

Preparation and Characterization of New Flame Retardant Polyurethane Composite and Nanocomposite

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ABSTRACT: In this work, a new flame retardant additive [2-phenyl-1,3,2 oxazaphospholidine 2-oxide (POPO)] containing phosphorus and nitrogen is synthesized using phenyl phosphonic dichloride, ethanol amine, and copper (II) chloride, as catalyst. POPO is characterized by ¹H-NMR, ¹³C-NMR, and ³¹P-NMR and used as additive in polyurethane composites. Moreover, two commercial flame retardant additives [tricalcium diphosphate and hexabromocyclododecane (HBCD)] as well as nanoclay are used to compare flame retardancy of the synthesized additive. Limited oxygen index (LOI) and time burning (flammability test) of polyurethane composites and nanocomposites are evaluated. The results of the LOI test demonstrate that POPO is an excellent flame retardant additive and can be used to improve flame retardancy of polyurethane composites. In addition, increasing the additive content leads to an improvement of the flame retardancy of the samples. The LOI results show, however, that POPO is a good flame retardant, but the high synthesis cost of this flame retardant is a major disadvantage. Thermogravimetric analysis results show that using POPO in polyurethane matrices leads to low thermal stability and high char residue. Moreover, the nanocomposite has better thermal stability than the other samples. Scanning electron microscope micrographs have been used to evaluate the char residue of the samples. These micrographs indicate that POPO is an intumescent flame retardant and HBCD follows a nonintumescent mechanism. Exfoliated/intercalated structures have been shown for nanocomposites by transmission electron microscope. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000-000, 2012

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INTRODUCTION

Polymeric materials are being used in ever more areas and under ever more demanding environmental conditions. Consequently, the demand for polymers is being increased. The fire hazards associated with polymeric materials. This problem is special concern among the government regulatory bodies, consumers and manufacturers. Because of that, noticeable attention has been paid in controlling the inherent flammability of flammable polymers.^{1,2} Hence, flame retardants are used to retard or suppress the combustion process. Polyurethane, like most of polymers, is flammable. Therefore, various flame retardants, consisting of halogen, phosphorus, sulfur, nitrogen, and so on, have been developed over the years. Flame retardants act in the vapor phase and/or the condensed phase through physical and chemical mechanisms. Considering flame-retardant mechanism, flame-retardant can be classified into intumescent and nonintumescent.

Many flame retarding agents are halogen based and harmful to the environment and also naturally toxic. Because these halogen compounds impart flame retardancy by vapor phases mechanism of free radical scavenging, toxic gases are being evolved in the process.³ The effective halogen-free flame retardants are intumescent flame retardants (IFRs).⁴ Recently, both academic and industrial communities are interested in halogen-free IFR for their multifold advantages including low toxic, low smoke, low corrosion, no corrosive gas, no dripping during a fire, and so on.⁵⁻⁷

By heating, intumescent material can form a charred layer on their surface. The charred layer acts as a physical barrier against both heat and mass transfer, giving good heat insulation, so that the underlying material is protected from a flame.⁵⁻⁷

Generally, the intumescent systems consist of three main substances: an acid source (e.g., phosphorus-containing substance),

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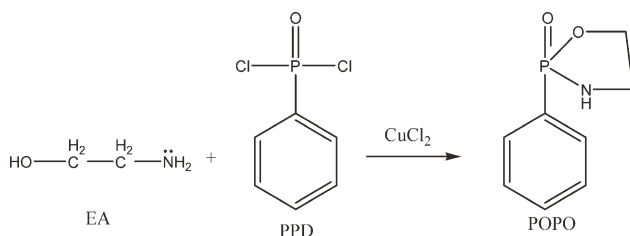


Figure 1. Scheme of synthesis of POPO.

a carbon source (e.g., polybasic alcohol), and a gas source (nitrogen-containing substance). Many various types of organophosphorus compounds have been synthesized for this purpose and some of them are commercially available.^{7,8} Phosphorus-based compounds act as flame retarding agents in a condensed phase by increasing char formation; hence, evolution of toxic gases during combustion is reduced.² Synergistic effect of phosphorus and nitrogen increases the flame retardants' limited oxygen index (LOI).^{8,9} Aromatic groups in the structures of flame retardant also play a very important role in improvement of the char yield.

