDP. LOI values as high as 44.8 were found for a particular formulation.

Keywords: ABS; Flame retardant; TPP nanocomposite

1. Introduction

Nowadays, a lot of emphasis has been placed on development of ecologically friendly polymers. In the area of flame retarding polymers, intense research has been performed to replace halogen-type flame retardants by non-halogen types and the flame retardants based on phosphorus-containing compounds are known to be the most promising candidates for this purpose [1,2]. Among various phosphorus-based flame retardants, Triphenyl phosphate (TPP) and its analogues are widely known to be the most effective for many polymers including acrylonitrile–butadiene–styrene copolymer (ABS) [3]. It has been reported that TPP generates phosphoric acids during thermal degradation and reaction takes place between phosphoric acids to yield pyrophosphoric acid, which acts as a heat transfer barrier in the condensed phase [4,5].

However, the use of TPP and its analogues has a shortcoming because their evaporation temperatures are lower than the processing temperature of ABS [6]. In order to overcome this problem a number of studies have been carried out to use mixtures of TPP with other polymers, mostly with phenols. The results showed that the evaporation of TPP is effectively suppressed due to the interaction between TPP and phenol, thus elevating the evaporation temperature of TPP [7–10]. It has also been reported that the flame retarding effects are enhanced if proper char forming agents are used [11–16].

In the meantime, a number of pioneering researchers have explored the feasibility of using organically modified mica-type silicates (OMTS) as a ceramic constituent in polymer–ceramic composites [17–22]. The

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ability to engineer the chemical nature of the silicate surface makes bonding at the polymer–silicate interface possible and allows nanocomposites to be fabricated from a broad range of polymers. These polymer–ceramic hybrids exhibit several unique properties; optical, electrical, barrier, and structural properties as well as thermal stabilization [23–27]. Blumstein already reported that the thermal stability of poly(methyl methacrylate) (PMMA) is improved by incorporation of montmorillonite clay [28]. As mentioned before, in the area of flame retarding polymers, intense research has been performed to replace the halogen type flame retardant by non-halogen types and attention has been paid to the use of polymer layered silicate nanocomposites as promising candidates for this purpose [29–31]. Several research groups have reported that the flammabilities of thermoplastics and thermosets are diminished by employing polymer layered silicate nanocomposites [32–35]. The peak and average heat release rate (HRR) are reduced in exfoliated and intercalated nanocomposites where mass fraction of silicates is well below 10 wt.%. The use of OMTS can be a very promising new method for flame retardance without usual drawbacks associated with other inorganic additives. The layered structure of nanocomposites is believed to improve the performance of the char formed on combustion. The char layer may act as an insulator and a mass transport barrier that slows down the escape of volatile products generated during the decomposition of polymer.

In a previous study, we incorporated various epoxy resins into TPP as flame co-retardants for enhancing the thermal stability of ABS and reported that the thermal stability of ABS is greatly enhanced by epoxy addition [36]. In this study, OMTS clay and silane coupling agent were added to that system and the synergistic effect of these materials on the flame retardancy of ABS investigated. Our approaches can be divided into two categories: (1) Suppression of TPP evaporation by using the TPP nanocomposite where TPP is inserted into the galleries of silicate layers. The motive for this approach can be easily understood by considering the advantages of nanocomposites mentioned before; and (2) Using a silane coupling agent which couples silicates and epoxy resins. The reason for using coupling agent is that it is well known that silicon-containing materials have fairly good thermal stability [37–41] and the silane coupling agent may help the coupling between clays and epoxy resins.

