Flame-Retardant ABS Resins from Novel Phenyl Isocyanate Blocked Novolac Phenols and Triphenyl Phosphate

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ABSTRACT: In an effort to prepare a novel novolac phenol (NP) based char former with good solubility, the hydroxyl functionalities of NP were blocked with phenyl isocyanate (PI) via a simple urethane-forming reaction. The chemical structure and properties of the obtained novolac phenol–phenyl isocyanate adduct (NP–PI) were characterized with gel permeation chromatography, Fourier transform infrared spectroscopy, ^{1}H-NMR, and differential scanning calorimetry. Adducts of two kinds of NPs (molecular weights = 450 and 800) with PI were used as potential char formers for this study. Thus, a two-component system using NP–PI as a char former and triphenyl phosphate (TPP) as a phosphorous-based flame retardant was blended with ABS, and the thermal degradation behavior and flame retardance were examined as a function of the molar mass of NP–PI and the TPP/NP–PI ratio with thermogravimetric analysis and limiting oxygen index (LOI) testing. ABS compositions with no NP–PI were also prepared for comparison. The mixtures showed a synergistic effect between TPP and NP–PI on the flame-retardance enhancement of ABS. Those containing the higher molar mass NP–PI adduct were the most flame retardant, and a LOI value as high as 41 was obtained. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 721–728, 2006

Key words: gel permeation chromatography (GPC); miscibility; intumescent

INTRODUCTION

Novolac phenols (NPs) are linear oligomers that are easily synthesized by the base-catalyzed condensation of phenols and formaldehyde. They have acquired unique applications in various polymer systems, and a number of studies have been carried out to examine the physical properties of NPs.[1–3] So far, there have been several approaches to the use of NPs as char formers in flame-retardant resin systems.[4–9] A few studies have reported on aryl phosphate–novolac combinations in ABS.[9–11] These approaches have been used in an effort to delay the volatilization of the degradation products of phosphorous-based flame retardants [e.g., triphenyl phosphate (TPP)] by the presence of barrier-producing components in the melted resin.[4]

Because high flame retardance can be achieved, NPs are very promising materials in terms of char formers. They consist of a relatively robust aromatic backbone and polar hydroxyl functionalities. NPs and phosphorous-based flame retardants in polymer compounds are expected to increase the flame-retardant properties of the system. However, most methods have used virgin NPs in flame-retardant resin formulations, and from a chemistry point of view, it is difficult to compound polar NPs with nonpolar polymers such as ABS because they are not miscible. NPs are expected to be microphase-separated due to the high content of hydroxyl units in the backbone. Thus, a NP derivative with good miscibility is desired.

In our laboratory, we have investigated the thermal stabilization of ABS in the presence of various organic[10–12] and inorganic[13] additives to develop efficient flame retardants for ABS. Our recent research into the application of intumescent flame retardants to ABS demonstrated that the introduction of intumescents based on phosphorous compounds and NPs onto ABS resins significantly increased the fire barrier performance.[11] These properties have been shown to result from the formation of a complex charred residue. Similar behavior was observed for certain styrene–acrylonitrile (SAN)/TPP/NP combinations.[4] Although virgin NPs can efficiently increase the flame retardance of various polymer systems, the flame-retardance enhancement of ABS with blocked NPs has not yet been investigated.

The polar nature of these NP-based char formers is not desirable for ABS systems. In an effort to prepare a new class of NP-based char formers with higher solubility, we attempted to synthesize blocked NPs

(a) Novolac phenol (NP)

(b) Phenyl isocyanate (PI)

(c) 1,4-Diazabicyclo[2,2,2]octane (DABCO)
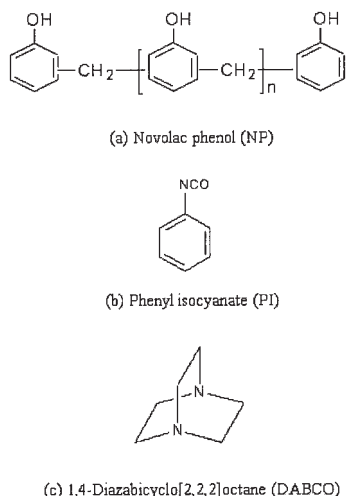
Scheme 1   Chemical structures of the NP, PI, and DABCO used in this study.

with phenyl isocyanate (PI). NPs with hydroxyl groups can react with PI via a simple urethane-forming reaction to form novolac phenol–phenyl isocyanate adducts (NP–PIs). The blocked NPs are expected to be highly soluble and, consequently, can be introduced into a ABS system along with TPP.

