Available online at www.sciencedirect.com
SCIENCE DIRECT®

Polymer Degradation and Stability 91 (2006) 1513–1521

Polymer Degradation and Stability
www.elsevier.com/locate/polydegstab

Towards the development of thermally latent novolac-based char formers for ABS resins

Kangjun Seo, Jinhwan Kim, Jin-Young Bae*

Department of Polymer Science and Engineering, Polymer Technology Institute, Sungkyunkwan University, 300 Chunchun-dong, Jangan-gu, Suwon, Kyunggi-do 440-746, South Korea

Received 9 August 2005; received in revised form 29 September 2005; accepted 4 October 2005
Available online 13 December 2005

Abstract

Novel novolac-based char formers for ABS resins, [PN–PI], [PN–BPI], [CN–PI] and [CN–BPI], were prepared from phenol formaldehyde novolac (PN), cresol formaldehyde novolac (CN), phenyl isocyanate (PI), and 4-biphenyl isocyanate (BPI) via a simple urethane-forming reaction. The four compounds were used as thermally latent char formers for this study. Thus, a two component system employing novolac–isocyanate adduct as a char former, and tetra-2,6-dimethyl phenyl-resorcinol diphosphate (DMP-RDP) as a phosphorous-based flame retardant was blended with ABS, and the thermal degradation behaviour and flame retardancy were determined by thermogravimetric analysis (TGA) and LOI test. The mixtures show a synergistic effect between DMP-RDP and novolac–isocyanate adduct on the flame retardance enhancement of ABS. Those containing higher molar mass CN–BPI adduct are found to be most flame retardant, and a LOI value as high as 35 is obtained.

© 2005 Elsevier Ltd. All rights reserved.

Keywords: Novolac; ABS; Char former; Flame retardancy

1. Introduction

Several publications report that phenol-containing polymers undergo some skeletal rearrangement in the course of their thermal degradation [1–10]. For example, poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is a well-known char-forming polymer sometimes blended with other polymers (e.g. ABS) to reduce flammability [10]. Despite the dissimilarity in structure to novolac-type polymers (e.g. PN or CN), which are condensation products of phenols and formaldehyde, these two materials both pyrolyse to produce cresols and xylenols, all of which are hydrogen rich when compared with the PPO. This is because PPO undergoes a skeletal rearrangement during thermal degradation to form a novolac-type structure [10]. Thus, it is postulated that the generation of the novolac-type structures formed by pyrolising some polymers (e.g. PPO or blocked novolacs) can be a means of cross-linking (with phosphorous-based flame retardants) and a route to char formation.

Nylon, polyamide, is also a well-known char-forming polymer, and the mechanism of thermal decomposition of nylon-6 especially in the presence of melamine has been given in the literature [11]. According to their IR study of char residue and high boiling products of nylon-6 chain scission through CH_2–C(O) bonds is likely to take place in the presence of melamines to give isocyanate (and carbodiimide) functionalities during the thermal decomposition. The resulting isocyanate chain ends undergo dimerisation to form carbodiimide or trimerisation to form *N*-alkylisocyanurate. These secondary reactions increase the thermal stability of the solid residue and increase the yield of the char. Thus, it is postulated that the generation of the isocyanate-type structures formed by pyrolysing some polymers (e.g. nylon or blocked isocyanate) can be a route to stabilization and char formation.

In this laboratory, we have investigated the thermal stabilization of ABS in the presence of various organic [12–14] and

---

* Corresponding author. Tel.: +82 31 290 7287; fax: +82 31 292 8790.
E-mail address: b521@skku.edu (J.-Y. Bae).

0141-3910/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymdegradstab.2005.10.010

inorganic [15] additives to develop efficient flame retardants for ABS. Our recent research into the application of intumescent flame retardants to ABS has demonstrated that the introduction of intumescents based on phosphorous compounds and novolacs onto ABS resins significantly increases the fire barrier performance [14]. These properties have been shown to result from the formation of a complex charred residue.

It was of obvious interest to extend the ideas inspired by the mechanistic studies of thermal decomposition of PPO [10] and nylon [11] to novel char former syntheses for ABS resins (vide supra). Therefore, we designed novolac–isocyanate adducts with two different functional groups (Ph–OH and –NCO) protected by each other (i.e. isocyanate-blocked novolac or novolac-blocked isocyanate, Scheme 1). Like other blocked phenols (or blocked isocyanates), these adducts contain both an electrophilic site (C(O)–O bond) for hydrolysis and a site (C–O bond) activated for thermal deblocking. Thus, the novolac–isocyanate adducts offer several options for additional applications (Scheme 1). Hydrolysis (or saponification) reactions of such adducts in the presence of water are expected to occur resulting in carbamic acid and novolac formation. However, the adducts can be treated by simple heating (i.e. thermal deblocking) to afford deblocked novolac and isocyanate. And these regenerated novolac and isocyanate are expected to enhance the char formation at high temperatures. Thus, the novolac–isocyanate adducts can act as thermally latent char formers in appropriate conditions. Scheme 1 presents this synthetic strategy concerning the scope of the synthesis of novolac–isocyanate adducts from novolac and isocyanate. Novolac with hydroxyl groups can react with isocyanate via a simple urethane-forming reaction to form the adducts. The blocked novolacs are expected to be highly soluble, and can consequently be introduced into an ABS system along with phosphorous flame retardant.

This article describes the synthesis and characterization of a new series of phenol (or cresol)-type novolacs with phenyl (or biphenyl) isocyanate blocking units. Four novel char formers, [PN–PI], [PN–BPI], [CN–PI] and [CN–BPI], were prepared based on modifications of novolacs with different isocyanates. We also report the effects of the amount of novolac–isocyanate adduct and DMP-RDP used in the ABS blend and the kind of adducts on LOI and the thermal properties of the systems.

