

Study of a Novel Halogen-Free Flame Retardant System through TGA and Structure Analysis of Polymers

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ABSTRACT: Butadiene-rubber toughened styrene polymers, such as acrylonitrile-butadiene-styrene (ABS) copolymer and high impact polystyrene (HIPS), are noncharring polymers. They are generally blended with polycarbonate (PC) or polyphenyleneether (PPE), which are char forming polymers, to improve char forming ability for styrenic blends containing conventional phosphate flame retardants. To achieve cost effective flame retardant system, PET was selected as a potential char-source for ABS blends through the thermogravimetric analysis (TGA) and chemi-

cal structure analysis of various polymers. PET may contribute to the enhancement of flame retardancy of ABS/PET blends, especially in the presence of small amounts of phenol novolac (PN). The effective flame retardancy of this system is believed to be accomplished through the enhancement of interchain reactions by PN. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 2669–2675, 2009

Key words: halogen-free; flame retardant; char; TGA; phosphate; ABS; HIPS; PET; novolac

INTRODUCTION

Because of environmental concerns with some halogenated flame retardants, halogen-free flame retardant systems have drawn continuous attention.^{1,2} The representative halogen-free flame retardants are organic phosphates, such as triphenyl phosphate (TPP), bisphenol A bis- (diphenyl phosphate) (BDP), and resorcinol bis (di-2, 6-xyryl phosphate) (RXP). There are several well-known halogen-free flame retardant polymer systems using aryl phosphates with polycarbonates (PCs) and polyphenyleneethers (PPEs).^{3,4} PC and PPE are char-forming polymers and have high limiting oxygen index (LOI), which is closely related to flame retardancy.⁵ LOI refers to the minimum oxygen concentration in a mixture of oxygen and nitrogen to sustain burning after ignition. Generally, char-forming polymers consist of the phenyl ring or oxygen linkage in their backbones, which can lead to further reactions for char formation. These polymers are readily flame-retarded using phosphorus containing flame retardants^{6–8} and are widely used for the use of halogen-free housing applications, although they are not cost-efficient.

On the other hand, the rubber toughened styrenic polymers, acrylonitrile-butadiene-styrene copolymer

(ABS) and high impact polystyrene (HIPS), widely used as housing materials for LCD and CRT monitors, are flame-retarded using conventional halogenated compounds as flame retardants. It is very difficult to achieve halogen-free flame retardant system for ABS and HIPS, because ABS and HIPS are noncharring polymers upon combustion. So it is difficult to achieve halogen-free flame retardant system with conventional flame retardants.⁹ Thus, ABS or HIPS are generally blended with PC or PPE to improve the char-forming ability. Generally, the content of PC in PC/ABS formulation is more than 50 mass percents and that of PPE in PPE/HIPS blend is more than 25 mass percents.

Van Krevelen set up the empirical relationship between char residue and LOI. According to this relationship, LOI is proportional to the char amount calculated through the numerical summation of each chemical group contribution.¹⁰ This theory uses only the char residue data in TGA tests under nitrogen. On the basis of this relationship, the flame retardancy of a polymer can be predicted. To facilitate the formulation of a potential flame retardant system, the group contribution method was simplified to three components, which are the concentration of phenyl ring, the presence of oxygen linkage in the backbones, and the hydrogen concentration in the polymer structure. Additionally, in this study, the thermal degradation of a polymer by TGA under both air and nitrogen was considered.

The widely used char forming polymers, PC and PPE, are engineering plastics, which show excellent

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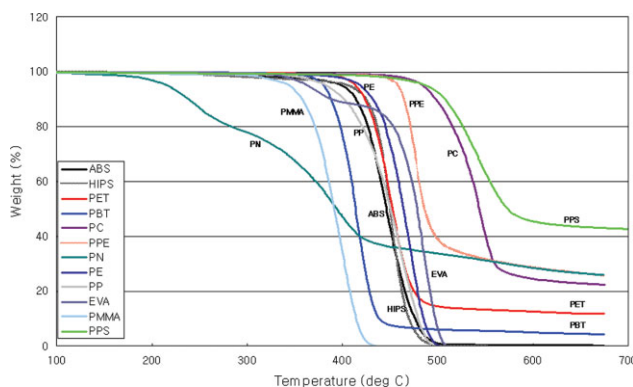