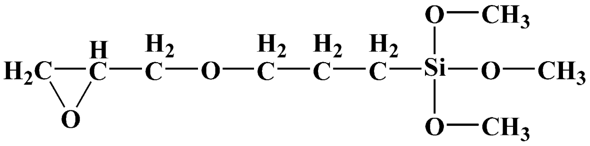
2. Experimental

2.1. Materials

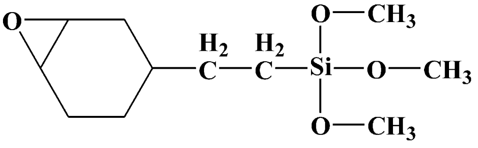
Two different epoxy resins were used; novolac and multi-functional. Both were supplied by the Nippon Kayaku Co. Japan. Their epoxy equivalent weights were 199 and 170, respectively, and their chemical structures can be found elsewhere [36]. Three different types of silane coupling agents which will be referred to as 'Silane' were used; gamma-glycidoxy propyl trimethoxy silane (S1), beta-(3,4-epoxy cyclohexy) ethyl trimethoxy silane (S2), and 3-methacrloxy propyl trimethoxy silane (S3). S1 and S2 were supplied by the Crompton Corporation and S3 by ShinEtsu Co., Japan. The chemical structures of silane coupling agents are presented in Fig. 1. Two different phosphorus type flame retardants (FR), TPP and tetra-2,6-dimethylphenyl resorcinol diphosphate (DMP–RDP), were supplied by Daihachi Co., Japan. ABS containing 18.0 wt.% butadiene and 35.9 wt.% acrylonitrile was manufactured by compounding g-ABS and bulk styrene–acrylonitrile copolymer (SAN), both of which were provided by Cheil Industries, Korea. Cloisite 30B of Southern Clay Products was used as an Organically modified Mica type Silicate (OMTS), which will be referred as 'Clay' hereafter.

2.2. Sample preparation

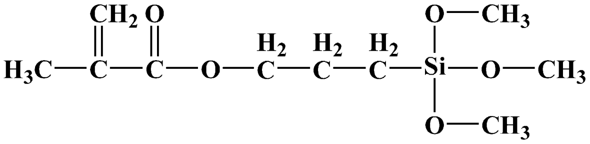
The mixture of TPP and clay, which will be referred to as 'Nano TPP', was melt-mixed in a heating mantle



r-Glycidoxy propyl trimethoxy silane (S1)



β-(3,4-Epoxycyclohexy) ethyl trimethoxy silane (S2)



$$H_3C-C(=CH_2)-C(=O)-O-CH_2-CH_2-CH_2-Si(O-CH_3)_3$$

3-Methacryloxy propyl trimethoxy silane (S3)

Fig. 1. The chemical structures of three silane coupling agents used in this study.

at 110 °C for 10 min. The desired amount of silane coupling agent was added to Nano TPP, followed immediately by the addition of epoxy resin to obtain the final flame retardant mixture. The mixing was performed at 110 °C for 5 min. The blends of ABS and flame retardant mixture containing TPP, Clay, Silane, and epoxy resin were processed in a Haake Plasti-Corder mixer at 230 °C and 60 rpm for 7 min. Specimens for limiting oxygen index (LOI) measurements were pressed on a Carver hot press at 180 °C for 10 min.

2.3. Thermogravimetry and LOI

Thermal stability was examined by a thermogravimetry (TGA) (TA instruments) under nitrogen and air. The flow rates for both cases were maintained at 10 and 90 ml/min for the balance part and for the furnace area, respectively. A dynamic method was employed at heating rate of 10 °C/min up to 700 °C. Limiting oxygen index (LOI) value was measured by a Fire Testing Technology instrument at a flow rate of 10.6 l/min.

2.4. Structure characterization by XRD and morphology observation

The structures of Nano TPP and NanoTPP/Silane mixture were analyzed by a X-ray diffractometer (XRD) with CuK_α radiation source ($\lambda = 0.154$nm) and a curved graphite crystal monochromator under 40 kV and 50 mA conditions. Scanning rate was 2°/min. The surface morphology of the char obtained after LOI test was observed by an optical microscope.

