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Studies on the thermal stabilization enhancement of ABS; synergistic effect by triphenyl phosphate and epoxy resin mixtures

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Abstract

Triphenyl phosphate (TPP) and its analogs are known to be the most effective flame retardant for acrylonitrile–butadiene–styrene copolymer (ABS) among various phosphorus-based compounds. But, its evaporation temperature is quite lower than the processing temperature of ABS. Therefore, it is inevitable to avoid a considerable amount of TPP to evaporate during processing. In order to overcome this undesirable phenomena, we incorporated various epoxy resins to TPP as coflame retardants and a series of ABS/TPP/epoxy compounds were made from them and their flame retardancy were evaluated by measuring the limiting oxygen index (LOI) values. Our results showed that the incorporated epoxy is very effective in suppressing the evaporation of TPP from the compounds and the LOI value as high as 38 is obtained. It is also found that more the epoxide ring contents in epoxy resins, the higher the LOI value of the compounds. The reason for this finding was postulated to come from the interaction between phosphoric acid and carboxylic acid generated from epoxy during thermal degradation. And some direct evidences from FTIR experiments were presented even though they were not conclusive. Moreover, the LOI values of quaternary mixtures of ABS, tetra-2,6-dimethyl phenyl resorcinol diphosphate, TPP, and epoxy resins were evaluated and that the same synergism of epoxy incorporation on flame retardancy was also found for them.

Keywords: Phosphorus flame retardant; Synergism; Epoxy resin

1. Introduction

Nowadays, a lot of emphasis has been laid to develop ecologically friendly polymers. In the area of flame retarding polymers, enormously intense researches have been performed to replace the halogen type flame retardant 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 analogs are widely known to be the most effective flame retardants for many polymers including acrylonitrile–butadiene–styrene copolymer (ABS) [3]. It has been reported that TPP itself generates phosphoric acid during thermal degradation and the reaction among phosphoric acids generated takes place and gives birth to pyro phosphoric acid, which acts as heat transfer barrier in condensed phase [4,5].

However, the evaporation temperatures of TPP and its analogs are quite lower than the processing temperature of ABS. Therefore, when manufacturing the flame retarding ABS by incorporating TPP, it is inevitable to avoid a considerable amount of TPP to evaporate during processing [6]. So, a number of studies have been carried out to utilize the mixtures of TPP with other polymers in order to overcome this problem [6–8]. Among them, the mixtures of TPP with novolac phenols are most intensively studied and the results showed that the evaporation of TPP is effectively suppressed due to the interaction between TPP and phenol, thus consequently elevating the evaporation temperature of TPP [6–10]. Also, it has been reported that polycondensates are produced from the rearrangements of phenol formaldehyde in the main thermal degradation routes and they act as char forming agents and the flame retarding effects are observed [11–16].

On the other hand, it has been reported that epoxide ring is converted into carboxylic acid during thermal oxidation [17–19]. Then, if the reaction between TPP and carboxylic acids generated can take place in the compounds containing epoxide rings during further thermal oxidation, one may expect the enhancement in thermal stabilization. In this

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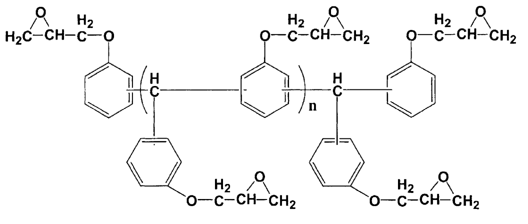
study, we employed various epoxy resins to investigate the synergistic effect of epoxy groups on the flame retardancy of ABS. Epoxy resins were used together with TPP and its analog as coflame retardants.

2. Experimental

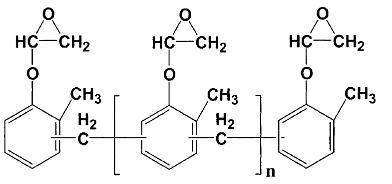
2.1. Materials

Three different types of epoxy resins were used; di-glycidyl ether of bisphenol-A (DGEBA), novolac, and multi functional. Novolac and multi type epoxy resins were supplied from the Nippon Kayaku Co., Japan. Epoxy equivalent weights (EEWs) for novolac and multi type epoxy resins are 199 and 170, respectively. DGEBA type epoxy resin was provided by the Kukdo Chemical Co., Korea and its EEW is 450. The chemical structures of epoxy resins are presented in Fig. 1. TPP and tetra-2,6-dimethylphenyl resorcinol diphosphate (DMP-RDP) were supplied from 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, both of which were provided by the Cheil Industries, Korea.