Figure 1 Thermogravimetric curves of each polymer under nitrogen at a heating rate of 20°C/min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

physical properties, but they are not cost-effective polymers, compared with ABS and HIPS. The objective of this study was to obtain an environmental friendly and a cost-effective flame retardant system by developing an effective char forming system. Through chemical structure analysis, a study of degradation pathways, an evaluation of thermal behavior and the consideration of the cost performance of the various polymers, which can be blended with ABS or HIPS, polyethyleneterephthalate (PET) was selected as a potential char forming polymer. Phenol novolac (PN) was used as the char forming accelerator. Although the char amount and the LOI of PET are much smaller than those of PC or PPE, if char forming accelerator is present, PET can act as a good char source in the formulation. In this study, it was shown that the contribution to flame retardancy of PET in ABS/PET blend was significantly improved by incorporating a small amount of PN, which is used as a char forming accelerator. The flame retardant mechanism is also discussed.

EXPERIMENTAL

Thermogravimetric analysis (TGA) data for various polymers were obtained at a heating rate of 20°C/min, using a TA TGA-2950. Polymers used were acrylonitrile-butadiene-styrene (ABS) terpolymer (SD-0150) of Cheil Industries (Uiwang, Korea), HIPS (HG-1760S) of Cheil Industries, PET (BL-7750) of SK Chemicals (Suwon, Korea), polybutyleneterephthalate (PBT; KP211) of Kolon (Kumi, Korea), PC (L1250W) of Teijin Chemicals (Matsuyama, Japan), PPE (P-402) of Asahi Chemicals (Mizshima, Japan), PN (KPH2002) of Kolon, polyethylene (PE; 4220S) of Samsung Total (Daesan, Korea), polypropylene (PP; HJ700) of Samsung Total, ethylene-vinylacetate (EVA) copolymer (E153A) of Samsung Total, polymethylmethacrylate (PMMA; IH830) of LG MMA, and polyphenylenesulfide (PPS; Torelina) of Toray Industries (Mizshima,

Japan). Resorcinol bis (di-2, 6-xylyl phosphate) (RXP; PX-200) of Daihachi Chemicals (Osaka, Japan) was used as a representative flame retardant among aryl phosphates. The polymers and RXP were used as obtained. The flame retardant formulations containing ABS or HIPS were prepared in a 45Φ and L/D 34 twin-screw extruder of SM Platek in the temperature range of 200–270°C, screw RPM 350. The flame retardancy of resin formulation was evaluated according to the UL 94 vertical burning test method.¹¹

RESULTS AND DISCUSSION

Because combustion always accompanies oxidation due to oxygen in air, it is worthwhile to compare TGA data obtained in both air and nitrogen for the purpose of the prediction and evaluation of flame retardancy. Figures 1 and 2 show TGA data for various polymers under nitrogen and air atmosphere, respectively. Mass loss rate and mass loss onset temperature exhibit different results with the chemical structures of polymers. PN begins to lose its mass at 180°C, whereas PPS begins to lose its weight after 400°C. Char residue at 700°C in nitrogen atmosphere of PPS shows the highest amount, 43%.

Comparing the Figures 1 and 2, it is noticeable that the mass loss behavior of a polymer varies significantly with the atmosphere. In nitrogen, some polymers give char residues at 700°C, whereas TGA data of all polymers under air provide no residues because polymers eventually lose their whole masses because of air oxidation at high temperature. The thermal mass loss depends on the atmosphere and it is different on a polymer-by-polymer basis. Some polymers show slower mass loss rate in air, whereas others exhibit faster mass loss rate in air. On the basis of this property, polymers used are classified with the changes of mass loss rate between air and nitrogen. Figure 3 shows an example of Type I