3. Results and discussion

3.1. Evidences for TPP/Clay nanocomposites

First, the evidence for the formation of Nano TPP was examined by XRD. Fig. 2 (a) shows the XRD profiles of Clay, Nano TPP, and Nano TPP/Silane mixture just after manufacturing at 110 °C. The composition of Nano TPP was 90/10 TPP/Clay and that of Nano TPP/Silane mixture was 81/10/9 TPP/Clay/Silane. It is observed in Fig. 2(a) that Clay itself shows a characteristic peak maximum at $2\theta = 4.9°$. For the mixture of TPP and Clay, i.e. Nano TPP, the first peak maximum moves to lower angle, indicating that intercalation of TPP into Clay galleries takes place. Therefore, it can be concluded that Nano TPP was successfully fabricated. It should be noticed moreover that the maximum peak position has not moved at all with further addition of silane coupling agent, meaning that the distance between silicate layers is the same for Nano TPP and Nano TPP/Silane mixture. This finding can be easily understood when considering that Silane preferentially reacts with–OH groups existing at the surfaces of silicate layers but the reaction of Silane with intercalated TPP is not possible at 110 °C, that is the temperature at which the mixtures were fabricated.

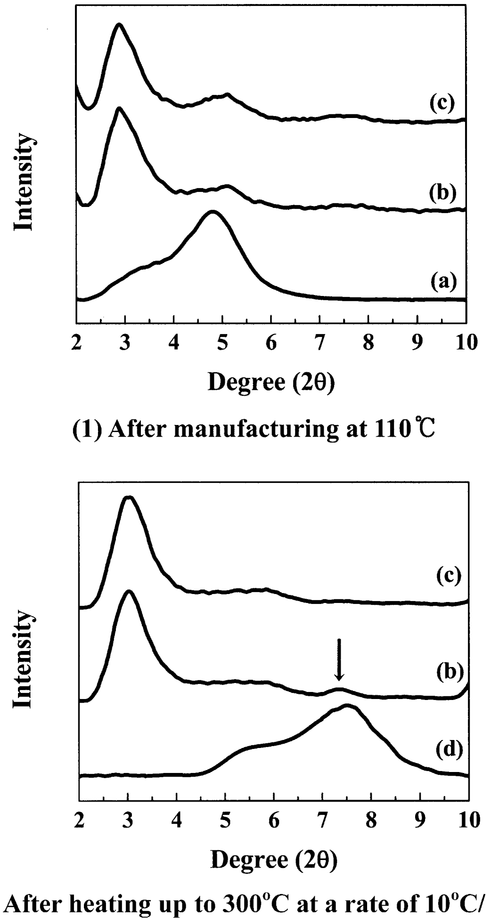


Fig. 2. XRD profiles for: (a) OMTS; (b) Nano TPP; (c) Nano TPP+Silane; (d) MMT. Top profiles were obtained just after melt mixing at 110 °C and bottom profiles after heating to 300°C.

Fig. 2(b) shows XRD profiles of Nano TPP and Nano TPP/Silane mixture after heating to 300 °C at a heating rate of 10 °C/min. For reference, the XRD profile of pristine montmorillonite (MMT) is also given. Comparing Fig. 2(a) and (b), it is noticed that a third peak maximum at $2\theta = 7.2°$, which corresponds to the peak maximum of MMT, is observed for the heated Nano TPP sample. This result indicates that not only intercalated TPP but also organic modifier in OMTS are escaping from Nano TPP upon heating.

3.2. Thermal stability enhancement of Nano TPP

Fig. 3 shows the TGA thermograms of TPP, Nano TPP, and Nano TPP/Silane mixtures employed in this study. When comparing their thermal stabilities under nitrogen atmosphere, it was found that Nano TPP and Nano TPP/Silane mixture have similar thermal stability and they exhibit much improved thermal stability over