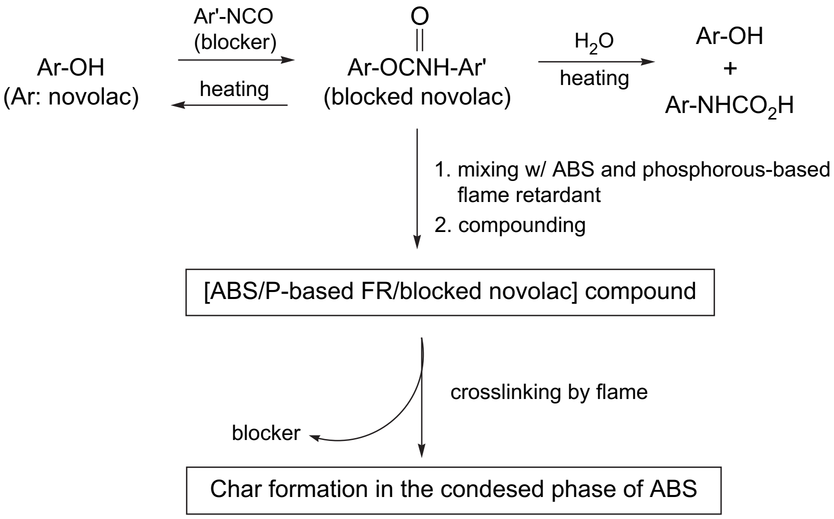
2. Experimental

2.1. Materials

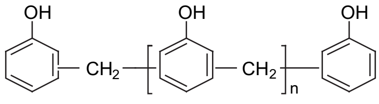
Two kinds of novolac resins differing in structures used in this study were PN and CN from the Kolon Co., Korea (MW = 800) and the Meiwa Co., Japan (MW = 800), respectively. All novolacs have the same hydrogen equivalent weights (HEW) of 106 g/OH mol. Phenyl- and 4-biphenyl isocyanates from Aldrich were used as blocking agents for PN and CN. One oligomeric aryl phosphate, tetra-2,6-dimethyl phenyl-resorcinol diphosphate (DMP-RDP), was supplied from the Daihachi Co., Japan. The chemical structures of PN, CN, phenyl isocyanate, 4-biphenyl isocyanate, the 1,4-diazabicyclo[2,2,2]octane (DABCO) reaction catalyst, and DMP-RDP are presented in Scheme 2. All other reagents were purchased from commercial sources (Aldrich or Lancaster) and used without further purification unless otherwise noted. Tetrahydrofuran (THF) was dried over CaH_2 and distilled. Novolacs were dried in vacuum before use. The products are coded for example CN–BPI. The code CN and BPI represent cresol novolac and 4-biphenyl isocyanate. 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.

2.2. Sample characterization

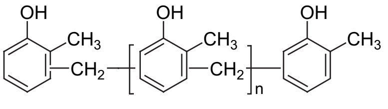
^{1}H NMR (500 MHz) spectra were recorded on a Varian Unity Inova Spectrometer in d_6-DMSO. The FT-IR spectra



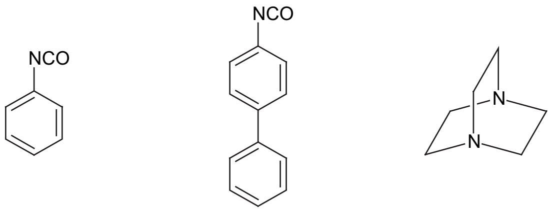
Scheme 1. Preparation of thermally latent char formers based on blocked novolacs for ABS resins.



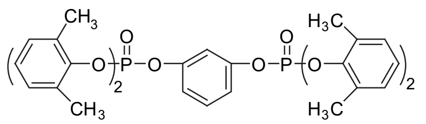
(a) Novolac phenol



(b) Cresol novolac



(c) Phenyl isocyanate (d) 4-Biphenyl isocyanate (e) 1,4-Diazabicyclo[2,2,2]octane



(f) Tetra-2,6-dimethyl phenyl resorcinol diphosphate

Scheme 2. The chemical structures of novolac phenol, cresol novolac, phenyl isocyanate, 4-biphenyl isocyanate, 1,4-diazabicyclo[2,2,2]octane, and tetra-2,6-dimethyl phenyl-resorcinol diphosphate employed in this study.

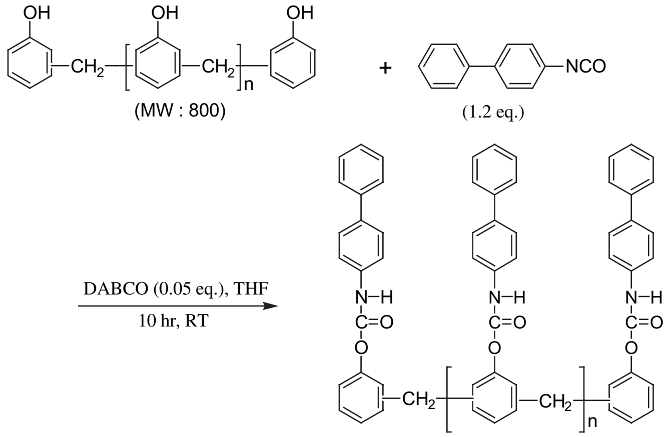
of the samples were recorded on a Unicam Mattson 500 FT-IR spectrometer using a KBr plate technique. Molecular weights of the novolac−isocyanate adducts were determined by gel permeation chromatography (GPC) with a Waters 515 LC instrument using THF as solvent and polystyrene as calibration standards. Thermogravimetric analyses (TGA) were carried out both in nitrogen and in air at a heating rate of 10 °C/min using a TGA 2050 (TA instruments). The flow rates in both cases were maintained at 10 and 90 cc/min for the balance part and for the furnace area, respectively. In each case, samples weighed ∼ 100 mg.

2.3. Limiting oxygen index test

The limiting oxygen index (LOI) was measured using 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 standard oxygen index test (ASTM D 2863/77).