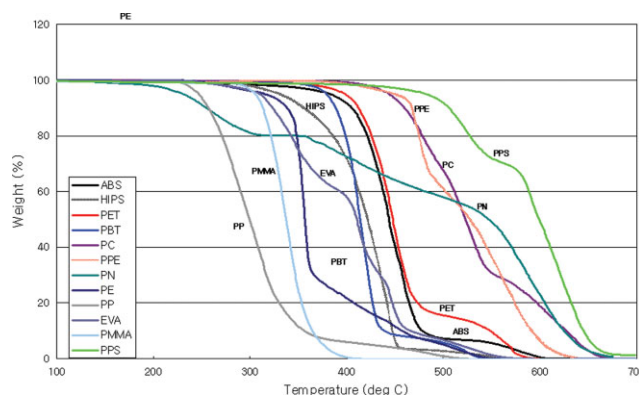


Figure 2 Thermogravimetric analysis of each polymer under air at a heating rate of 20°C/min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

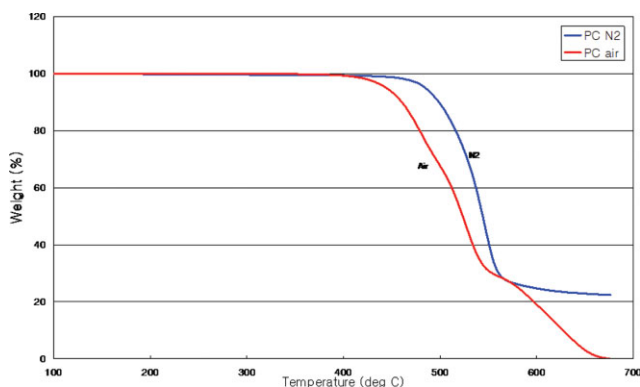


Figure 3 TGA example of Type I polymer, PC. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

polymers. PC, HIPS, PMMA, PP, PE, and EVA are included in this category. Type I polymers show faster mass loss in air than in nitrogen. This means that the oxygen in air accelerates the mass loss of polymer through oxidation. With the exception of PC, these polymers have vinyl based structures and they are thermally degraded by radical process.^{12–14} In the case of Type II polymers, the presence of oxygen during heating does not significantly affect the mass loss behavior as shown in Figure 4. ABS, PET, and PBT belong to this category. Figure 5 exhibits the typical behavior of Type III polymers. A polymer in this category exhibits slower mass loss in air. It is speculated that oxygen in air catalyzed interchain reactions for Type III polymers.

Referring to Table I, thermal mass loss and degradation behavior depend on the polymer structure. The Type III polymer generally loses its mass at high temperature and gives a large amount of char residue in nitrogen. Vinyl based Type I polymers give no char residues and begin to lose their masses at relatively low temperature. The manifest structural differences between these two groups are the

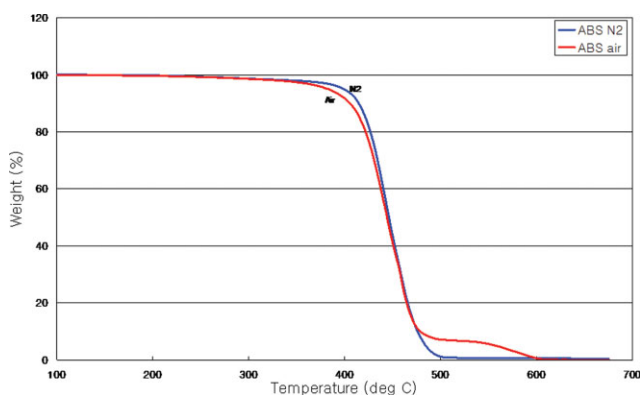


Figure 4 TGA of ABS. An example of Type II polymer. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