This article describes the synthesis and characterization of a new series of NPs with PI blocking units. Two NP–PIs, NP450–PI, and NP800–PI, were prepared based on modifications of NPs of different molecular weights (MWs) reacted with phenyl isocyante. We also report the effects of the amount of NP–PI and TPP used in the ABS blend and the length of NP–PI segments on the limiting oxygen index (LOI) and the thermal properties of the systems.

EXPERIMENTAL

Materials

The two kinds of NP resins differing in MW used in this study were NP450 and NP800 from Kolon Co. (Korea; MW = 450) and Meiwa Co. (Japan; MW = 800), respectively. All NPs had the same hydrogen equivalent weight of 106 g/mol of —OH. PI from Aldrich was used as a blocking agent for the NPs. The chemical structures of NP, PI, and the 1,4-diazabicy-clo-2,2,2-octane (DABCO) reaction catalyst are presented in Scheme 1. All other reagents were purchased from commercial sources (Aldrich or Lancaster) and used without further purifications unless otherwise noted. Tetrahydrofuran (THF) was dried over CaH_2 and distilled. NPs were dried *in vacuo* before use. The products were coded, for example, NP450–PI. The NP part was coded by MW. ABS containing 18.0 wt % butadiene and 35.9 wt % acrylonitrile was manufactured by compounding *g*-ABS and bulk SAN copoly-

mer, both of which were provided by Cheil Industries (Korea).

Sample characterization

^{1}H-NMR (500-MHz) spectra were recorded on a Varian Unity Inova spectrometer in d_6-dimethyl sulfoxide (DMSO). The Fourier transform infrared (FTIR) spectra of the samples were recorded on a Unicam Mattson 500 FTIR spectrometer with a KBr plate technique. MWs of the blocked NPs were determined by gel permeation chromatography (GPC) with a Waters 515 LC instrument with THF as the solvent and polystyrene as the calibration standard. The thermal characterization of the blocked NPs was carried out by differential scanning calorimetry (DSC) at a heating rate of 10°C/min on a DSC TA 2910 instrument. Samples weighing 5–9 mg were quenched from room temperature (RT) to −10°C by liquid nitrogen and were run under a nitrogen atmosphere over a temperature range of 0–300°C. Indium (mp = 156.6°C) was used for temperature calibration. Thermogravimetric analyses (TGAs) were carried out in both nitrogen and air at a heating rate of 10°C/min with a TGA 2050 (TA instruments). The flow rates in both cases were maintained at 10 and 90 cc/min for the balance part and the furnace area, respectively. In each case, the sample weighed about 100 mg.

LOI test

LOI was measured with a Fire Testing Technology instrument on sheets (length = 120 mm, width = 60 mm, thickness = 3 mm) at a flow rate of 10.6 L/min according to a standard oxygen index test (ASTM D 2863/77).

Synthesis of blocked NPs: NP–PI adducts

The synthetic route to the NP–PIs of two MWs is shown in Scheme 2, and only a representative example
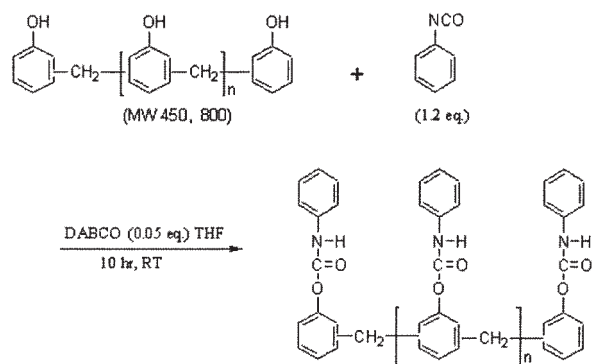
Scheme 2   Preparation of blocked NPs by the use of PI.