2.4. Synthesis of blocked novolacs: novolac−isocyanate adducts

The synthetic routes to the novolac−isocyanate adducts of different structures are shown in Schemes 3 and 4, and only a representative example (i.e. PN−BPI) is given here. In a 250 mL round-bottom flask were placed PN (30 g, 37.5 mmol), DABCO (0.37 g, 3.3 mmol), and THF (150 mL). To this solution was added dropwise 4-biphenyl isocyanate (7.32 g, 37.5 mmol) 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 aq. HCl and water, respectively. The solvent was evaporated yielding a white solid: yield = 32 g (86%); ^{1}H NMR (500 MHz, d_6-DMSO), δ 3.70 (m, $-CH_2-$), δ 6.90 (m, aromatic protons from PN moieties), δ 7.30 (m, aromatic protons from 4-biphenyl isocyanate moieties); FT-IR, 2300 cm^{-1} (−NCO), 1215 (−CONH−).



Scheme 3. Preparation of 4-biphenyl isocyanate-blocked novolac phenol.

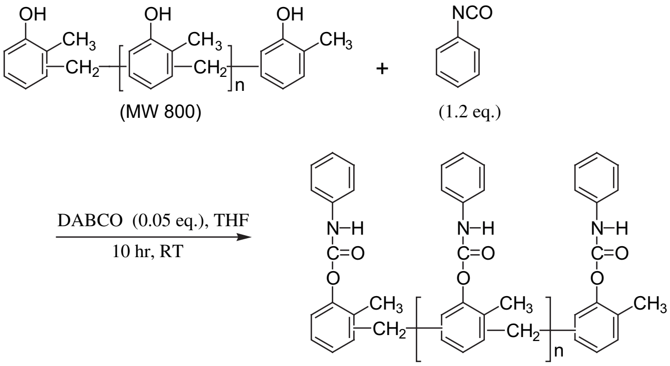
2.5. Polymer sample preparation

The ABS polymer, DMP-RDP, and novolac−isocyanate adducts were mixed in an HAAKE plasticorder mixer at 230 °C and 60 rpm for 7 min, followed by moulding 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 LOI tests.

3. Results and discussion

3.1. Synthesis and characterization of novolac−isocyanate adducts

The highly polar phenolic group can be converted to a blocked phenol by reacting it with a suitable blocking agent.



Scheme 4. Preparation of phenyl isocyanate-blocked cresol novolac.

This phenol-blocker adduct is relatively inert at room temperature, but it can generate free phenol either by chemicals such as aq. NaOH (i.e. saponification) or by simple heating (i.e. thermal deblocking), which then reacts with the available electrophile [16]. The phenols can be blocked through one of the several methods [17]. In this study, hydroxyl functionalities of novolacs (PN and CN) were blocked to make a thermal deblocking reaction possible upon heating at high temperatures. Aromatic isocyanates (e.g. phenyl isocyanate and 4-biphenyl isocyanate) instead of aliphatic isocyanates were the blocking agent of choice because of its high evaporation property. Thus, blocked PN and CN were prepared in >80% yield by reacting the novolacs both with phenyl- and 4-biphenyl isocyanates in the presence of DABCO catalyst via a simple urethane-forming reaction (Schemes 3 and 4).

3.1.1. Solubility test

With regard to the use of the established char formers based on virgin novolacs, two major drawbacks are evident within the ABS areas. Firstly, they have relatively high solubilities in water. Secondly, they are not miscible with ABS at the molecular level. From a chemistry point of view, it is difficult to compound polar novolacs with non-polar polymers such as ABS because they are not miscible. Novolacs are expected to microphase-separate due to the high content of hydroxyl units in the backbone. Thus, a novolac derivative with good miscibility is desired.

The virgin PN and CN were soluble in hot water and methanol, but insoluble in benzene and methylene chloride (Table 1). However, as expected, the resulting four adducts (PN–PI, PN–BPI, CN–PI and CN–BPI) were insoluble in water, but soluble in benzene and methylene chloride. Thus, the polar-nature of novolacs is significantly reduced due to the blocking. When the mixture of DMP-RDP and novolac–isocyanate adducts was incorporated as flame retardant into ABS, the thin film of the ABS compounds was completely transparent, indicating that the novolac–isocyanate adducts have good compatibility with ABS.

3.1.2. GPC study

4-Biphenyl isocyanate adducts of novolacs showed slightly higher molecular weights than the phenyl isocyanate-blocked novolacs (Table 2). From the GPC trace of CN–BPI, a clear trimodal molecular weight distribution was observed. This is due to a trimodal molecular weight distribution of the starting CN. However, all adducts showed relatively narrow molecular weight distributions (PDI < 1.4).

Table 2
GPC results of various novolac–isocyanate adducts

Sample	GPC results		
	Mn	MW	Polydispersity
PN	810	1050	1.30
PN–PI	1300	1550	1.20
PN–BPI	1360	1760	1.29
CN	790	1030	1.31
CN–PI	1200	1620	1.34
CN–BPI	1390	1820	1.31

3.1.3. ^{1}H NMR study

Fig. 1(a) shows the 500 MHz ^{1}H NMR spectrum of the PN, as it is, for comparison. Fig. 1(b) shows the ^{1}H NMR spectrum of the CN–PI adduct. It can be noticed that the main PN structure remains in the adduct spectrum; also, aromatic peaks at 7.3 ppm due to phenyl isocyanate moiety can be detected. Since the PN as received shows 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. Fig. 2 shows the ^{1}H NMR spectra of CN and CN–BPI in d_6-DMSO.

3.1.4. FT-IR study

Ideally, the PN (or CN)-based char formers should be hydrophobic both at the ambient temperatures and the processing temperature (~200 °C) enough to be miscible with ABS, and at the burning conditions they should expose hydroxyl functionalities which can interact with phosphate flame retardants resulting in char formation. To date, no PN (or CN) derivatives having double roles at different temperatures have been synthesized and successfully applied to ABS.

In this study, we tried to show that by reacting PN (or CN) with phenyl (or 4-biphenyl) isocyanate, a novolac–isocyanate adduct, which has double roles at different temperatures, may be synthesized. On heating this it was postulated that the isocyanate is released which induces blocked PN into deblocked PN (i.e. char-forming species). To demonstrate this, we performed the FT-IR studies of PN–PI adduct at varying temperatures.