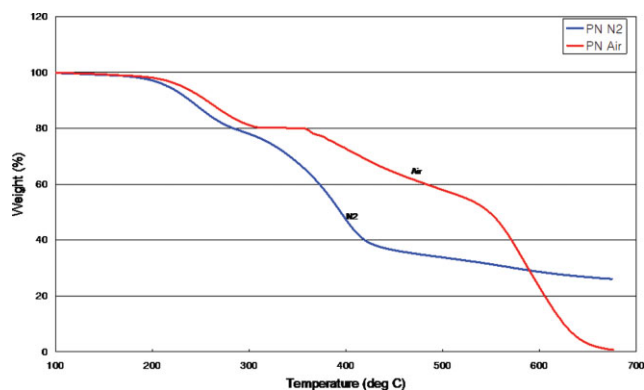


Figure 5 TGA of PN. An example of Type III polymer. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

presence of an aromatic ring and an oxygen (sulfur for PPS) linkage in their backbones.

A comparison of LOI values and the polymer type is shown in Table I. Type III polymers have high LOI numbers and Type I polymers show low LOI. ABS belongs to Type II polymers and HIPS is in Type I. These two polymers give no char residue upon combustion. Therefore, it is difficult to achieve sufficient flame retardancy for these polymers by incorporating an aryl phosphate as a flame retardant, because aryl phosphate flame retardants generally work in char forming polymer systems. PC or PPE are blended with ABS or HIPS to provide the char forming ability and thus enable flame retardancy with aryl phosphates.

The use of aryl phosphates to achieve a UL-94 V-0 or V-1 rating generally requires that PC/ABS contain 70% PC and PPE/HIPS contain 30% PPE. These flame retardant polymer blends are commercially available and widely used for the housing materials of electrical appliances. On the basis of the chemical structure of PC and PPE, the flame retardancy of PPE can be expected to be better in terms of char residue and LOI. However, this fails to explain why the required PC dosage in ABS/PC blends for UL94 V0 or V1 flame retardancy using aryl phosphate is twofold or more, compared with the PPE content in ABS/PPE or HIPS/PPE blends (Table II). Considering LOI value, char residue and chemical composition of PC, PC should have exhibited better flame retarding performance than shown in Table II. This can be explained by the degradation characteristics of PC. It appears that PC undergo decarboxylation reaction in the presence of air as shown in Scheme 1,^{15,16} and PC belongs to Type I polymers, which is not preferable for good flame retardancy. The vulnerable carbonate linkage may be readily attacked by oxygen with the evolution of carbon dioxide and small molecules and/or radicals. This may explain why the flame retardancy of PC is

TABLE I
LOI Residue at 700°C in Nitrogen, Concentration of Specific Functional Groups in Polymer Structure, Temperature at 5% and 30% Mass under Nitrogen and Air and TGA Type of Polymer

Polymer	LOI	Residue at 700°C	Concentration in structure (%)			Temperature at 5% mass loss (°C)		Temperature at 30% mass loss (°C)		TGA Type
			Φ^a	—O— ^b	—H ^c	Nitrogen	Air	Nitrogen	Air	
PPS	44	43	70.4	—	3.7	488	482	541	563	III
PN	35	28	70.7	15.1	5.6	215	217	341	415	III
PPE	29	27	60.0	13.3	6.7	458	448	476	483	III
PC	27	22	56.7	12.6	5.5	484	444	528	495	I
PET	21	11	37.5	16.7	4.2	414	398	440	436	II
PBT	20	4	32.7	14.5	5.5	380	379	404	403	II
ABS	19	0	—	—	7.9	399	383	434	431	II
HIPS	19	0	—	—	7.1	405	330	441	402	I
PMMA	17	0	—	—	8.0	344	305	379	328	I
PP	18	0	—	—	14.3	383	247	434	281	I
PE	18	0	—	—	14.3	419	315	453	352	I
EVA	18	0	—	—	12.1	364	310	465	360	I

^a Phenyl group content in chain backbone of polymer.

^b Oxygen linkage content in chain backbone of polymer.

^c Hydrogen content in whole structure.

worse than PPE and why more PC than expected is required to achieve the UL94 V0 or V1 rating in ABS/PC.