Organic montmorillonite (OMMT) has been used for improving flame retardancy.^{10,11} Modified or organophilic clay can be dispersed in an appropriate polymer matrix by various methods. These methods can be classified into three categories: intercalation of prepolymer or polymer from solution, melt intercalation, and *in situ* intercalative polymerization.^{11,12}

In this article, we attempt to reduce the flammability of commercial polyurethane through introducing a new phosphorus–nitrogen-containing additive in matrix of the polymer. For this purpose, aromatic phosphorus–nitrogen-containing additive, 2-phenyl-1,3,2-oxazaphospholidine 2-oxide (POPO), is synthesized and used as an additive in commercial polyurethane. POPO consists of an acid source, carbon source, and a gas source. Therefore, it can be acted as a strong flame retardant additive. In addition, the properties of POPO are compared with the properties of two commercial flame retardant and nanoclay. For preparing nanocomposite, intercalation of prepolymer or polymer from solution is used. Finally, the flame retardant polyurethanes are prepared and the effects of amount and kind of the flame retardant additive on thermal and burning resistance properties of them are studied.

EXPERIMENTAL

Material

Hexabromocyclododecane (HBCD) was purchased from Great lakes, Michigan (USA). Tricalcium diphosphate (TCP), phenyl phosphonic dichloride (PPDC), ethanol amine (EA), copper (II) chloride, and dimethylformamide (DMF) were purchased from Merck, Hohenbrunn (Germany). All reagents were used without purification. A commercial grade of TPU (thermoplastic polyurethane), 5377A Desmopan, was purchased from the Bayer Materials, Germany. It is used as polymer. Cloisite 30B, from Southern Clay Products, Texas (USA), was used in this study as organically modified layered silicate. The Cloisite series of organosilicates are based on a natural montmorillonite (MMT) with a cation exchange capacity of 0.92 mequiv/g and

has a 0.9 mequiv/g organic quaternary ammonium ions N(CH₂CH₂OH)₂(CH₃)T, where T represents an alkyl group with approximately 65% C18H37, 30% C16H33, and 5% C14H29. Cloisite 30B, prior to use was dried in a vacuum oven at 70°C for 12 h.

Synthesis of POPO

Because of the reaction of nucleophile molecules with PPDC,¹ the EA was chosen in this article. A 250 mL reaction vessel was equipped with a temperature controller, magnetic stirrer, an N₂ inlet, and an aqueous sodium hydroxide trap (which was used for neutralizing hydrochloric acid) and charged with 1 mol of PPDC, 2 mol of EA (excess amount), and copper (II) chloride (1 wt %). The mixture was stirred in ice bath until hydrochloric acid evolution subsided. Thereafter, the mixture was gradually heated to 50°C and refluxed until no hydrochloric acid gas was emitted. Flame retardant was separated and washed with mixture of acetone and ethanol (75/25, v/v) for removing the excess amount of EA. Figure 1 shows the scheme of synthesis of POPO.

Preparing Flame Retardant Polyurethane Composites and Nanocomposites

Commercial polyurethane was added to DMF and stirred until complete dissolution (Mixture 1) was achieved. Flame retardant additive was added to Mixture 1. The mixture was stirred with high shear mixer for 30 min. To prepare nanocomposites, Cloisite 30B was added to DMF and dispersed by high shear mixer for 3 h. This mixture was added to Mixture 1 and stirred by high shear mixer for an hour at room temperature. To obtain films of flame retardant polyurethane composites and nanocomposites, every mixture was poured on Teflon plates. The Teflon plates were put in oven at 60°C until the entire solvent was evaporated. As DMF is toxic compound, the oven was placed under hood. Detail description of samples has been illustrated in Table I.