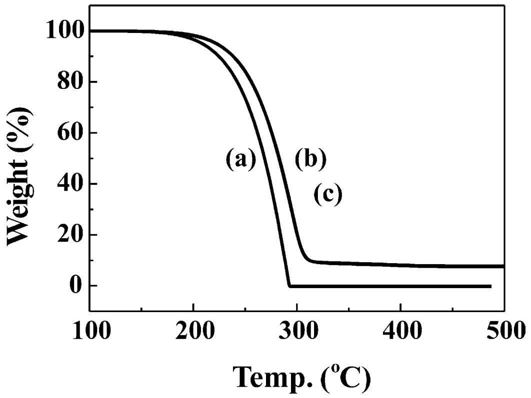
TPP. The initial thermal degradation temperature (T_i), the temperature at which weight loss begins, are in the order TPP (190 °C) < Nano TPP (219 °C) = Nano TPP/Silane mixture (219 °C) and the terminal thermal degradation temperature (T_f), the temperature after which no significant weight loss is observed, are also in the order TPP (292 °C) < Nano TPP (307 °C) = Nano TPP/Silane mixture (307 °C). Under air atmosphere, T_i are in the order TPP (201 °C) < Nano TPP (215 °C) = Nano TPP/Silane mixture (215 °C) and the same trend is observed for T_f. Therefore, it can be concluded that under both nitrogen and air conditions, the thermal stability of TPP is improved by fabricating nanocomposites with Clay.

It is also noticed from Fig. 3 that no residues remain above T_f for TPP but significant amounts of residues remain for both Nano TPP and Nano TPP/Silane mixture, which is believed to be related to the presence of Clay. Although no discernable difference in residue weight is found between Nano TPP and Nano TPP/Silane mixture under nitrogen atmosphere, the residue weight of Nano TPP/Silane mixture (11. 6 wt.%) is significantly higher than that of Nano TPP (8.22 wt.%) under air atmosphere. This is quite natural when comparing the compositions of Nano TPP and Nano TPP/Silane mixture.

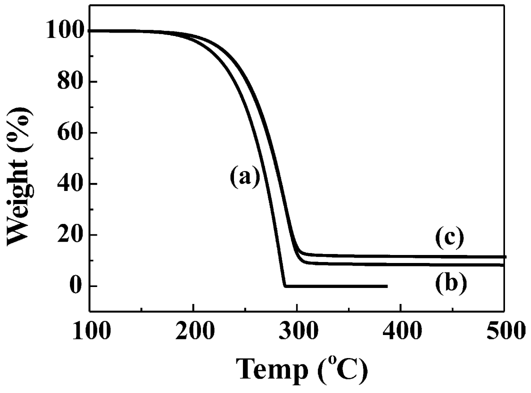
3.3. Thermal stability enhancement of ABS with Nano TPP

In the previous section, we presented experimental evidence that the thermal stability of TPP is enhanced by making nanocomposites. Therefore, Nano TPP or Nano TPP/Silane mixture were incorporated to ABS as a flame retardant and it was investigated whether there is any enhancement on the thermal stability of ABS, with the results given in Fig. 4. It was found under both nitrogen and air conditions that the thermal stability of the 85/15 mixture ABS with Nano TPP or Nano TPP/Silane is slightly enhanced. The slight enhancement is believed to result from the delayed evaporation of TPP in the compounds containing Nano TPP.

A series of flame retardants differing in TPP and Silane contents and Silane types was manufactured and compounded with ABS. LOI values of those compounds were measured and the results are presented in

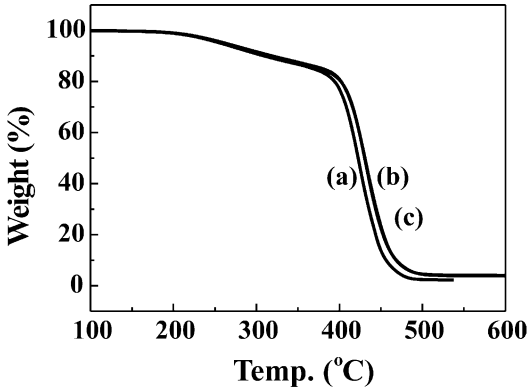


(1) Under nitrogen condition

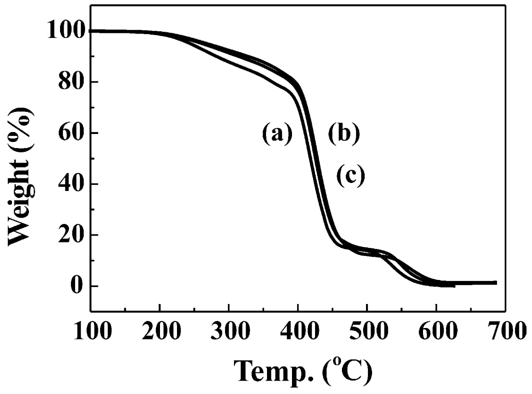


(2) Under air condition

Fig. 3. TGA thermogram for: (a) TPP; (b) NanoTPP; (c) NanoTPP/Silane.