TABLE I
Solubility Tests of NP and NP–PI

	Solvent					
Sample[a]	Benzene	Methanol	Water	Methylene chloride	THF	Acetone
NP450	Insoluble	Soluble	Soluble in hot water	Insoluble	Soluble	Soluble
NP800	Insoluble	Soluble	Partly soluble in hot water	Insoluble	Soluble	Soluble
NP450–PI	Soluble	Soluble	Insoluble	Soluble	Soluble	Soluble
NP800–PI	Soluble	Soluble	Insoluble	Soluble	Soluble	Soluble

[a] The NPs are coded by molecular weight.

(i.e., NP450–PI) is given here. In a 250-mL, round-bottom flask were placed NP450 (30 g, 66 mmol), DABCO (0.37 g, 3.3 mmol), and THF (150 mL). To this solution, PI (9.43 g, 79.2 mmol) was added dropwise over 30 min at RT. The mixture was stirred at RT under N_2 for 10 h. The reaction mixture was then poured into ice-cold water. The organic layer was separated and washed with aqueous HCl and water, respectively. The solvent was evaporated, yielding a white solid (yield = 35 g, 92%).

^{1}H-NMR (500 MHz, d_6-DMSO, δ): 3.70 (m, —CH_2—), 6.90 (m, aromatic protons from NP moieties), 7.30 (m, aromatic protons from PI moieties).

Polymer sample preparation

The ABS polymer, TPP, and NP–PI adducts were mixed in a Haake plasticorder mixer at 230°C and 60 rpm for 7 min and then molded at 180°C in a Carver laboratory hot press for 10 min. The resulting sample plate was cut into test specimens of specific sizes required for the LOI tests.

RESULTS AND DISCUSSION

### Synthesis and characterization of NP–PI adducts

The highly polar phenolic group can be converted to a blocked phenol by reacting it with a suitable blocking agent. This phenol-blocker adduct is relatively inert at RT, but it can generate free phenol either by chemicals such as aqueous NaOH (i.e., saponification) or by simple heating (i.e., thermal deblocking), which then reacts with the available electrophile.[14] The phenols can be blocked through one of several methods.[15] In this study, the hydroxyl functionality of NPs was blocked to make a thermal deblocking reaction possible on heating over 200°C. PI was the blocking agent of choice because of its high evaporation properties (deblocking temperature > 200°C, vide infra). Thus, blocked NP450 and NP800 were prepared at yields greater than 90% by the reaction of NPs with PI in the presence of the DABCO catalyst via a simple urethane-forming reaction (Scheme 2).

Solubility tests

The virgin NPs were soluble in hot water and methanol but insoluble in benzene and methylene chloride (Table I). However, as expected, the resulting NP–PIs were insoluble in water but soluble in benzene and methylene chloride. Thus, the polar nature of NPs was significantly reduced because of the blocking. When the mixture of TPP and NP–PIs was incorporated as a flame retardant into ABS, the thin film of the ABS compounds was completely transparent, which indicated that the NP–PI adducts had good compatibility with ABS.

GPC study

PI adducts of the two NPs were prepared by the reaction of PI with the corresponding NPs (MW = 450 and 800; Scheme 2), which resulted in two blocked NPs of different MWs. Figure 1 shows the GPC results, from which it can be found that the MW of the blocked NP increased as the higher MW NP was introduced [number-average molecular weights (M_n's) = 1337 vs 1791]. In the GPC trace of NP450–PI, a clear
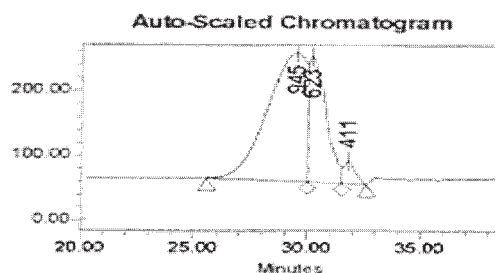
Sample	GPC results		
	Mn	Mw	Polydispersity
NP450-PI	1337	1782	1.33
NP800-PI	1791	2507	1.40

Figure 1 GPC trace of NP450–PI relative to polystyrene standards (M_w = weight-average molecular weight).