CHARACTERIZATION TECHNIQUES

Polymer films were characterized by using Du Pont TGA 951 thermogravimetric apparatus at air condition with a heating rate of 10°C/min under a nitrogen flow rate of 10 mL/min. The

Table I. Description of Samples used in this Study

Sample	Additive	PU amount (g)	Wt % additive by polymer
PU	-	10	-
PUPh2.5	POPO	10	2.5
PUT2.5	TCP	10	2.5
PUB2.5	HBCD	10	2.5
PUN2.5	Nanoclay	10	2.5
PUPh5	POPO	10	5
PUT5	TCP	10	5
PUB5	HBCD	10	5
PUN5	Nanoclay	10	5

Nomenclature of samples is based on: PU, polyurethane; ph, 2-phenyl-1,3,2-oxazaphospholidine 2-oxide; T, tricalcium diphosphate; B, hexabromocyclododecane; N, nanoclay; numbers indicate wt % of used flame retardant additive.

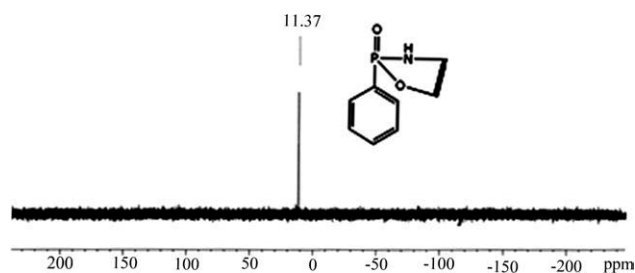


Figure 2. ^{31}P -NMR spectrum of POPO.

scanned temperature was in the range of ambient temperature to 600°C and reference material was calcium oxalate. The POPO was characterized by ^1H , ^{13}C -NMR, and ^{31}P -NMR spectroscopies. ^{13}C -NMR, ^{31}P -NMR, and ^1H -NMR spectra in D_2O were obtained on BRUKER DRX500 AVANCE. The NMR proton, carbon, and phosphorous frequency were 500, 125, and 202 MHz, respectively. A scanning electron microscope (SEM, Philips XL30, The Netherlands) equipped with a detector of secondary electrons was used to investigate char residue of the samples PUPh2.5 and PUB2.5 at electron beam energy of 15 kV.

Transmission electron microscopy (TEM, CEM902A, company of Zeiss) measurements were performed at a voltage of 50 kV. Samples provided in the form of thin films, and those were placed on a Cu grid.

To investigate burning behavior of the samples, LOI and ignitability tests were carried out. ASTM 2863-09 test method was used to measure LOI of the samples. LOI measures the mini-

mum oxygen concentration (in a flowing mixture of oxygen–nitrogen gas) required to support candle-like downward flame combustion.¹³ Burning time of 2 cm mark lines was measured according to Clause 6.2.5 of DIN 4102 standard (ignitability test).

RESULTS AND DISCUSSION

Characterization of POPO

The electrons around a nucleus circulate through a magnetic field and create a secondary-induced magnetic field. As stipulated by Lenz's law, this field opposes the applied field and atoms with higher electron density (i.e., higher induced fields) are called shielded, relative to those with lower electron density.

The chemical milieu of an atom can influence its electron density. Electron-donating groups lead to increased shielding, whereas electron-withdrawing substituents lead to deshielding of the nucleus. In addition to substituent that causes local induced fields, bonding electrons, for example, π bonds in benzene, can lead to shielding and deshielding effects. Trends in chemical shift are explained based on the degree of shielding or deshielding. When the applied magnetic field is static (normal case in FT spectrometers), and when the nucleus is more deshielded, the frequency is higher (higher chemical shift). Inversely when the nucleus is more shielded, the frequency is lower (lower chemical shift). The purified POPO was characterized by ^1H -NMR, ^{13}C -NMR, and ^{31}P -NMR. Figure 2 shows the ^{31}P -NMR spectrum of POPO. As can be seen from the figure, the shifting and splitting pattern of ^{31}P -NMR at 11.37 ppm correspond to