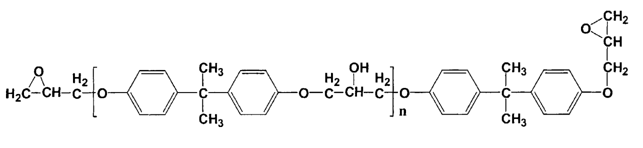
The mixtures were processed in a Haake Plastic-Corder mixer at 230 °C and 60 rpm for 7 min. Sample for FTIR was melt-mixed in a heating mantle at 130 °C and 60 rpm for 10 min. Specimens for limiting oxygen index (LOI) measurements were pressed by a Caver hot press at 180 °C for 10 min.



(a) Multi type (EEW = 170)



(b) Novolac type (EEW = 199)



(c) DGEBA type (EEW = 450)

Fig. 1. The chemical structures of three epoxy resins employed in this study.

2.2. Thermogravimetry and LOI

Thermal stability was examined by a thermal gravimetry (TGA) of TA instruments under nitrogen and air conditions. The flow rates for both cases were maintained at 10 and 90 cc/min for the balance part and for the furnace area, respectively. Dynamic method was employed at the heating rate of 10 °C/min up to 700 °C. LOI value was measured by a fire testing technology instruments at the flow rate of 10.6 l/min.

2.3. FTIR spectrophotometry

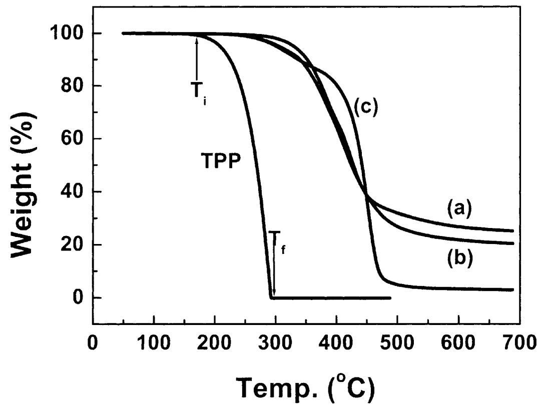
The char residues remained after TGA experiments were characterized with a FTIR spectrophotometry using KBr pellets.

3. Results and discussion

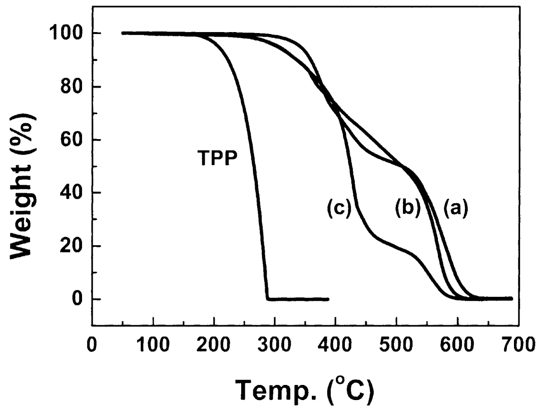
3.1. Thermal stability

First, thermal properties of three different epoxy resins were compared with that of TPP. Fig. 2 shows the TGA thermograms of three different epoxy resins employed in this study. It was found that all epoxies exhibit greater thermal stability over TPP. When comparing thermal stabilities of three epoxies under nitrogen atmosphere, the initial thermal degradation temperatures (T_i), the temperature at which weight loss begins, are in order of multi (316 °C) $\gg$ novolac (257 °C) $\approx$ DGEBA (253 °C) and the residue weights at the temperatures above 450 °C are also in order of multi > novolac $\gg$ DGEBA. Under air atmosphere, initial thermal degradation temperatures are in order of multi (337 °C) $\gg$ novolac (263 °C) > DGEBA (252 °C) and the terminal thermal degradation temperatures (T_f), the temperature after that no significant weight loss is observed, are in order of multi (637 °C) > novolac (622 °C) > DGEBA (605 °C). Therefore, it can be concluded that under both nitrogen and air conditions, the thermal stabilities of epoxy resins are much better compared to TPP and are in order of multi > novolac > DGEBA among three epoxies.