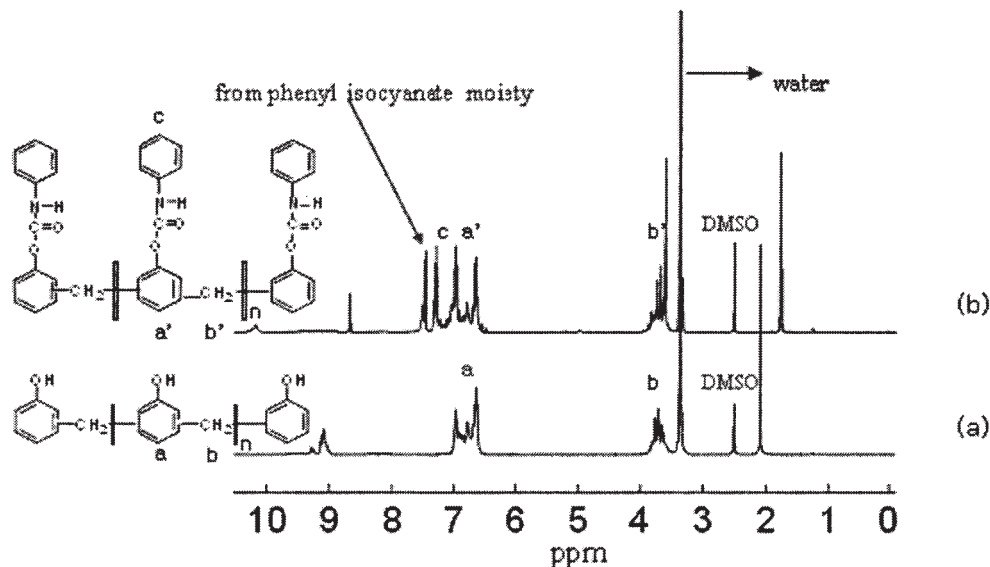**Figure 2** ^{1}H-NMR spectra of (a) NP450 and (b) NP450–PI in d_6-DMSO.

trimodal MW distribution was observed. This was due to a trimodal MW distribution of the starting NP450.

^{1}H-NMR study

Figure 2(a) shows the 500-MHz ^{1}H-NMR spectrum of the NP450, as it was, for comparison. Figure 2(b) shows the ^{1}H-NMR spectrum of the (NP450–PI) adduct. The main NP450 structure remained in the adduct spectrum; also, aromatic peaks at 7.3 ppm due to the PI moiety were detected. Because the NP450 as received showed a complicated ^{1}H-NMR spectrum, probably due to the presence of various constitutional isomeric structural units, the phenylene unit protons of the adduct backbone were not fully characterized.

FTIR study

IR spectra of the blocked NPs were recorded with an FTIR unit in KBr pellets, and all adducts showed no
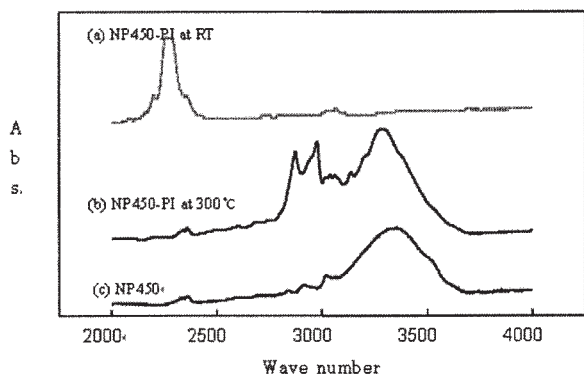

Figure 3 FTIR spectra of (a) NP450–PI at RT, (b) NP450–PI after it was heated at 300°C for 5 min in the neat state, and (c) NP450.

hydroxyl absorption band at about 3300 cm^{-1} [Fig. 3(a)], and this indicated the complete blocking of the phenolic groups with PI. The formation of NP from the PI-blocked NP was attempted via thermal deblocking. In the spectrum of PI-blocked NP, the hydroxyl stretching mode frequency, the 3300-cm^{-1} band, was absent, whereas in the heat-treated sample, the regeneration of the phenolic group was clearly observed [Fig. 3(b)]. The FTIR studies clearly demonstrated the formation of NP from the PI-blocked NP after it was heated at a temperature of about 300°C for 5 min in the neat state.