On the basis of van Krevelen's study and our flame retardant formulation study, it is thought that the flame retardancy of polymers is closely related to the char forming tendency and is mainly governed by three factors: (1) the concentration of aromatic rings in polymer backbone, (2) the presence of oxygen linkage in the backbone, and (3) the hydrogen concentration in the polymer structure. Char consists of highly aromatized structures, thus the aromatic groups in backbone are likely to form char-like structures upon heating. Char is the outcome of interchain reactions such as dehydrogenation and dehydroxylation and its chemical structure is the graphite-like structure. The oxygen or sulfur linkage in polymer chain is a potential site for the interchain reactions, which make mass loss rate slower upon heating, eventually leading to char structure through dehydroxylation, etc. Hydrogen is the ultimate fuel upon combustion, so a polymer having a high hydrogen concentration tends to show a low LOI number. Flammability of the polymers used in this study can be explained and predicted in terms of these three factors as well as considering the TGA Type of polymer.

The objective of this study is to form a cost-effective flame retardant system for ABS and HIPS using phosphate flame retardants. Thus, it is prerequisite to impart char forming ability to ABS or HIPS. Although PPE and PC are well known char formers for ABS or HIPS, they are not cost-effective. PPS may be a good char former, but PPS has a process-

ing temperature range where ABS or HIPS cannot be processed. In the case of PN, its mass loss rate was significantly lowered in air as shown in Figure 5, which means increased interchain reaction in the presence of oxygen and high char forming efficiency. However, its thermal stability is not good enough in the processing temperature region of ABS or HIPS, 200–250°C, so a large amount of PN cannot be used to formulate an efficient char forming system. Other candidates would be the use of PET or PBT.

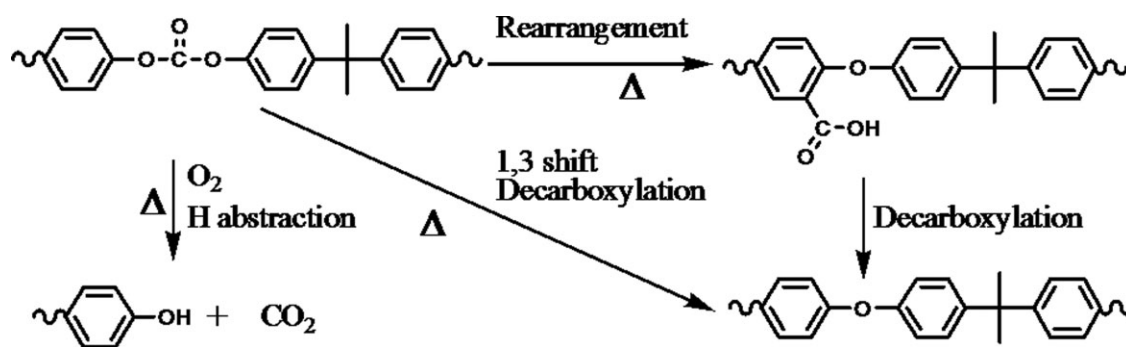
As indicated in Table I, PET and PBT have an aromatic portion and an oxygen linkage in their back

TABLE II
UL 94 Results of Each Formulation

Formulation	UL94 V
ABS/PN/RXP = 80/20/20	V1
ABS/PN/RXP = 90/10/20	Fail ^a
ABS/PPE/RXP = 70/30/20	V1
ABS/PPE/RXP = 80/20/20	Fail
ABS/PC/RXP = 30/70/20	V0
ABS/PC/RXP = 40/60/20	Burn ^b
ABS/PET/RXP = 10/90/20	V1
ABS/PET/RXP = 20/80/20	Burn
HIPS/PN/RXP = 80/20/20	Fail
HIPS/PN/RXP = 90/10/20	Burn
HIPS/PPE/RXP = 70/30/20	V0
HIPS/PPE/RXP = 80/20/20	Fail
HIPS/PC/RXP = 30/70/20	V0
HIPS/PC/RXP = 40/60/20	Fail
HIPS/PET/RXP = 10/90/20	Fail
HIPS/PET/RXP = 20/80/20	Burn

^a Fail: Self-extinguishing, not-satisfying UL94 specification.