Next, the mixtures of TPP and epoxy were incorporated to ABS as flame retardant and it was investigated if there is any synergistic effect of epoxy addition on the thermal stability of ABS, whose results are given in Fig. 3. It can be seen in Fig. 3 that the initial weight loss observed at 200–400 °C which is mainly caused by TPP evaporation is greatly hampered for the compound containing epoxy resin. Also, thermally stable zone that is observed at 450–500 °C right after rapid decomposition zone of ABS observed at 400–450 °C becomes richer by epoxy addition.



(1) Under nitrogen condition



(2) Under air condition

Fig. 2. TGA thermograms of three epoxy resins and TPP under nitrogen and air conditions: (a) multi; (b) novolac; (c) DGEBA.

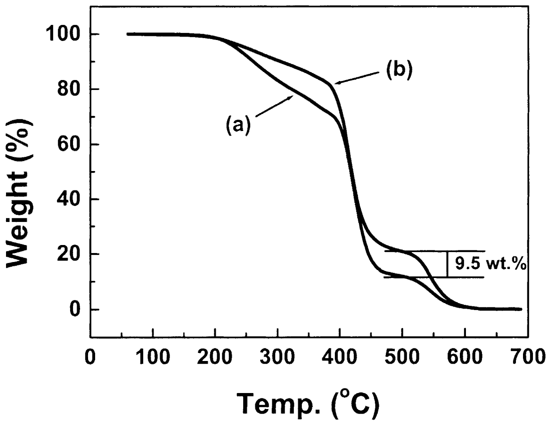


Fig. 3. TGA thermograms under air condition: (a) ABS/TPP 75/25; (b) ABS/(multi/TPP) 75/(15/10).

Therefore, it is concluded from these results that the residue of ABS mixture is greatly enhanced by adding epoxy as a coflame retardant.

3.2. LOI value

Now, a series of flame retardants differing in epoxy resin to TPP ratio were manufactured and they were compounded with ABS. For all the compounds, the amount of flame retardant was fixed at 25 wt% and the LOI values of compounds were measured, whose results are given in Fig. 4. When 25 wt% TPP was added alone, LOI value was found to be 21.6. When 25 wt% epoxy resin was added alone, the LOI values were 20.2 for the compound with multi, 21.0 for the compound with novolac, and 19.4 for the compound with DGEBA, respectively. Those LOI values are a little bit lower than the LOI value of the ABS compound containing TPP only. But, when the mixture of TPP and epoxy resin was incorporated into ABS, dramatic increases in LOI values were observed and the LOI value as high as 38 was obtained for the formulation containing 4/6 TPP/epoxy mixture. It is also worth to note that the increase in LOI value becomes more profound in order of multi $>$ novolac $>$ DGEBA, which exactly matches the order discussed in thermal stabilities of epoxy resins themselves. And, it is interesting to notice that this order is congruous with EEW in a reciprocal manner. That is, the more the oxirane ring in epoxy resin unit, the higher the LOI value of the compound.

At this moment, it is postulated that the increase in LOI value of the compound containing epoxy resin is resulted from the interaction of TPP with epoxy resin. In order to examine the validity of interaction between TPP and epoxy resin, mixture of TPP and multi type epoxy at 4/6 ratio was analyzed by TGA as shown in Fig. 5. For comparison reasons, the TGA thermogram for this mixture is constructed from the experimental data given in Fig. 2 by adopting the additive rule and is also presented in Fig. 5. It is noticed in Fig. 5 that T_i experimentally observed is higher

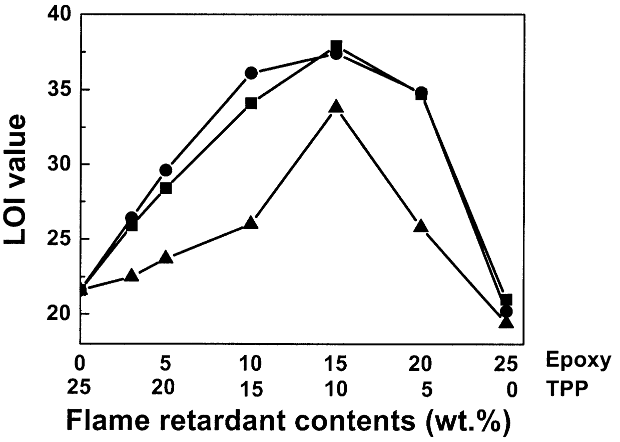


Fig. 4. LOI values for various ABS/TPP/epoxy resin ($75/(25-x)/x$) mixtures: ●; multi, ■; novolac, ▲; DGABA).