DSC study

The thermal properties of NP450 and NP450–PI were studied by DSC. Their representative DSC thermograms are shown in Figure 4, and the phase-transition temperatures derived from DSC were based on the first heating scan at a rate of 10°C/min. The adduct of NP450 with PI resulted in an increase in the endothermic melting peak, as expected. No other transitions were observed in the curve of NP450–PI in a temperature range from RT to 300°C. This indicated that the
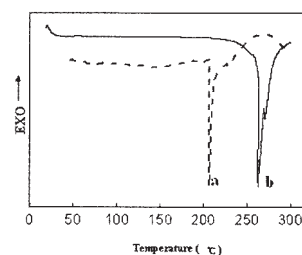

Figure 4 DSC thermograms scanned at a heating rate of 10°C/min under nitrogen: (a) NP450 and (b) NP450–PI.

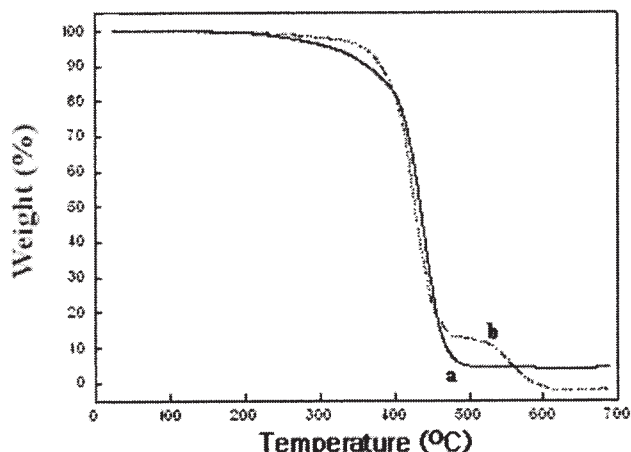**Figure 5** TGA thermograms for ABS at a scanning rate of 10°C/min in (a) nitrogen and (b) air.

Figure 7 TGA thermograms scanned at a heating rate of 10°C/min under nitrogen: ABS/TPP/NP450–PI at ratios of (a) 75/25/0, (b) 75/18.75/6.25, (c) 75/12.5/12.5, (d) 75/6.25/18.75, and (e) 75/0/25.

adduct was thermally stable at ambient temperatures because no exothermic event (due to the deblocking of NP450–PI) was discernible in the DSC heating trace.

Thermal degradation of the ABS/TPP/NP–PI compounds

Results under an inert atmosphere

Next, the mixture of TPP and NP450–PI was incorporated as a flame retardant into ABS, and the thermal degradation behavior of these compounds was investigated through TGA. These data were compared with those for pure ABS and pure TPP. Figures 5(a) and 6 show the TGA thermograms of pure ABS and pure TPP, respectively, under a flow of nitrogen. Pure ABS showed one degradation step in the TGA curve at about 380°C, with almost total weight loss. Pure TPP evaporated almost completely in one step at about 200°C. As shown in Table II (entries 1–5) and Figure 7,
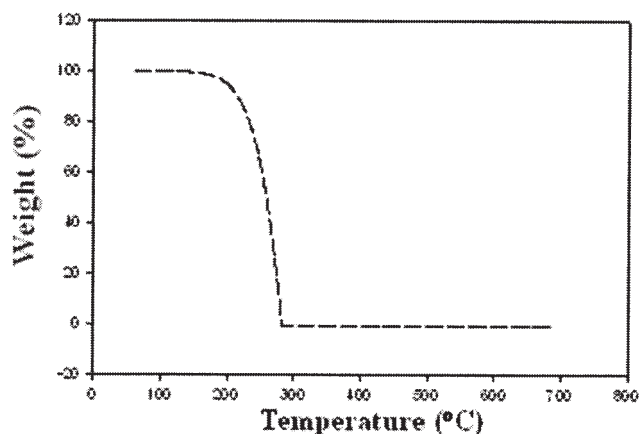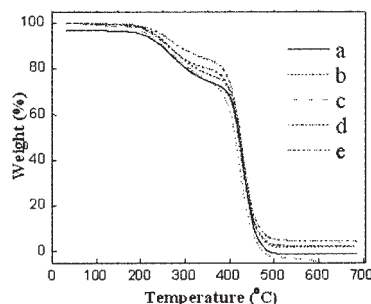

Figure 6 TGA thermogram for TPP at a scanning rate of 10°C/min in nitrogen.

all of the ABS compounds containing TPP and NP450–PI had very similar thermal degradation behaviors with a weight loss of 20% of the initial weight at about 280°C due to the volatilization of TPP. Another major weight loss occurred at about 400°C, which was caused by the degradation of ABS. With NP450–PI addition, the initial weight loss observed at 240°C (temperature for 10% mass loss) shifted to a higher temperature under nitrogen. A much enhanced amount of char was observed at 700°C for the compounds containing NP450–PI, whereas no char was observed for pure ABS in nitrogen.