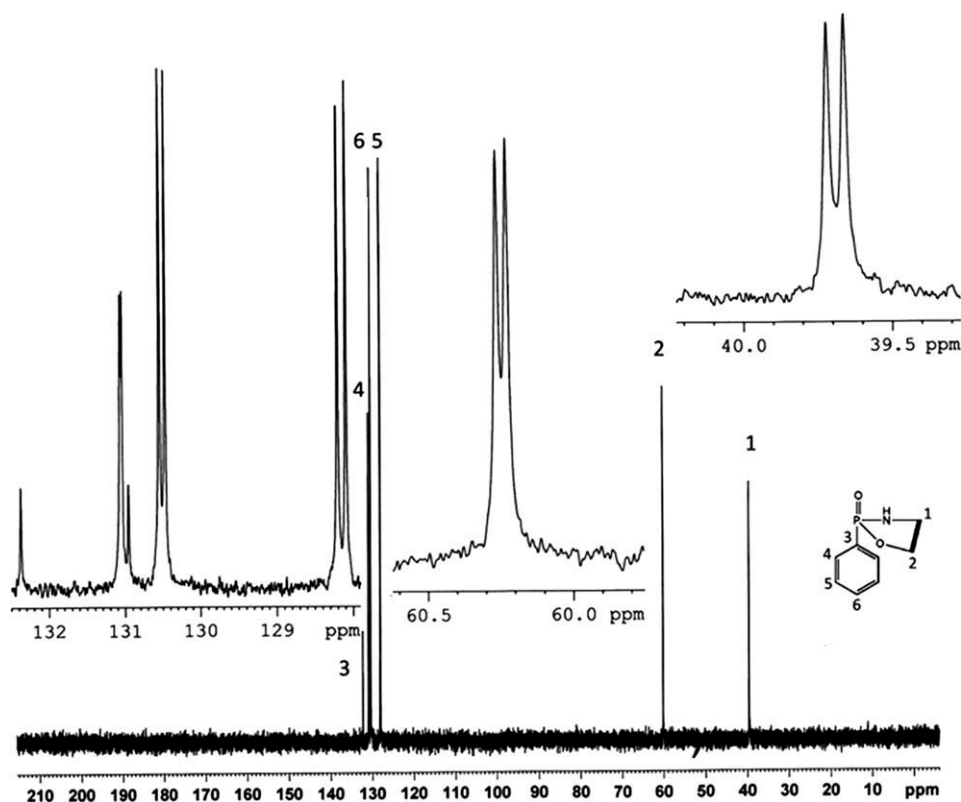


Figure 3. ^{13}C -NMR spectrum of POPO.

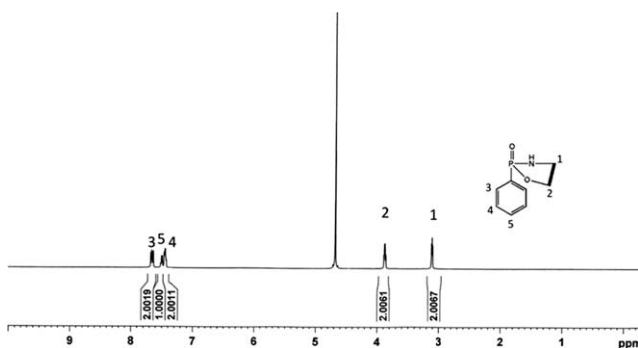


Figure 4. ^1H -NMR spectrum of POPO.

phosphorous atom. Figure 3 shows the ^{13}C -NMR spectrum of POPO. According to Figure 3, the shift and splitting pattern of ^{13}C -NMR at 132.3, 131, 130.5, 128.2, 60.2, and 32.7 ppm correspond to various carbons (C) of POPO that have different chemical milieu. All carbons in this figure were marked by numbers. We used these numbers to refer to each carbon, for example, C¹ and C² refer to carbons that were marked with 1 and 2, respectively. In the POPO, the oxazaphospholidine group is linked to the aromatic ring and causes the aromatic carbons to become nonequivalent and the signal to be split into a multiplet owing to their coupling. As oxazaphospholidine group is electronegative group, aromatic ring's peaks are shifted to higher chemical shift. Moreover, influence of oxazaphospholidine group on all ring's carbon is not equal. As mentioned before, electronegative groups are deshielding carbon and other NMR active atoms. Therefore, peaks appear in higher chemical shift. Deshielding amount of various carbons is different; consequently, related peaks appear in different chemical shift. Generally, distance and resonance stats affect the deshielding amount. Effects of oxazaphospholidine group on deshielding properties increase in the order carbon in meta position < carbon in para position < carbon in ortho position < carbon that is linked to oxazaphospholidine group. On the other hand, oxygen is more electronegative than nitrogen. Regarding above descriptions, the shift and splitting pattern of ^{13}C -NMR at 132.3, 131, 130.5, 128.2, 60.2, and 32.7 ppm correspond to C³, C⁴ (and other