(1) Under nitrogen condition



(2) Under air condition

Fig. 4. TGA thermogram for: (a) ABS/TPP 85/15; (b) ABS/NanoTPP 85/15; (c) ABS/(NanoTPP/Silane) 85/15.

Table 1. The clay content was fixed at 1.5 wt.% in all the compounds. When 15 wt.% TPP was added alone, LOI value was found to be 20.7 which is a little higher than 18.2 of ABS. When 15 wt.% Nano TPP was added, the LOI value was 20.9. When various Nano TPP/Silane mixtures were added to ABS, LOI value increases a little but not significantly. It is concluded that Nano TPP alone cannot effectively enhance the thermal stability of ABS.

3.4. Thermal stability enhancement of ABS with Nano TPP and novolac epoxy mixture

LOI values of various ABS compounds containing Nano TPP/Silane/multi epoxy resin FR are presented in Table 2. From these results, the following things are worthy to note: (1) No significant increase in LOI value by adding TPP or multi epoxy only as a FR; (2) Dramatic increases in LOI values when epoxy resin is incorporated into ABS together with TPP (LOI value of 85/9/6 ABS/Multi epoxy/TPP is 34.7 while that of 85/15 ABS/TPP is 20.7); (3) Further increases in LOI values by applying Nano TPP; (4) LOI value goes up with increasing amount of Silane (See the results for the formulations containing S2 type Silane); and (5) Most significant increase in LOI value is obtained with S2 type Silane among three different coupling agents used in this study. Therefore, we conclude that our ideas described in the Introduction section, that is, the application of Nano TPP together with silane coupling agent, are working successfully.

Table 1
LOI values of various mixtures of ABS with Nano TPP and Nano TPP/Silane (the numbers in table represent wt.% of each component)

ABS	Clay	TPP	Coupling agent (x)			LOI value
			S1	S2	S3	
100	–	–	–	–	–	18.2
85	–	15	–	–	–	20.7
85	1.5	15-x	0.150	–	–	20.9
85	1.5	15-x	–	0.075	–	21.2
85	1.5	15-x	–	0.150	–	21.3
85	1.5	15-x	–	0.750	–	21.8
85	1.5	15-x	–	–	0.075	20.9
85	1.5	15-x	–	–	0.150	21.0

Table 2
LOI values of various mixtures of ABS with Nano TPP/Silane/multi epoxy mixture (the numbers in table represent wt.% of each component)

ABS	Multi epoxy	Clay	TPP	Coupling agent (x)			LOI value
				S1	S2	S3	
100	–	–	–	–	–	–	18.2
85	15	–	–	–	–	–	20.2
85	–	–	15	–	–	–	20.7
85	9	–	6	–	–	–	34.7
85	9	0.6	5.4-x	0.054	–	–	37.7
85	9	0.6	5.4-x	–	0.027	–	36.1
85	9	0.6	5.4-x	–	0.054	–	38.0
85	9	0.6	5.4-x	–	0.270	–	39.2
85	9	0.6	5.4-x	–	0.540	–	41.2
85	9	0.6	5.4-x	–	–	0.027	36.0
85	9	0.6	5.4-x	–	–	0.054	36.0