Table 1
Solubility tests of various novolac derivatives

Sample	Solvent					
	Benzene	Methanol	Water	Methylene chloride	Tetrahydrofuran	Acetone
PN	Insoluble	Soluble	Soluble in hot water	Insoluble	Soluble	Soluble
PN–PI	Soluble	Soluble	Insoluble	Soluble	Soluble	Soluble
PN–BPI	Soluble	Insoluble	Insoluble	Soluble	Soluble	Soluble
CN	Insoluble	Soluble	Partly soluble in hot water	Insoluble	Soluble	Soluble
CN–PI	Soluble	Soluble	Insoluble	Soluble	Soluble	Soluble
CN–BPI	Soluble	Insoluble	Insoluble	Soluble	Soluble	Soluble

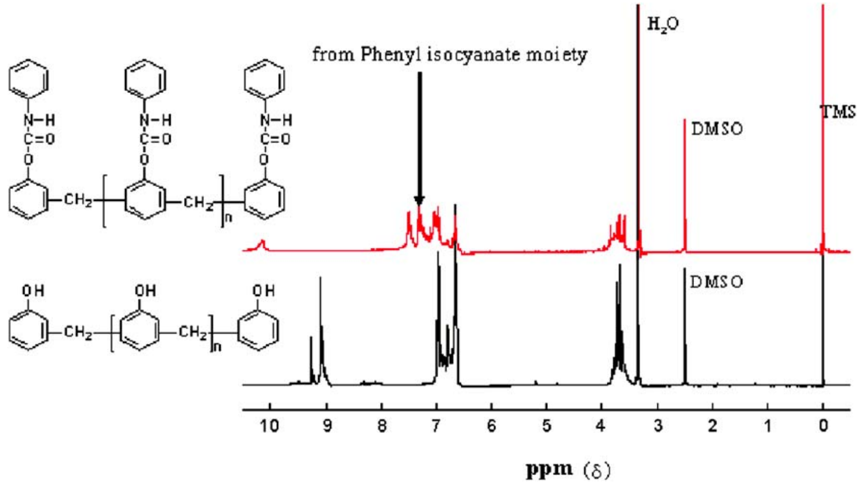


Fig. 1. ^{1}H NMR spectra of (a) PN and (b) PN–PI in d_6-DMSO.

IR spectra of PN–PI at different temperatures were recorded using a FT-IR unit in KBr pellets, and the adduct showed no isocyanate (–NCO) absorption band at ~2300 cm^{-1} from room temperature up to 100 °C (Fig. 3), and this indicated the complete blocking of isocyanate groups with phenolic groups and vice versa. A stretching vibration band at 1210–1220 cm^{-1} showed the presence of C=O combined with N–H in the spectrum (i.e. urethane bond). The release of phenyl isocyanate from the PN–PI adduct was attempted via thermal deblocking. In the spectrum of PN–PI at 100 °C the isocyanate stretching mode frequency, the 2300 cm^{-1} band, is absent, whereas in the heat-treated sample (110 °C, 5 min), the regeneration of the isocyanate group is clearly observed. The increase in the intensities of the isocyanate group with an increase in temperature is seen in Fig. 3. The FT-IR studies clearly demonstrate the deblocking of the phenyl isocyanate-blocked PN after heating over 110 °C for 5 min in the neat state.

3.1.5. Thermal stabilities of novolacs and novolac–isocyanate adducts: TGA study

In this experiment, thermal stabilities of four adducts, [PN–PI], [PN–BPI], [CN–PI] and [CN–BPI], and their thermal deblocking behaviours were investigated. First, thermal stabilities of PN and PN–PI were investigated. Fig. 4(a) shows the TGA thermograms of PN and PN–PI under nitrogen. Initial thermal degradation temperatures (Ti) are in order of PN (215 °C) > PN–PI (110 °C) and the residue weights at 700 °C are also in order of PN (23 wt%) > PN–PI (17 wt%). Under air atmosphere, initial thermal degradation temperatures are also in order of PN (215 °C) > PN–PI (110 °C) (i.e. the presence of oxygen does not affect the Ti of the adduct) although no char is observed for both cases at 700 °C (Fig. 5(a)). That is, both in nitrogen and in air the PN–PI adduct releases phenyl isocyanate by heating over 110 °C via thermal deblocking pathway. And this observation corresponds to the results obtained from the FT-IR study at varying temperatures (vide supra).

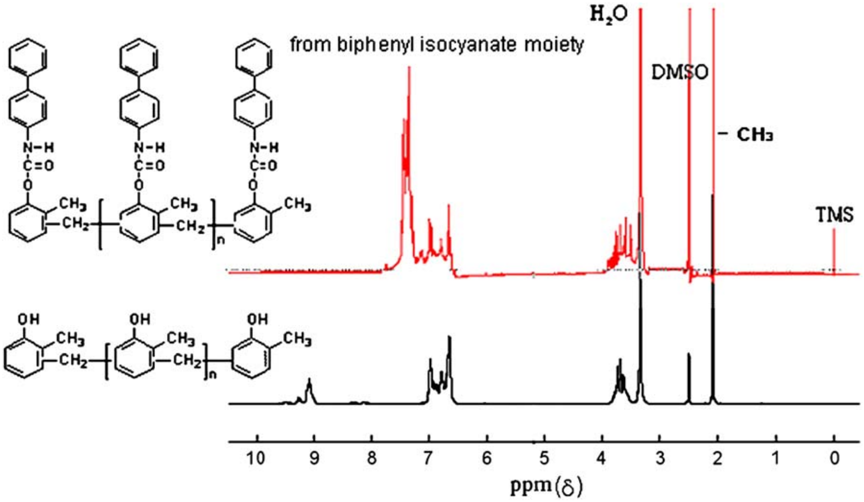


Fig. 2. ^{1}H NMR spectra of (a) CN and (b) CN–BPI in d_6-DMSO.