^b Burn: Burned to the clamp, not self-extinguishing.



Scheme 1

bone and their hydrogen concentrations are low. Comparing PET with PBT, PET might be better for flame retardancy in terms of aromatic content and hydrogen concentration. Even though the aromatic portion of PET is low, compared with Type III polymers, it has high oxygen content and has the lowest hydrogen concentration among polymers used. This implies that PET can act as a good char former upon combustion. However, its char forming ability is not efficient to impart flame retardancy to ABS/PET or HIPS/PET blends. Table II shows UL94 results for possible ABS or HIPS containing blends using PN, PPE, PC, and PET as char forming polymers, when resorcinol bis (di-2, 6-xylyl phosphate) (RXP) was used as a flame retardant at 20 parts.

The UL94 results in Table II reflect the char forming ability of polymers applied to ABS or HIPS formulations. As in the order of LOI and char residue data of Table I, the most effective char former is PN and then PPE, etc. The amount of each char forming polymer in the formulation containing ABS or HIPS for UL94 V0 or V1 was determined; 20 parts of PN in ABS/PN, 30 parts for PPE in ABS/PPE, 70 parts of PC in ABS/PC, and 90 parts of PET in ABS/PET. The required amount of PC is much more than those of PN and PPE. This may relate to the degradation characteristics of PC as described in the previous section. Even though PN imparts very good char forming performance to the formulation, its heat and color stability are not good, so a large amount of PN cannot be applied. In the case of PET, its char forming ability is not sufficient, so a large amount (as much as 90 parts of PET) is required to achieve UL94 V1 rating for an ABS/PET blend. Considering the chemical structure of PET, PET has an aromatic ring and an oxygen linkage in backbone. PET, which is one of the widely used polymers for bottles and clothing, also has a low hydrogen concentration. However, PET itself hardly forms char during combustion because of its degradation mechanism. PET undergoes thermal degradation through intrachain transesterification to form small, volatile mole-

cules.^{17,18} Thus, it is difficult for ABS/PET blend to achieve good flame retardancy. To overcome and compensate these drawbacks of PN and PET, a small amount of PN was incorporated into an ABS/PET blends.

Table III shows representative flame retardant test results on ABS and HIPS containing PET, PN, and a conventional phosphate flame retardant (RXP). PN was incorporated into the system at 0 to 5 parts. If only PET is blended with ABS, ~ 90 parts are required to achieve an UL-94 V-1 or V-0 rating. If PN is incorporated with a small amount at three parts in the formulation, an UL 94 V1 performance is obtained even at 35 parts of PET in the ABS/PET blend. Comparing this result with a PC/ABS/Phosphate formulation, which needs 70 parts of PC, it is remarkable that such a relatively small amount of PET can exhibit V1 flame retardancy by the small addition of PN. This implies that the addition of PN brings about the enhancements in char forming ability of PET and ABS during thermal degradation. On the other hand, a HIPS/PET/PN system did not exhibit sufficient flame retardancy. The difference between ABS and HIPS (butadiene-styrene) is the presence of acrylonitrile in their chemical

TABLE III
UL94 Results for PN Containing FR System

Formulation	UL94 V
ABS/PET/PN/RXP = 10/90/0/20	V1
ABS/PET/PN/RXP = 65/35/0/20	Burn ^a
ABS/PET/PN/RXP = 65/35/1/20	Fail ^b
ABS/PET/PN/RXP = 65/35/3/20	V1
ABS/PET/PN/RXP = 65/35/5/20	V1
HIPS/PET/PN/RXP = 10/90/0/20	Fail
HIPS/PET/PN/RXP = 65/35/0/20	Burn
HIPS/PET/PN/RXP = 65/35/1/20	Burn
HIPS/PET/PN/RXP = 65/35/3/20	Fail
HIPS/PET/PN/RXP = 65/35/5/20	Fail

^a Burn: Whole polymer sample burned.

^b Fail: Self-extinguishing, not-satisfying UL94 specification.