Therefore, we concluded from the results that the thermal stability of ABS was greatly enhanced by the addition of NP450–PI as a co-flame-retardant. However, the factors affecting the increase of the thermal stability in ABS were not only the addition of NP450–PI but also the reduction of TPP content in the compounds. The increase in both initial weight loss temperature and charring became profound when the MW of NP–PI was larger (NP450–PI vs NP800–PI; Table II, entries 6–10, and Fig. 8). At this moment, we postulated that the increase in the char residue of the compound containing NP–PI resulted from the interaction of TPP with NP–PI at high temperatures. That is, the evaporation of TPP in the presence of NP–PI in the initial thermal degradation was delayed to some extent, and during further thermal degradation, more thermally stable char was formed through some reaction between TPP and NP–PI.

Results under air

Figure 5(b) shows the TGA curve of pure ABS and pure TPP under a flow of air. The thermogram of pure ABS showed two steps of weight loss. The behaviors of ABS in air and nitrogen were very similar, with one main step of degradation that occurred at about 460°C in air because of some action of oxygen. In this case, the second step was probably due to the effect of oxygen in causing a temporary carbonization, which

Entry	Sample (w/w)	Temperature for 10% mass loss (°C)		Nonvolatile residue at 700°C (wt %)		LOI (vol %)
		Nitrogen	Air	Nitrogen	Air	
1	ABS/TPP/NP450–PI (75/25/0)	240	235	1.77	0.00	19.7
2	ABS/TPP/NP450–PI (75/18.75/6.25)	250	248	4.16	0.34	33.5
3	ABS/TPP/NP450–PI (75/12.5/12.5)	255	260	0.10	0.57	29.3
4	ABS/TPP/NP450–PI (75/6.25/18.75)	260	255	2.93	1.09	27.7
5	ABS/TPP/NP450–PI (75/0/25)	280	275	4.27	0.00	21.0
6	ABS/TPP/NP800–PI (75/25/0)	240	235	1.77	0.00	19.7
7	ABS/TPP/NP800–PI (75/18.75/6.25)	265	262	2.92	0.87	32.0
8	ABS/TPP/NP800–PI (75/12.5/12.5)	290	275	5.10	0.91	41.3
9	ABS/TPP/NP800–PI (75/6.25/18.75)	320	305	6.61	0.51	36.3
10	ABS/TPP/NP800–PI (75/0/25)	319	306	5.70	0.28	21.0

later got oxidized. As for TPP, the thermogram in air was exactly the same as that described before.

All of the ABS compounds containing TPP and NP–PI also had the same behavior in the presence of air with a first step of weight loss of 20% at about 280°C due to the volatilization of TPP (Figs. 9 and 10). Second, there was a weight loss of 80% at about 430°C, due to the loss of ABS, as shown by the thermogram of pure ABS in Figure 5(b). There was a third step, which was not present in the thermograms under a flow of nitrogen, revealed by a step at about 500°C in the TGA. This again, corresponded to the second step in the thermogram of pure ABS. However, the levels of transitory residue formed from ABS/TPP/NP–PI system were higher than the amount of transitory residue obtained from pure ABS. All of the weight loss steps occurred at lower temperatures than those in the presence of nitrogen because of the degrading action of oxygen.