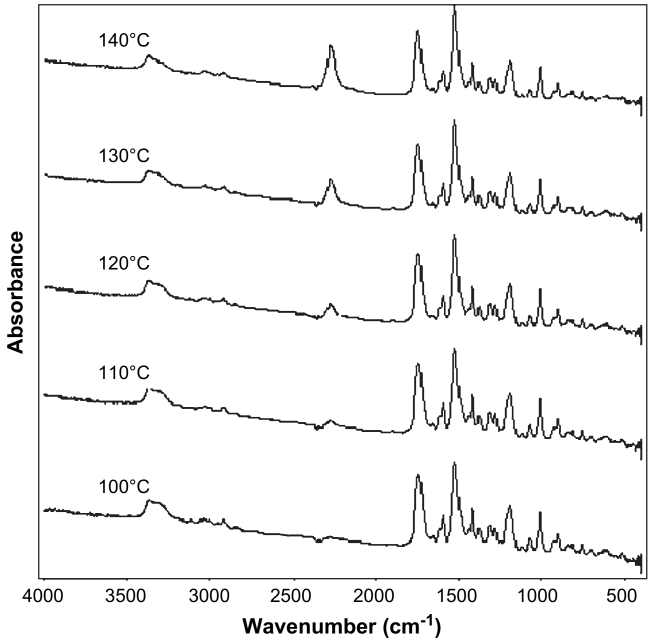


Fig. 3. FT-IR spectra of PN–PI at varying temperatures (heating time: 5 min).

The thermal properties of CN and CN–PI were also studied by TGA. Their representative TGA thermograms are shown in Figs. 4(b) and 5(b), and it was found that the adduct of CN with phenyl isocyanate results in slight decrease of Ti (=92 °C) compared with PN–PI. This indicates that the CN–PI adduct is thermally less stable than PN–PI (i.e. lower deblocking temperature), and both PN–PI and CN–PI are not desirable as char formers for flame retardant ABS formulations because of low deblocking temperatures. However, the adduct of PN (or CN) with the more rigid 4-biphenyl isocyanate blocker results in much enhanced increase of Ti (=220 °C) compared with the corresponding phenyl isocyanate adducts (Fig. 6). When comparing thermal stabilities of all four novolac derivatives under nitrogen atmosphere, initial thermal degradation temperatures (Ti) are in the order of PN–BPI (220 °C) > CN–BPI (215 °C) > PN–PI (110 °C) > CN–PI (92 °C).

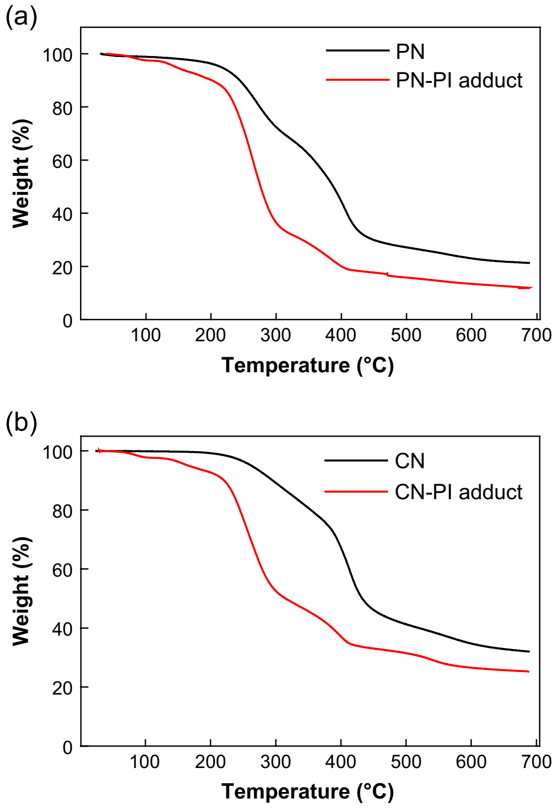


Fig. 4. TGA thermograms scanned at a heating rate of 10 °C/min under nitrogen condition: (a) PN and PN–PI and (b) CN and CN–PI.

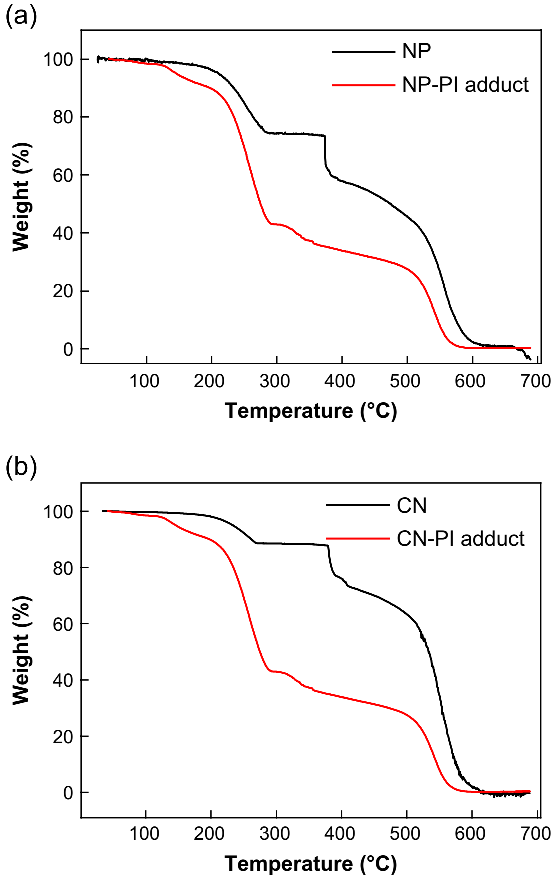


Fig. 5. TGA thermograms scanned at a heating rate of 10 °C/min under air condition: (a) PN and PN–PI and (b) CN and CN–PI.

In summary, the more rigid the molecular structure of isocyanate, the higher the deblocking temperature of the novolac–isocyanate adduct. Therefore, it can be concluded that the more thermally stable novolac-4-biphenyl isocyanate adducts (Ti > 200 °C) are expected to be inert at the ABS processing temperature (~200 °C) and more suitable as thermally latent char formers.