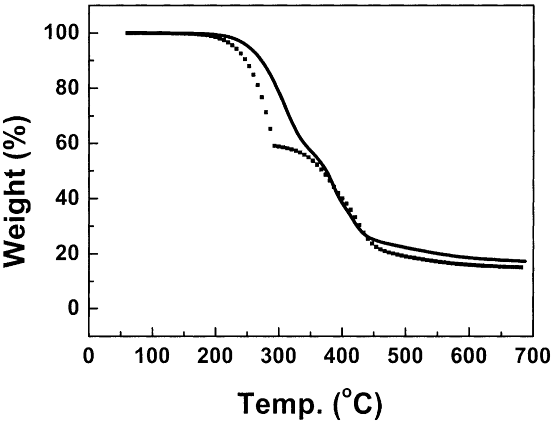


Fig. 5. TGA thermograms of TPP/multi (4/6) mixture under nitrogen condition: (line) experimental (symbol), by additive rule.

than T_i predicted from the additive rule. In addition, the residue observed experimentally at 700 °C is 2.3 wt% more than the residue predicted from the additive curve. From these results, it is postulated that, epoxy resin delays the evaporation of TPP in the initial thermal degradation and, during further thermal degradation, more thermally stable char is formed through some reaction between TPP and epoxy resin even though it is not clear at this moment. However, the earlier results are far enough to claim that epoxy can be a very efficient synergistic coflame retardant to ABS.

3.3. Evidences for the reaction between TPP and epoxy resin by FTIR

In an attempt to elucidate the reaction between TPP and epoxy resin, the mixtures of TPP and multi epoxy in 4/6 ratio undergone different thermal treatment were analyzed by FTIR and the results are presented in Fig. 6. For these purposes, the samples were obtained: (a) as mixed at 130 °C; (b) after experiencing thermal degradation at 400 °C on TGA; and (c) from the residue degraded at 600 °C on TGA.

For the mixture obtained right after mixing at 130 °C which is shown in Fig. 6(a), one observes the absorptions at 907 and 832 cm^{-1} which can be ascribed to the oxirane ring deformation, and the absorption at 1295 cm^{-1} which can be ascribed to the P=O stretching in pentavalent phosphorus compounds. In addition, the absorptions at 1187 and 949 cm^{-1} can be ascribed to the Aro-O and P–O stretchings in the pentavalent phenyl phosphates, respectively [20,21]. The earlier results indicate that TPP and epoxy resin are intact during mixing. After experiencing thermal degradation up to 400 °C, the absorptions of oxirane ring deformation have disappeared but the absorption of P=O stretching in newly generated POH bond has appeared at 1096 cm^{-1} as shown in Fig. 6(b) [6,20,21]. The absorptions of Alkyl-O and P–O stretchings in the pentavalent alkyl phosphates have also appeared at 1034 and 816 cm^{-1}, respectively [20,21]. And the absorption at 1709 cm^{-1} which can be ascribed to the carboxylic acid generated from epoxy is observed. However, as shown in Fig. 6(c), the absorption at 1724 cm^{-1} which can be ascribed to the ester formed from the reaction between –OH of POH and –COOH generated from oxirane ring opening has appeared on further oxidation when the residue experienced thermal degradation up to 600 °C [22]. And one can observe the existence of phenyl ether judging from the absorption at 1042 cm^{-1}. From these FTIR spectrophotometry results, one can clearly see the formation of a phosphoric acid from TPP and the creation of a carboxylic acid from epoxy resin at 400 °C and the presence of ester formed from the reaction between them at 600 °C. Therefore, it can be concluded that the interaction between TPP and epoxy resin deters the evaporation of TPP and the generation of phenyl ether and ester may be related to the formation of thermally stable char [11,23]. And this char formation must be responsible for the enhancement of flame retardancy for the compounds containing epoxy. However, the evidences given above are not conclusive yet and further study should be carried out. At this juncture, it should be mentioned that the interaction between the nitrile groups in ABS and the carboxylic acid is also possible [24–26]. Then, that interaction would be helpful for the enhancement of thermal stability, too.