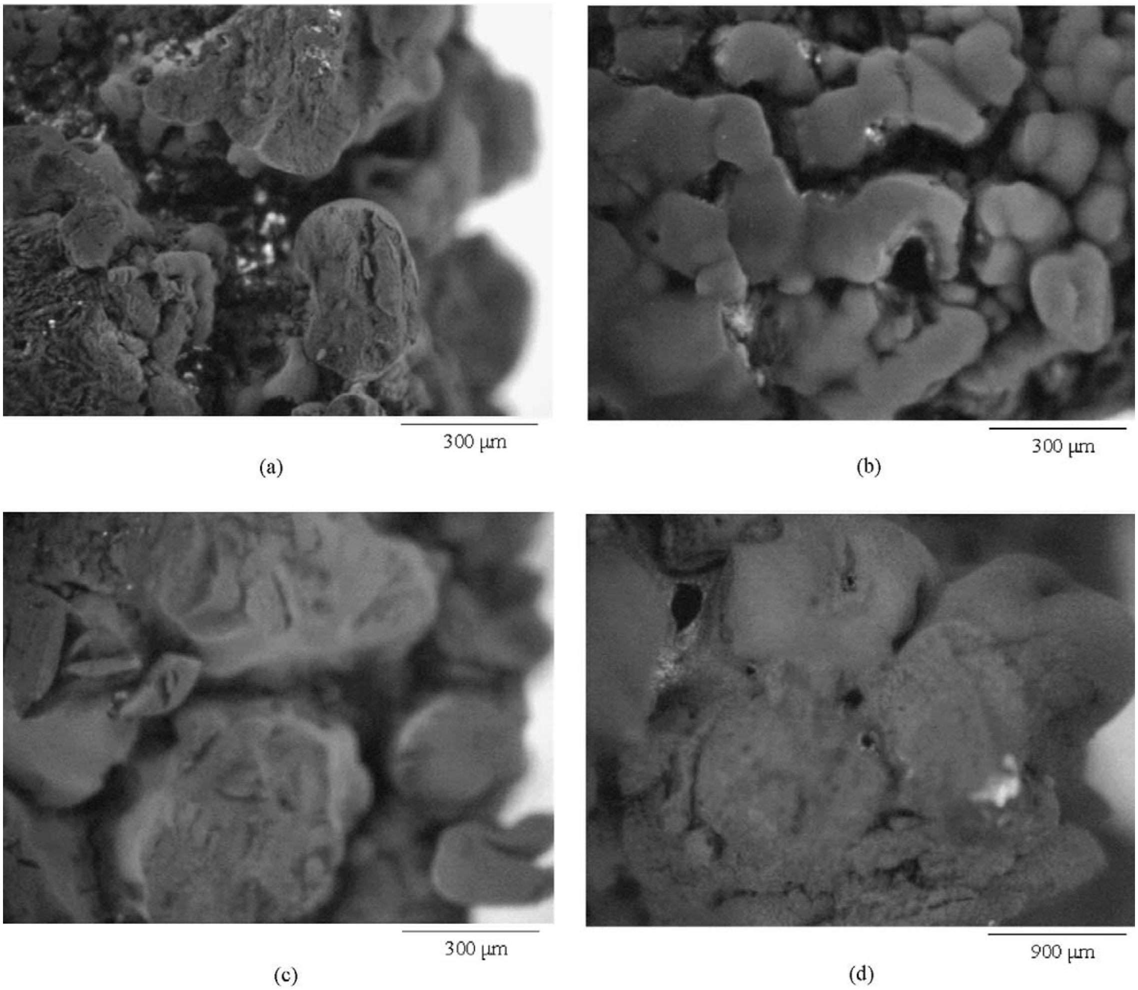
Finally, DMP–RDP which is one of the phosphorus flame retardants exhibiting higher evaporation temperature than TPP was used to examine whether the same synergistic effect could be observed. The LOI value (22.3) of a formulation containing 25 wt.% DMP–RDP alone was a little higher than the value (21.6) of a formulation containing the same amount of TPP. However, in the case of ternary mixtures of ABS, DMP–RDP, and novolac epoxy, huge increases in LOI values are observed. Table 3 shows the LOI values for various formulations containing Nano FR when the amounts of FR were fixed at 25 wt.%. LOI values as high as 44.8 is observed for a specific formulation. From Table 3, it becomes manifest that the same synergistic effects are found for the mixtures containing DMP–RDP. Again, it can be concluded from the results given in Table 3 that thermal stability enhancements are found when Nano FR together with epoxy and coupling agent is incorporated to ABS as a flame retardant.