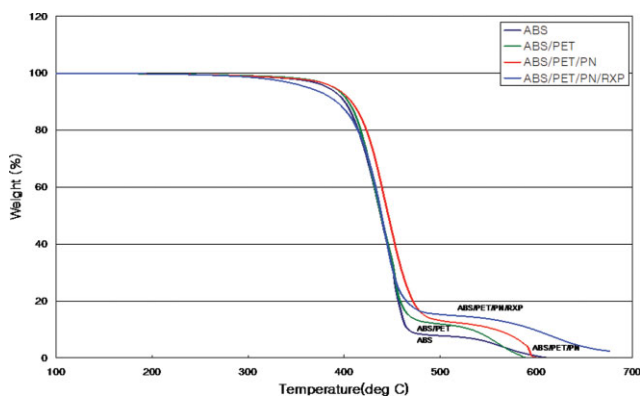


Figure 6 Thermogravimetric mass loss data of virgin ABS, ABS/PET = 65/35, ABS/PET/PN = 65/35/3, and ABS/PET/PN/RXP = 65/35/3/20 in air. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

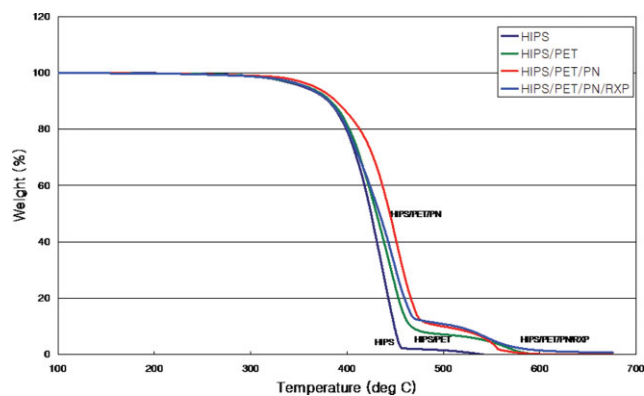
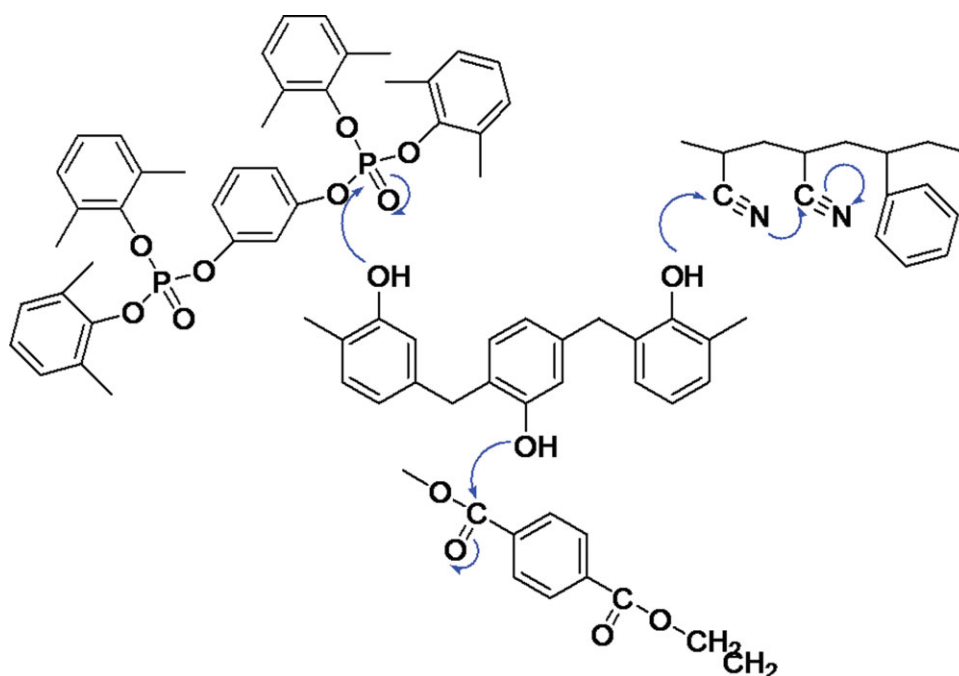