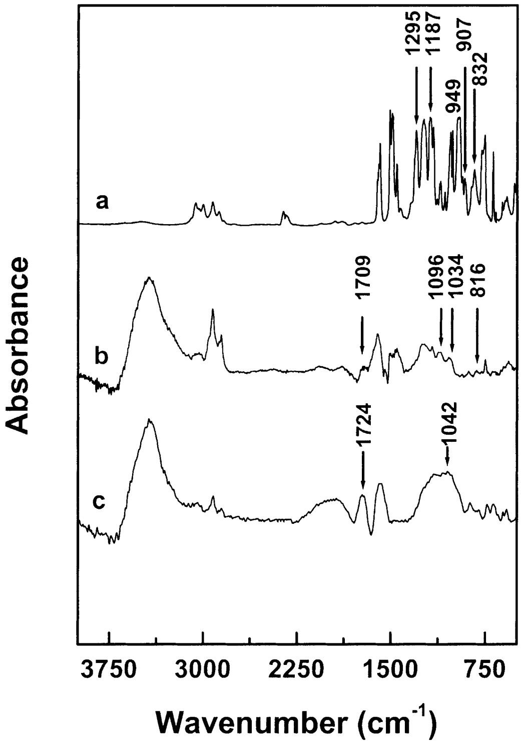


Fig. 6. FTIR spectra of 60 wt% multi epoxy + 40 wt% TPP: (a) after melt-mixing at 130 °C; (b) residue at 400 °C; and (c) residue at 600 °C. Residues were obtained from heating the specimen on TGA at heating rate of 10 °C under air condition.

3.4. Quaternary mixtures of ABS/TPP/DMP-RDP/epoxy

Finally, DMP-RDP, which is one of the phosphorus flame retardants exhibiting higher evaporation temperature compared to TPP, was employed to examine whether the same synergistic effect of epoxy addition could be observed. The LOI value (22.3) of a formulation containing 25 wt% DMP-RDP was a little higher than the value (21.6) observed for formulation containing the same amount of TPP. However, in the case of quaternary mixtures of ABS, DMP-RDP, TPP, and novolac epoxy, enormously huge increases in LOI values were observed. Fig. 7 shows the LOI values for various mixtures where the amount of flame retardants were fixed at 25 wt%. The LOI value as high as 44 is observed for a specific formulation. From Fig. 7, it becomes manifest that the same synergistic effects are found for quaternary mixtures containing DMP-RDP and that effect are more profound for DMP-RDP/epoxy mixtures than for TPP/epoxy mixtures. Therefore, it can be concluded that the most profound synergistic effects are found when a ternary mixture of TPP, DMP-RDP, and epoxy is incorporated to ABS as a flame retardant.

4. Conclusions

In this study, we incorporated various epoxy resins as coflame retardants to TPP and its analogs and a series of ABS/TPP/epoxy compounds were made from them and their LOI values were measured. The results showed that the incorporated epoxy is very effective in suppressing the evaporation of TPP from the compounds and the LOI value as high as 38 is obtained for a certain formulation. The reason for these findings were postulated to be due to the formation of thermally stable char originated from the reaction between the phosphoric acid generated from TPP and the carboxylic acid generated from epoxy during thermal degradation. And some evidences from FTIR experiments were given to support this assertion even though they are not conclusive. We note that there are several studies reported in the literatures supporting that the interaction between the nitrile groups in ABS and the carboxylic acid is also possible. Therefore, more profound study on this subject should be carried out in the future.

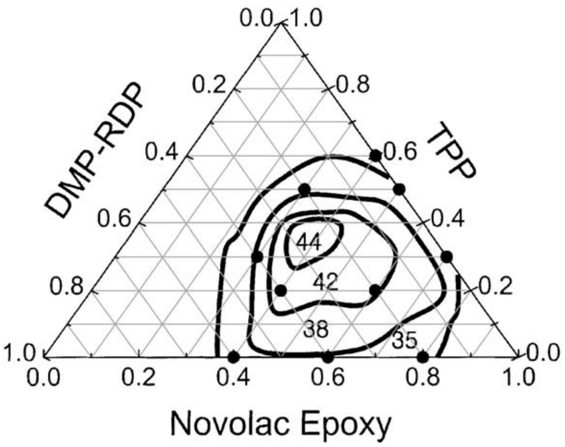


Fig. 7. LOI values for the quaternary mixtures of ABS, DMP-RDP, TPP, and novolac type epoxy. The amount of flame retardant, i.e. the amount of DMP-RDP, TPP, and novolac mixture, was fixed at 25 wt% in entire formulations.

Synergistic effect of epoxy addition was also confirmed for the quaternary mixtures of ABS, DMP-RDP, TPP, and epoxy. The LOI value as high as 44 was found for a certain formulation. However, any effort to interpret the results analytically has not been made and that will be the main direction of our next study.

Acknowledgements

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