3.5. Morphological consideration

In an attempt to elucidate the reason for the enhancement of flame retardancy by Nano FR and coupling agent addition, the morphologies of four different formulations after LOI testing (oxygen contents: 21.0 vol.%) were examined by optical microscopy and the results are presented in Fig. 5. It is observed from Fig. 5(a) that for the ABS/clay mixture the crevices between grains generated after combustion are very wide. These crevices become pathways for gas molecules generated from the combustion and heat evolved during burning. Although layered silicates are known to play an important role in flame retardance by exerting a heat

Table 3
LOI values of various mixtures of ABS with Nano DMP-RDP/Silane/novolac epoxy mixture (the number in table represent wt.% of each component)

ABS	Novolac epoxy	Clay	DMP–RDP	Coupling agent (S2)	LOI value
100	–	–	–	–	18.2
75	–	–	25.00	–	22.3
75	10	–	15.00	–	34.1
75	10	1.50	12.15	1.35	42.6
75	15	–	10.00	–	37.7
75	15	1.00	9.00	1.00	44.8



(a) (b) (c) (d)

Fig. 5. Optical micrographs of the chars formed after LOI test: (a) ABS/Clay 99/1; (b) ABS/NanoTPP 85/15; (c) ABS/(NanoTPP/Silane) 85/15; (d) ABS/Epoxy/(Nano TPP/Silane) 85/9/6.

transfer barrier, the enhancement must be limited judging from the above mentioned morphological observation. Fig. 5(b) shows the morphology of the residue after burning the ABS/Nano TPP mixture. The distances between grains become closer and the crevices are narrower. It is presumed that this morphological change is caused by the coating effect of Nano TPP. Fig. 5(c) shows the morphology of the residue after burning ABS/Nano TPP/Silane mixture. When compared with Fig. 5(b), bigger grains are observed but the distance between crevices is not changed much. In conclusion, no significant change in morphology is observed when clay or Nano TPP is added alone and that is the reason why the LOI values are not increased significantly for these systems as presented in Table 1. However, the burned residue of ABS/epoxy/Nano TPP/Silane mixture exhibits a quite different morphology as shown in Fig. 5(d). In this system, crevices are clogged and hardly observed and only small holes gushing flammable gas are observed. We believe that this difference in morphology is responsible for the huge thermal stability enhancement of ABS compounds containing epoxy resin. However, more profound study to support this assertion should be carried out in the future.

4. Conclusions

In this study, we synthesized TPP nanocomposites by intercalating TPP into the galleries of OMTS and investigated if there is any retarding effect of the nanocomposite on the evaporation of TPP. It was found that Nano TPP has higher evaporation temperature compared to TPP and the thermal stability is slightly enhanced by using Nano TPP in ABS. Next, epoxy resin was incorporated as flame co-retardant and three different silane coupling agents were also used to help the coupling between epoxy and Clay. A huge increase in the LOI value was observed with epoxy addition and further enhancement in thermal stability was obtained for the compounds containing small amount of coupling agent. It is also worthy to note that significant increase in the LOI value is observed with increasing the silane contents. For a specific formulation of 85/9/6 ABS/multi epoxy/(Nano TPP + Silane), an LOI value as high as 41.2 is obtained. Microscopy results revealed that this enhancement is closely related to the morphologies observed for the chars formed after burning the ABS/epoxy resin/Nano TPP/Silane mixture. In this system, crevices were hardly found and only small holes gushing flammable gas were observed.

The synergistic effect of using the flame retardant nanocomposites and addition of epoxy resin and coupling agent as flame co-retardants was also confirmed for the compounds based on DMP–RDP. An LOI value as high as 44.8 was found for a specific formulation. However, any effort to interpret the results analytically has not been made and will be the main direction of our future work.

Acknowledgements

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