carbon in ortho position), C⁶, C⁵ (and other carbon in meta position) C², and C¹, respectively. Figure 4 shows the ^1H -NMR spectrum of POPO. Regarding above descriptions, the shift and splitting pattern of ^1H -NMR at 7.65, 7.5, 7.46, 3.87, and 3.12 ppm, correspond to hydrogens that are linked to C³ (and other carbon in ortho position), C⁵, C⁴ (and other carbon in meta position), C², and C¹, respectively. These results confirm that the POPO was successfully synthesized.

Studies on Nanostructure of Nanocomposites

TEM technique provides a qualitative understanding of the internal structure in real space in a localized area.¹⁴ Nanoclay platelets have a higher electron density than the polyurethane, thus presents a higher resistance to electron transmission. This effect is seen in the TEM images as darker shapes.¹⁵ The TEM microphotograph of nanocomposites, PUN5 and PUN2.5, is shown in Figure 5, where exfoliated/intercalated structures were created in both samples. This may be because of hydrogen bonding, polar nature of polyurethane chains, and using Cloisite 30B for nanoclay. Large intragallery of Cloisite 30B caused to decrease the electrostatic interaction between adjacent Cloisite 30B layers, which provides an occasion for polymer chains to diffuse into the Cloisite 30B intragalleries during high shear mixing. The PUN2.5 shows better dispersion than PUN5. This phenomenon is because of the fact that the nanoclay particles have electrostatic interactions and increasing the amount of nanoclay in polymer matrix leads to increasing of interaction. Consequently, nanoparticles extremely agglomerate.

TGA Analysis

Saunders and Frisch¹⁶ summarized the four possible types of reactions that may take place in the thermal decomposition of urethanes. The tendency for a particular mechanism depends on the chemical nature of the groups, adjacent to the urethane linkage, and the environmental conditions. Polyurethane degradation usually starts with dissociation of the urethane bonds, carbon dioxide and isocyanate evaporation. Figure 6 shows thermogravimetric analysis (TGA) curves of PUPh2.5, PUT2.5, PUB2.5, and PUN2.5. Results illustrate that the degradation profiles of polyurethanes under investigation depend on the

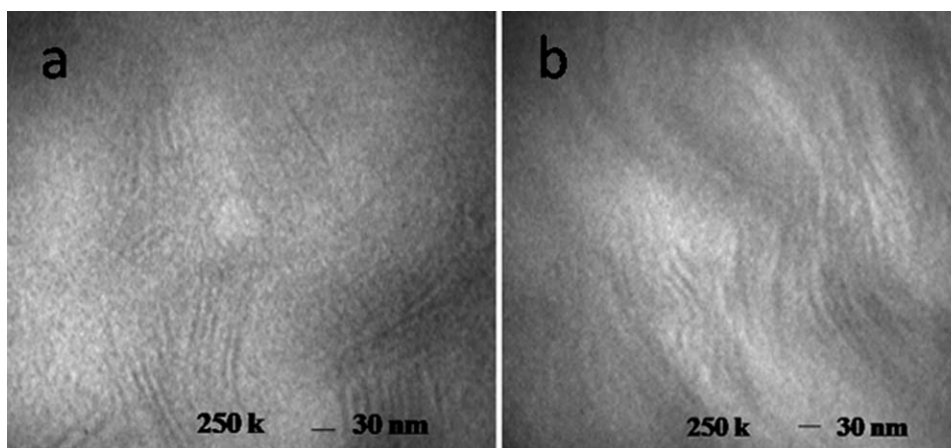


Figure 5. TEM microphotographs. (a) Sample PUN2.5. (b) Sample PUN5.