Evaluation of flammability of various compositions: LOI tests

To select the mixture composition with the highest flame retardance, a study was conducted, and 10 samples were prepared containing TPP/NP–PI at various concentrations. These samples were tested for LOI values. The LOI improved as the amount of total additive increased. However, guided by the foregoing study, one ABS composition (75%) with different amounts of total fire retardant was chosen for all of the NP–PI adducts, and they are shown in Table II. The samples containing both the TPP and the NP450–PI as flame retardants reached higher LOI values than the corresponding samples with the same total flame-retardant concentration but containing only one of the two additives (Table II, entries 1–5 and Fig. 11). This indicated the occurrence of synergism between TPP and NP450–PI. Furthermore, for the mixtures with the same total flame-retardant amount, the best sample
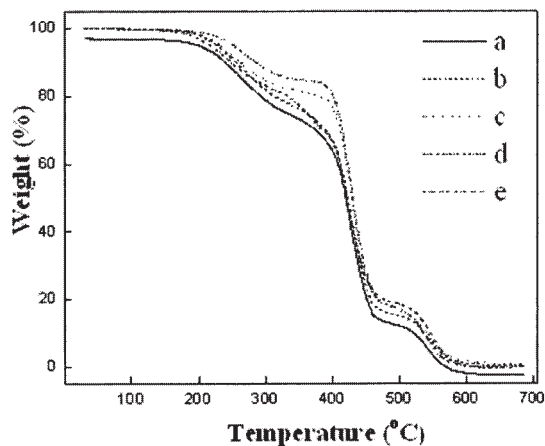

Figure 8 TGA thermograms scanned at a heating rate of 10°C/min under nitrogen: ABS/TPP/NP800–PI at ratios of (a) 75/25/0, (b) 75/18.75/6.25, (c) 75/12.5/12.5, (d) 75/6.25/18.75, and (e) 75/0/25.
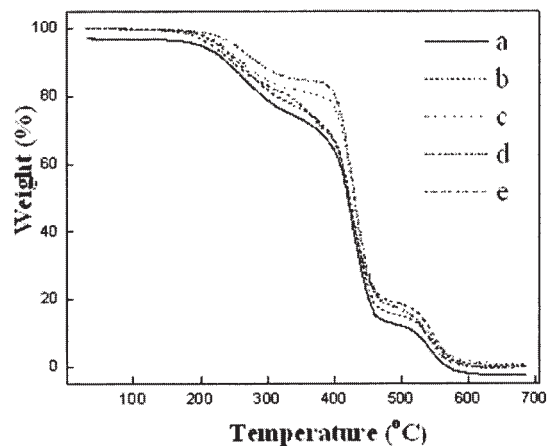
Figure 9 TGA thermograms scanned at a heating rate of 10°C/min under air: ABS/TPP/NP450–PI at ratios of (a) 75/25/0, (b) 75/18.75/6.25, (c) 75/12.5/12.5, (d) 75/6.25/18.75, and (e) 75/0/25.
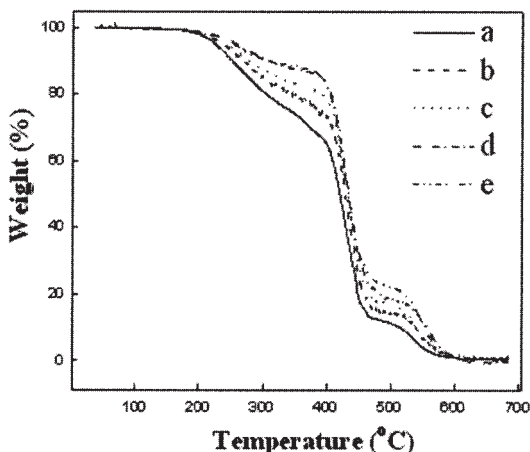
Figure 10 TGA thermograms scanned at a heating rate of 10°C/min under air: ABS/TPP/NP800–PI at ratios of (a) 75/25/0, (b) 75/18.75/6.25, (c) 75/12.5/12.5, (d) 75/6.25/18.75, and (e) 75/0/25.

was that containing a 3 : 1 ratio of TPP/NP450–PI (LOI = 33.5), as shown in Figure 11.

Among the different MWs of NP–PI adducts used, the higher MW NP800–PI was better as a flame retardant because the mixtures containing it reached higher LOIs (up to 41.3) than the others at the same concentration (Table II, entries 6–10, and Fig. 12). Because the higher the MW of NP–PI was, the higher the char-forming ability (due to the reduced volatility), we postulated that the increase in the LOI value of the compound containing higher MW NP–PI was resulted from the interaction of TPP with the less volatile NP.

From the LOI experiments, we concluded that our flame-retardant ABS systems required the presence of TPP, together with a char-forming material such as a blocked NP. Thus, this flame-retardant system had some activity in the surface of the material that was very close to that of intumescent additives (*vide infra*).