3.2. Thermal degradation of (ABS/DMP-RDP/novolac–isocyanate) compounds

3.2.1. Results under inert atmosphere

Next, the mixture of DMP-RDP and novolac-4-biphenyl isocyanate adduct (i.e. PN–BPI or CN–BPI) was incorporated

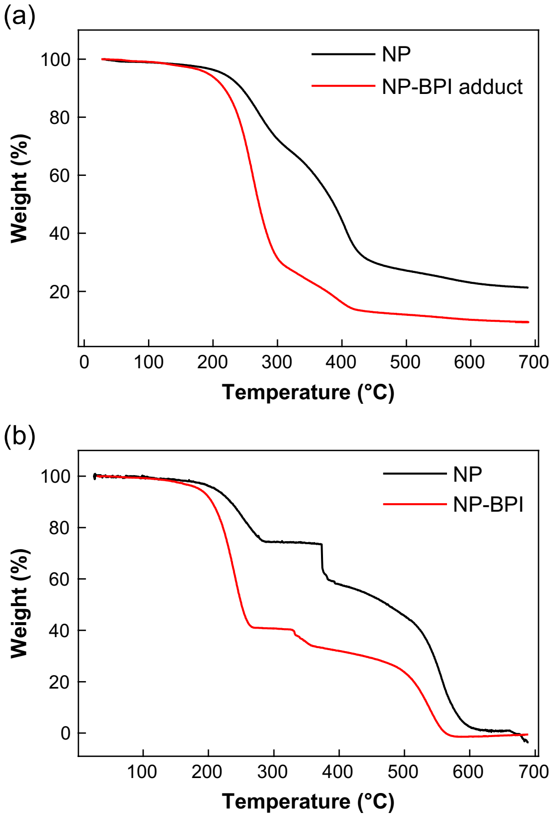


Fig. 6. TGA thermograms for PN and PN–BPI at a scan rate of 10 °C/min: (a) in nitrogen and (b) in air.

as flame retardant into ABS and the thermal degradation behaviour of these compounds was investigated through TGA analysis (Table 3). These data were compared with that of pure ABS, pure DMP-RDP, and (ABS/DMP-RDP/virgin novolac) compound. Pure ABS shows one degradation step in the TGA curve at ∼380 °C, with almost total weight loss under a flow of nitrogen (Fig. 7(a), [15]). Pure DMP-RDP evaporates almost completely in one step at ∼300 °C (Fig. 7(b), [14]). When the mixture of DMP-RDP and virgin novolac was incorporated into ABS, the initial weight loss of DMP-RDP observed at ∼300 °C was shifted to higher temperature (up to ∼400 °C) (Fig. 7(c), [14]). It can be seen in Table 3 and Fig. 8 that all the ABS compounds containing DMP-RDP and CN–BPI (or PN–BPI) have very similar thermal degradation behaviour with a weight loss of 10–20% of the initial weight at about 300 °C, due to deblocking and volatilisation of 4-biphenyl isocyanate together with the evaporation of DMP-RDP. Another major weight loss occurs at ∼400 °C, caused by degradation of ABS. With PN–BPI addition, the initial weight loss observed at 265 °C (temperature for 10% mass loss, entry 6) is shifted to higher temperature (up to 364 °C) under nitrogen (Fig. 8). And, much enhanced amount of char is observed at 700 °C for the compounds containing PN–BPI (up to 7.1 wt% of char yield) while no char is observed for pure ABS in nitrogen [15].

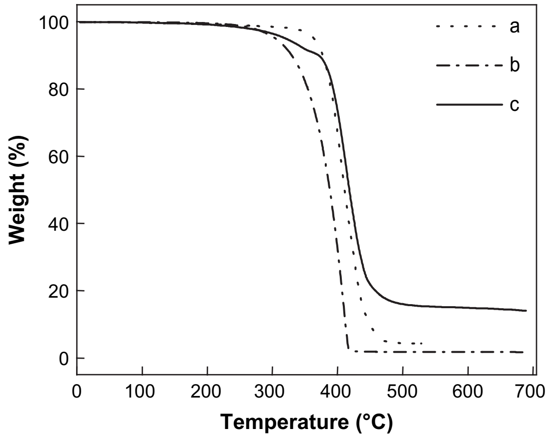


Fig. 7. TGA thermograms scanned at a heating rate of 10 °C/min under nitrogen condition: (a) ABS, (b) DMP-RDP, and (c) ABS/DMP-RDP/PN (75/12.5/12.5).

Therefore, it is concluded from results that the thermal stability of ABS is greatly enhanced by adding not only virgin novolac but also CN–BPI (or PN–BPI) as a co-flame retardant. It is worthy to note that the increase both in initial weight loss temperature and in charring becomes profound when the structure of novolac becomes more rigid (CN–BPI vs. PN–BPI, Table 3, entries 2 and 7). At this moment, it is postulated that the increase in char residue of the compound containing novolac–isocyanate adduct resulted from interaction of DMP-RDP with the deblocked adduct at high temperatures. That is, the evaporation of DMP-RDP in the presence of

Table 3
Temperatures for 10% mass loss, amount of non-volatile residue at 700 °C and LOI values for various (ABS/DMP-RDP/novolac–isocyanate) blends

Entry	Sample (wt ratio)	Temperature (°C) for 10% mass loss		Non-volatile residue at 700 °C (wt%)		LOI (vol.%)
		Nitrogen	Air	Nitrogen	Air	
1	ABS/DMP-RDP/CN–BPI (75/25/0)	265	290	1.13	0.05	21.0
2	ABS/DMP-RDP/CN–BPI (75/18.75/6.25)	350	334	3.20	3.20	28.5
3	ABS/DMP-RDP/CN–BPI (75/12.5/12.5)	338	325	5.91	3.21	31.5
4	ABS/DMP-RDP/CN–BPI (75/6.25/18.75)	311	322	3.80	1.01	29.4
5	ABS/DMP-RDP/CN–BPI (75/0/25)	280	289	2.10	0.05	21.2
6	ABS/DMP-RDP/PN–BPI (75/25/0)	265	290	1.13	0.05	21.0
7	ABS/DMP-RDP/PN–BPI (75/18.75/6.25)	364	345	4.22	5.24	30.8
8	ABS/DMP-RDP/PN–BPI (75/12.5/12.5)	350	339	7.10	4.35	35.1
9	ABS/DMP-RDP/PN–BPI (75/6.25/18.75)	320	335	4.93	2.75	30.2
10	ABS/DMP-RDP/PN–BPI (75/0/25)	299	295	3.27	0.10	19.7