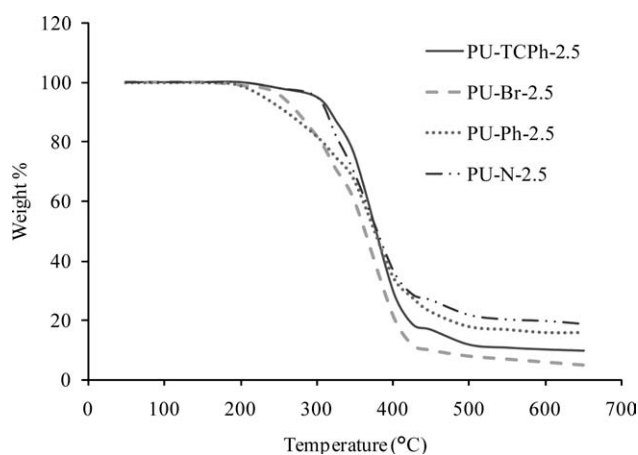


Figure 6. TGA thermograms of PUPh2.5, PUT2.5, PUB2.5, and PUN2.5.

kind of flame retardant and can be described with different values of the thermal parameters, which are collected in Table II.

It is obvious that the initiation degradation temperature (IDT) of PUPh2.5 containing POPO is much less than that of PUT2.5, PUB2.5, and PUN2.5. Table II shows IDT of PUPh2.5, PUB2.5, PUT2.5, and PUN2.5 at 208°C, 217°C, 249°C, and 243°C, respectively. The IDT for PUPh2.5 is 9°C less than PUB2.5, 41°C less than PUT2.5, and 35°C less than PUN2.5. In pure polyurethane, the specimen surface gradually degrades to volatile oligomers, monomer, and some molecules, whereas the presence of phosphorous flame retardant additive causes delay in degradation of polymer matrix. It is the result of this fact that the phosphorous flame retardant additive compounds have low thermal stability, are decomposed earlier, and protect underlying polyurethane matrix. From the combustion point of view, decomposition of PU and phosphorous flame retardant additive causes formation of a phosphorous-rich layer.¹⁷ This stable physical protective barrier on the surface of polyurethane may insulate the underlying polyurethane matrix from the heat source and slow down mass transfer between the gas and condensed phases. These phenomena lead to broadening of TGA curve for PUPh2.5.

HBCD such as many halogenated flame retardant acts in gaseous phase. TGA results from Barontini et al.'s study show that the HBr formed was about 58% of the HBCD initial weight, corresponding to 76% of the bromine initially present in the sample.¹⁸ In general, halogenated flame retardants have low char residue than phosphorous flame retardants. The data of char residue in air at 500°C of all samples are illustrated in

Table II. As shown in Table II, due to the presence of aromatic ring as well as phosphorus–nitrogen atoms in POPO, the char residue of PUPh2.5 is twice of the char residue for PUB2.5.

TGA result of the nanocomposite shows that the degradation rates of the nanocomposite is significantly slower than the other samples. Furthermore, results illustrate that the improvement of thermal stability of polyurethanes is due to the introduction of Cloisite 30B. This phenomenon relates to this fact that inorganic material can prevent the heat to expand quickly and limits further degradation.

The thermal stabilization effect of nanoclay is explained by the so-called Labyrinth barrier effect, which is generated by the highly anisotropic layered silicate platelets dispersed on the nanometer scale in the nanocomposite, which hinders the diffusion of the volatile degradation products (carbon dioxide, carbon monoxide, water molecules, etc.) from the bulk of the polymer matrix to the gaseous phase.¹⁹

Moreover, at higher temperature, this phenomenon is related to decomposition of polyurethane and OMMT, which in turn form a glassy coating and stable carbonaceous charred layers. This stable physical protective barrier on the surface of polyurethanes may insulate the underlying polyurethane matrix from the heat source and slow down heat and mass transfer between the gas and condensed phases.^{20,21} Furthermore, formation of this layer caused broadening of TGA curve for PUN2.5.

Flame Retardancy

LOI is a parameter for evaluating flame retardancy and flammability of polymeric materials in the same conditions. It denotes the lowest volume concentration of oxygen sustaining candle-like burning of materials in mixing gases of nitrogen and oxygen. The higher value of LOI illustrates that the flame-retardant treatment is more effective.^{6,22–24} The test was carried out according to ASTM 2863-09. LOI results of samples (PUPh5, PUT5, PUB5, PUN5, PUPh2.5, PUT2.5, PUB2.5, and PUN2.5) are shown in Table III.