Mechanistic considerations for the synergistic effect of TPP and NP–PI adducts on the flame-retardance enhancement of ABS

Previously, studies have focused on TPP as a flame retardant to determine whether it acts primarily in the
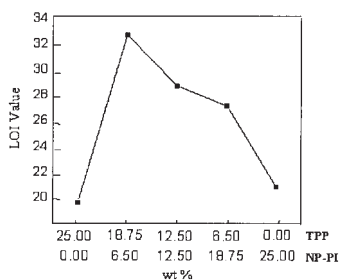

Figure 11 LOI values for various additive composition ratios (25 x/x) between TPP and the NP450–PI mixture.
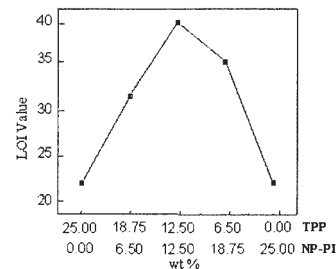

Figure 12 LOI values for various additive composition ratios (25 x/x) between TPP and the NP800–PI mixture.

gas phase or the condensed phase. Both gas-phase and condensed-phase mechanisms have been shown to occur.[16–18] Gas-phase effects are due to flame inhibition by the volatilization of TPP and/or its degradation products.[17,18] Condensed-phase activity is due to interaction with other flame-retardant additives (i.e., char former) or with oxygen-containing polymers such as PC or PPO.[16,17] This interaction delays the evaporation of TPP, which, therefore, undergoes thermal degradation in the condensed phase. Consequently, increasing char formation can limit the production of combustible gases, decrease the exothermicity of the pyrolysis reaction, and inhibit the thermal conductivity of the burning sample. Therefore, through the condensed-phase mechanism, the flame retardance of resins is leveled up.

It was reported that pure TPP tends to evaporate completely, but in the presence of novolacs, part of it undergoes a reaction because it is retained in the sample at higher temperatures (e.g., SAN/TPP/novolac system[4]). In a previous study, TPP underwent interaction with a novolac epoxy at high temperatures.[10] We also reported that the increase in the LOI value of the ABS compounds containing a phosphorous flame retardant and NP resulted from the interaction of a phosphorous compound with NP in the condensed phase.[11]

As shown by the FTIR studies (*vide supra*), the PI-blocked NPs did not thermally decompose in the relatively low temperature region. However, at the region of temperatures higher than 200°C, the deblocking of blocked NPs was observed. This regenerated NPs could have delayed the evaporation TPP. In fact, as shown in Figures 7–10, the first step of weight loss corresponding to loss of TPP occurred at slightly higher temperatures than in the thermogram of pure TPP. Therefore, similarly to previous related studies,[4] the degrading TPP in the presence of blocked NPs at high temperatures produced OH-containing structures that were not stable at the surface temperature of the burning ABS polymer, and they condensed to pyrophosphoric esters. That is, on heating the blocked NP-containing ABS resins, blocked NP first decomposed to regenerate NP, which further prevented the

volatilization of TPP through some interaction between TPP and NP and, consequently, resulted in some char formation at higher temperatures.

As for the TPP/blocked NP system, synergism was proven between these two additives because the LOI values tended to increase much more with increasing concentration of the total of the two additives than with increasing concentration of one of the two in binary mixtures with ABS. Also, the volatilization of TPP occurred at higher temperatures, probably due to the interaction of these additives. Similarly to the previous related works,[4,10–12] it was likely that our flame-retardant system worked in both the gas-phase and the condensed-phase because TPP was active not only in the gas phase but also in the condensed phase.

CONCLUSIONS

Novel PI-blocked NP derivatives (NP–PIs) with good solubility were successfully synthesized in high yield by the reaction of NPs with PI. Their basic features were examined by ^{1}H-NMR, FTIR, and DSC. Their potential possibilities as char formers by a deblocking reaction were investigated via IR studies. The thermal and flame-retardant properties of blocked NPs in mixtures with TPP and ABS resins were evaluated. In LOI tests, the mixtures showed a synergistic effect between TPP and NP–PI. Those containing a higher MW NP–PI were more flame retardant. From a mechanistic point of view, we postulated that the evaporation of TPP in the initial thermal degradation was delayed to some extent, and during further thermal degradation, a more thermally stable char was formed through some reaction between TPP and regenerated NPs. Our re-

sults show that TPP/NP–PI mixture could be a very efficient synergistic flame retardant to ABS.

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