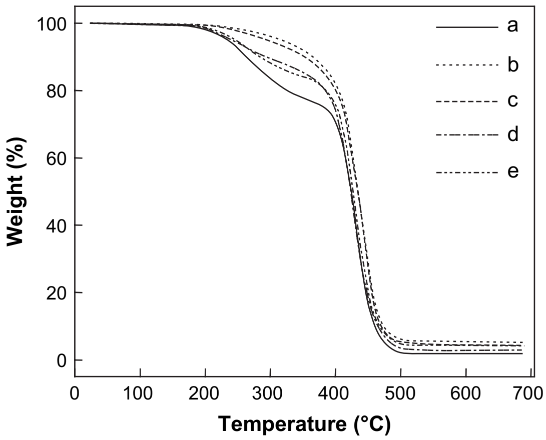


Fig. 8. TGA thermograms scanned at a heating rate of 10 °C/min under nitrogen condition: (a) ABS/DMP-RDP/PN–BPI (75/25/0), (b) ABS/DMP-RDP/PN–BPI (75/18.75/6.25), (c) ABS/DMP-RDP/PN–BPI (75/12.5/12.5), (d) ABS/DMP-RDP/PN–BPI (75/6.25/18.75), and (e) ABS/DMP-RDP/PN–BPI (75/0/25).

novolac–isocyanate adduct in the initial thermal degradation is delayed to some extent and, during further thermal degradation, more thermally stable char is formed through some reaction between DMP-RDP and the deblocked adduct.

3.2.2. Results under air

All the ABS compounds containing DMP-RDP and CN–BPI (or PN–BPI) adduct have the same behaviour also in the presence of air with a first step of weight loss of 20% at ~280 °C, due to volatilisation of 4-biphenyl isocyanate and DMP-RDP (Fig. 9). Secondly, there is a weight loss of 80% at ~430 °C, due to loss of ABS, as can be seen from the thermogram of pure ABS [15]. There is a third step, which was not present in the thermograms under flow of nitrogen, revealed by a step at ~500 °C in the TGA. This step is probably due to the effect of oxygen in causing a temporary carbonisation, which later gets oxidized [15]. However, the levels of transitory residue formed from ABS/DMP-RDP/novolac–isocyanate system are higher than the amount of transitory residue obtained from pure ABS. All the weight loss steps occur at lower temperature than in the presence of nitrogen, because of the degrading action of oxygen.

3.3. Evaluation of flammability of various ABS compounds: LOI tests

To select the mixture composition with the highest flame retardancy a study was conducted and various ABS compounds were prepared containing the DMP-RDP/novolac-4-biphenyl isocyanate adduct in various concentrations. These samples were tested for LOI values. The LOI improves as the amount of total additive increases. However, guided by the foregoing study, one ABS composition (75%) with different amounts of total fire retardant was chosen for all the samples, and they are shown in Table 3. It has been noticed that the samples containing both the DMP-RDP and the novolac-4-biphenyl isocyanate adduct as flame retardants reach higher LOI values than the corresponding samples with the same total flame retardant concentration, but containing only one of the two additives (Table 3 and Fig. 10). This indicates the occurrence of synergism between DMP-RDP and novolac-4-biphenyl isocyanate adduct. Furthermore, for the mixtures with the same total flame retardant amount, the best sample is that containing a DMP-RDP/PN–BPI ratio 1:1 (LOI = 35.1), as is shown in Fig. 10.

Among the different chemical structure of novolac-4-biphenyl isocyanate adducts used, the relatively rigid PN–BPI was better as a flame retardant, because the mixtures containing it reached higher LOI than the others (31.5 vs. 35.1), at the same concentration (Table 3, entries 3 and 8). Since 4-biphenyl isocyanate has relatively high boiling point, it is postulated that the increase in LOI value of the compound containing CN–BPI (or PN–BPI) has also resulted from the additional charring effect of high boiling 4-biphenyl isocyanate released by

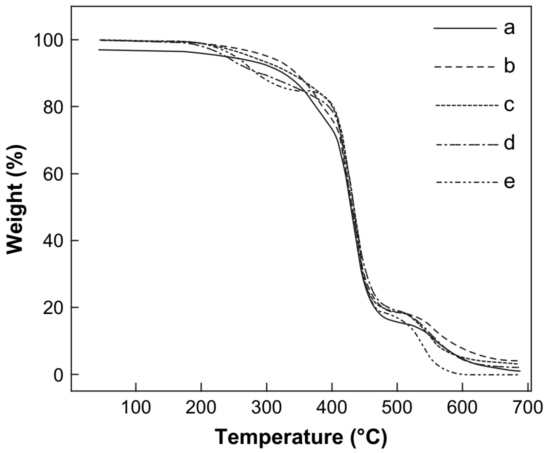


Fig. 9. TGA thermograms scanned at a heating rate of 10 °C/min under air condition: (a) ABS/DMP-RDP/PN–BPI (75/25/0), (b) ABS/DMP-RDP/PN–BPI (75/18.75/6.25), (c) ABS/DMP-RDP/PN–BPI (75/12.5/12.5), (d) ABS/DMP-RDP/PN–BPI (75/6.25/18.75), and (e) ABS/DMP-RDP/PN–BPI (75/0/25).