Although the halogen-containing flame retardants act in the gas phase, the phosphorus-containing flame retardants mainly influence the reactions proceeding in the condensed phase. They are particularly effective on materials with high oxygen content, such as polyurethane. The flame retardant is converted to phosphoric acid by thermal decomposition, which in the condensed phase extracts water from the pyrolysing substrate, thereby causing it to char. A possibility of forming unsaturated compounds with subsequent charring is for the acid-catalyzed elimination of water from the polymer.²⁵

Table II. Results of the Thermo Gravimetric Analysis of Samples

Sample	IDT (°C)	T10% (°C)	T20% (°C)	T30% (°C)	T50% (°C)	Char residue (%)
PUPh2.5	208	260	304	341	378	18
PUT2.5	249	310	341	349	379	12
PUB2.5	217	266	303	322	372	8
PUN2.5	243	308	325	344	380	22

Txx% refers to temperature which where xx% of samples is lost.

Table III. Results of LOI Test

Samples	Environmental condition	Title of test	Results	Time of burning (s)	Visual data	
					Char content	Dripping
PUPh2.5	$T = 23.4$ $H = 34\%$	LOI	22.2	Self-extinguished	High	Low
PUT2.5	$T = 23.4$ $H = 34\%$	LOI	21.3	Self-extinguished	High	Low
PUB2.5	$T = 23.4$ $H = 34\%$	LOI	21.1	Self-extinguished	Low	High
PUN2.5	$T = 23.4$ $H = 34\%$	LOI	19.7	54	High	Low
PU	$T = 23.4$ $H = 34\%$	LOI	18.3	38	Low	High
PUPh5	$T = 19.1$ $H = 38\%$	LOI	23.8	Self-extinguished	High	Low
PUT5	$T = 19.1$ $H = 38\%$	LOI	22.5	Self-extinguished	High	Low
PUB5	$T = 19.1$ $H = 38\%$	LOI	22.5	Self-extinguished	Low	High
PUN5	$T = 19.1$ $H = 38\%$	LOI	20.6	73	High	low

H and T refer to % humidity and temperature of tests condition, respectively.

LOI for POPO is high, which can be related to the low thermal resistance of the synthesized additive. Generally, phosphorous flame retardants with lower thermal stability show higher flame retardancy properties. In flame, the phosphorus-containing groups of polyurethane are decomposed more rapidly than the polymer matrix, resulting in high yields of char residuals. This phenomenon produces a flame resistant effect toward the polymers.¹⁷

Nanoclay has the weakest effect on the flame retardancy properties. In general, the nanocomposites' flame retardant mechanism involves a high-performance carbonaceous-silicate char, which builds up on the surface during burning. On heating, the viscosity of the molten polymer/layered silicate nanocomposite decreases with increasing temperature and facilitates the migration of the clay nanolayers to the surface. Furthermore, nanoclay migration is enhanced by the formation of gas bubbles, initiated by the decomposition of both the quaternary ammonium organomodifiers and the polymer chains. Such gas bubbles may in fact be nucleated by the surface of the MMT. These gas bubbles could also help in the convection of the MMT sheets to the surface. Therefore, accumulation of the clay on the surface of the material acts as a protective barrier. This protective barrier layer insulates the underlying material and serves as a barrier to both mass and energy transport.^{26,27} Consequently, the combustion process of nanocomposite is retarded or suppressed. According to the authors,²⁶ the nanoclay must be nanodispersed to affect the flammability of the nanocomposites. However, the clay does not need to completely be delaminated. Intercalated nanocomposites show better flame retardancy properties rather

than exfoliated nanocomposites. This is due to tortuous phenomenon. When nanoclay is intercalated, the combustible degradation product should pass a maze path. So the rate of transfer of these products to gas phase is reduced. Consequently, intercalated nanocomposites show better flame retardancy. In this work, prepared nanocomposites are intercalated; consequently, they show good flame retardancy properties. As can be seen in Table III, LOI for PUN5 is higher than PUN2.5. These results are related to this fact that as the fraction of clay increases, the amount of char that can be formed increases, and the rate at which heat is released decreases. On the other hand, as can be seen from TEM micrographs, the PUN5 is mostly intercalated nanocomposite, whereas the PUN2.5 mainly is exfoliated/intercalated.