Figure 7 Thermogravimetric mass loss data of virgin HIPS, HIPS/PET = 65/35, HIPS/PET/PN = 65/35/3, and HIPS/PET/PN/RXP = 65/35/3/20 in air. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

compositions. This means that the nitrile group of ABS may participate in the interchain reactions in the presence of PN and PET. In addition, HIPS was classified as a Type I polymer as shown in Table I, whereas ABS belongs to Type II. Another thing to consider in this case is the miscibility between each phase; PN is more miscible in ABS than HIPS. So, the miscibility between components could be another factor for the flame retardancy of the formulation. Meanwhile, if PN is involved in the ABS/PC or HIPS/PPE system as a char forming catalyst, the flame retardancy of the formulation is not significantly enhanced, probably because the char forming ability of PC and PPE is sufficient by themselves.

Figure 6 shows the thermal mass loss behavior of ABS-containing formulations in air. The residue occurring around 500°C in each formulation is an intermediate char, which clearly show differences with the formulation change. The thermal property at this temperature in air is very important, because the temperature of a burning polymer surface corresponds to this temperature region and the burning surface is exposed to air. As PET is added to ABS, the residue at 500°C is increased in a significant amount. The incorporation of PN and phosphate flame retardant further increases the residue at this temperature region and delays thermal degradation even more, to around 600°C.



Scheme 2

On the other hand, in the case of HIPS containing formulations, the incorporation of PN and phosphate flame retardant does not show a significant enhancement of intermediate char in the temperature region of 500–600°C (Fig. 7). The difference in intermediate char amounts between the ABS and HIPS formulations may reflect the UL94 flame retardancy, as shown in Table III. ABS formulations gave an UL94 V1 rating with 35 parts of PET, 20 parts of RXP, and three parts of PN, whereas HIPS formulations gave no rating with the UL-94 test. The incorporation of PN in ABS/PET blend is believed to increase the interchain reactions between components through transesterification and electron donation as shown in Scheme 2. The interchain reactions caused by PN may delay the degradation of the polymer matrix for some time and thus give more opportunity for the phosphate flame retardant to provide condensed phase flame retardancy as well as vapor phase flame retardancy. Because HIPS does not contain any functional groups for the interchain reactions, the effect of incorporation of PN in HIPS containing formulations is not significant.

Scheme 2 proposes how the interchain reactions could occur during the combustion of ABS/PET blend in the presence of small amount of PN. Because these interchain reactions are enhanced by PN, the flame retardant performance using phosphate flame retardant is significantly improved. In ABS/PET/RXP system, the phenolic group of novolac may react with the phosphate linkage and the ester group via transesterification, and it may accelerate the cyclization among nitrile groups to induce a crosslinked structure and ultimately form a nonflammable char on the surface of burning polymer. Because PN contains a large number of phenolic groups in the structure, it assists PET to form crosslinked structures and exhibits a very efficient flame retardant performance through the interchain reactions.

CONCLUSIONS

Various polymers were blended with rubber toughened styrene polymers, such as ABS copolymer and HIPS to formulate a cost effective and environmental

friendly flame retardant system. A TGA analysis was used to explain the polymer degradation characteristics and was used to classify polymers according to the difference in mass loss rate in air and nitrogen. Although char amount and LOI of PET are smaller than those of PC or PPE, PET was selected as a potential char-source for ABS and or HIPS blends. The selection was based upon TGA, chemical composition, and cost-performance. In this study, it was shown that PET can act as a potential char source. The flame retardancy of an ABS/PET blend is increased significantly by the presence of small amounts of PN. It appears that PN catalyzes interchain reactions either by transesterification with the ester linkage of a phosphate flame retardant or by reaction with the nitrile group of ABS. Regarding HIPS/PPE blends, efficient flame retardant systems were not formed, probably because there are no significant interchain reactions between components.

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