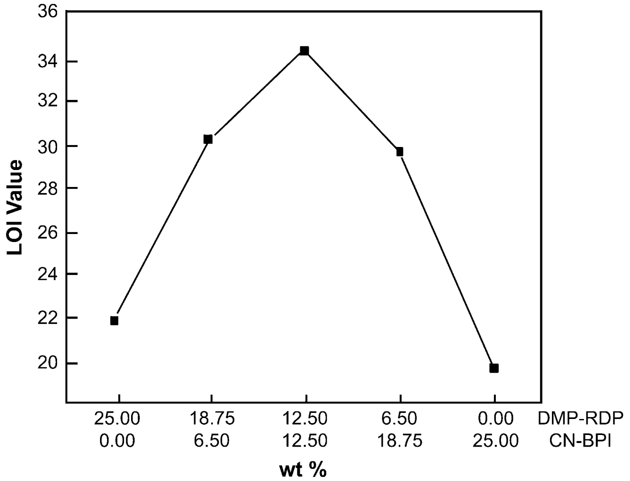


Fig. 10. LOI values for various additive composition ratio (25 – *x*/*x*) between DMP-RDP and PN–BPI mixture.

thermal deblocking, as well as the interaction of DMP-RDP with the deblocked novolac.

From LOI experiments, it can be concluded that our flame retardant ABS systems require the presence of DMP-RDP, together with a char-forming material like a novolac–isocyanate adduct. Thus, this flame retardant system has some activity in the surface of the material that is very close to that of intumescent additives (vide infra).

3.4. Mechanistic considerations for the synergistic effect of DMP-RDP and novolac–isocyanate adducts on the flame retardance enhancement of ABS

From our previous studies it was found that triphenyl phosphate undergoes interaction with the novolac epoxy at high temperatures [12]. We also reported that the increase in LOI value of the ABS compounds containing DMP-RDP and novolac phenol results from interaction of DMP-RDP with novolac phenol in the condensed-phase [14].

From TGA studies (vide supra) it is seen that the 4-biphenyl isocyanate-blocked novolacs do not thermally decompose in the relatively low temperature region. However, in the region of temperatures higher than 200 °C, the deblocking of the adducts was observed. This regenerated novolacs can delay the evaporation DMP-RDP. That is, on heating the blocked novolac-containing ABS resins blocked novolac first decomposes to regenerate novolac, which prevents further volatilisation of DMP-RDP through some interaction between DMP-RDP and novolac [14], and consequently results in some char formation at higher temperatures (Scheme 1).

As for the DMP-RDP/novolac–isocyanate adduct system, synergism has been proved between these two additives, because LOI values tend 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. It has also been noticed that the volatilisation of DMP-RDP occurs at higher temperatures probably due to the interaction of these additives. Similarly to the previous related works [12–14], it is likely that our flame retardant system works in the condensed-phase because high boiling DMP-RDP is retained in the condensed-phase.

4. Conclusions

In this paper, we show that by reacting PN (or CN) with phenyl (or 4-biphenyl) isocyanate, a novolac–isocyanate adduct is synthesized in high yield. On heating this adduct it is observed that the isocyanate is released via thermal deblocking, which induces blocked novolacs into deblocked novolacs (i.e. char-forming species). The use of isocyanate as blocking agent for novolacs is considered as means of preparing a thermally latent char former which has dual roles at different temperatures.

The thermal and flame retardant properties of novolac–isocyanate adducts in mixtures with DMP-RDP and ABS resins were evaluated. From LOI tests it is seen that the mixtures show a synergistic effect between DMP-RDP and novolac–isocyanate adduct. Those containing more rigid PN–BPI are found to be more flame retardant. From a mechanistic point of view, it is postulated that the evaporation of DMP-RDP in the initial thermal degradation is delayed to some extent and, during further thermal degradation, more thermally stable char is formed through some reaction between DMP-RDP and regenerated novolacs. Our results show that DMP-RDP/novolac–isocyanate adduct mixture can be a very efficient synergistic flame retardant to ABS.

Acknowledgements

This paper was supported by 63 Research Fund, Sungkyunkwan University, 2004.

References

[1] Jackson WM, Conley RT. J Appl Polym Sci 1964;8:2163.
[2] Conley RT. Thermal stability of polymers. New York: Dekker; 1970. p. 459.
[3] Nyden MR, Broun JE, Lomakin SM. Fire and polymers II. In: ACS symposium series, vol. 599. Washington, DC: American Chemical Society; 1995.
[4] Costa L, Rossi di Montelera L, Camino G, Weil ED, Pearce EM. J Appl Polym Sci 1998;68:1067.
[5] Fyfe CA, Mckinnon MS, Rudin A, Tchir WJ. Macromolecules 1983; 16:1216.
[6] Chetan MS, Ghadago RS, Rajan CR, Gunjikar VG, Ponrathnam J. J Appl Polym Sci 1993;50:685.
[7] Jackson WM, Conley RT. J Appl Polym Sci 1964;8:1263.
[8] Boscoletto AB, Checchin M, Tavan M, Cammino G, Costa L, Luda MP. J Appl Polym Sci 1994;53:121.
[9] Weil ED, Zhu W, Patel NG, Mukhopadhyay SM. Polym Degrad Stab 1996;54:125.
[10] Jachowicz J, Kryszewski M, Kowalski P. J Appl Polym Sci 1978; 22:2891.
[11] Camino G, Martinasso G, Costa L. Polym Degrad Stab 1990;27:285.
[12] Lee K, Kim J, Bae J, Yang J, Hong S, Kim HK. Polymer 2002;43:2249.
[13] Kim J, Lee K, Lee K, Bae J, Yang J, Hong S. Polym Degrad Stab 2003;79:201.
[14] Lee K, Yoon K, Kim J, Bae J, Yang J, Hong S. Polym Degrad Stab 2003; 81:173.
[15] Jang J, Kim JH, Bae JY. Polym Degrad Stab 2005;88(2):324.
[16] Doyle EN. The development and use of polyurethane products. New York: McGraw-Hill Book Co.; 1971. p. 125–44.
[17] Green TW, Wuts PGM. Protective groups in organic syntheses. New York: John Wiley & Sons, Inc.; 1991. p. 425.