HBCDs were chosen as halogenated flame retardant additive because of some reasons mentioned as follows; the effectiveness of halogen compounds depends on the ease of liberation of the halogen. In general, aliphatic or alicyclic halogen compounds are more effective than aromatic halogen compounds, due to the lower carbon-halogen bond energies, and hence relatively easier halogen release.²⁸ From the energy point of view, the effectiveness of halogen-containing flame retardants increases in the order $F \ll Cl < Br < I$. Fluorine- and iodine-based flame retardants are not used in practice. Because of the fluorine strong bond to the carbon, it cannot become effective as a radical interceptor in the gaseous phase. In contrast, iodine is attached to the carbon so weakly that it is liberated even by negligible energy supply; as a result, the flame-retardant effect is already lost in the temperature range of the pyrolysis.

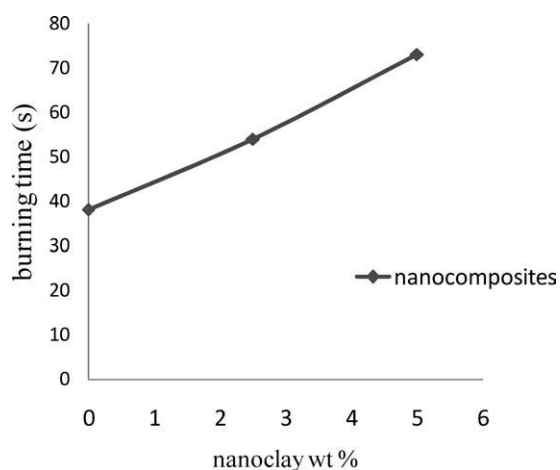


Figure 7. Burning time of pure polyurethane and nanocomposites.

Bromine flame retardants are more effective than chlorine flame retardants. Halogen-containing flame retardants act by interfering with the radical chain mechanism, which takes place in the gaseous phase. The very high-energy OH and H radicals, formed by chain branching, are removed by the reaction with HX and replaced with the lower-energy X radicals. Thus, the actual flame retardant effect is produced by HX.²⁴ Furthermore, HX acts as a catalyst. Moreover, bromine compound generates bromine-containing heavy gases, which suppresses the access of oxygen, which in turn suppress the combustion of polyurethanes.

Like other halogenated flame retardant, HBCD acts in gas phases and follows nonintumescent mechanism. HBDC has

many bromine atoms in its structure and during burning with mentioned ways reduces the rate of burning of the samples. As can be seen in Table III, LOI value of polyurethanes was improved with increase in flame retardant additives amount as well as nanoclay amount. Results of ignitability tests are shown in Table III and Figure 7. All samples show self-extinguished behavior except pristine polyurethane and nanocomposites.

SEM Microphotographs

Figure 8 shows SEM microphotographs of internal structure [Figure 8(a,b)] and surface [Figure 8(c,d)] of char residue of samples PUPh2.5 and PUB2.5 after LOI test. SEM microphotographs show more uniform surface of char residue of sample PUB2.5 in comparison with the sample PUPh2.5.

During combustion of PUPh2.5, a char-like foam was formed on the flame zone. As shown in SEM microphotographs ([Figure 8(a,b)]), foam-like structure is seen in sample PUPh2.5. Foam-like structure implies that the sample PUPh2.5 follows intumescent mechanism. Similar results, that phosphorous flame retardants are IFR, have been reported by some researchers.^{29–37}

However, additional study is necessary to prove the proposed mechanism for POPO. As can be seen in Figure 8(b), foam-like structure in sample PUB2.5 cannot be seen. This microphotograph shows that HBDC is non-IFR and acts in the gaseous phase. As shown in Figure 8(c,d), some holes are visible in samples PUPh2.5 (50–300 μm) and PUB2.5 (1–50 μm). These holes may be related to leaving of some volatile degradation products (carbon dioxide, carbon monoxide, water molecules, etc.) from the bulk to the gaseous phase. PUPh2.5 is IFR, so the amount of formed char and pressure in pyrolysis zone is high.

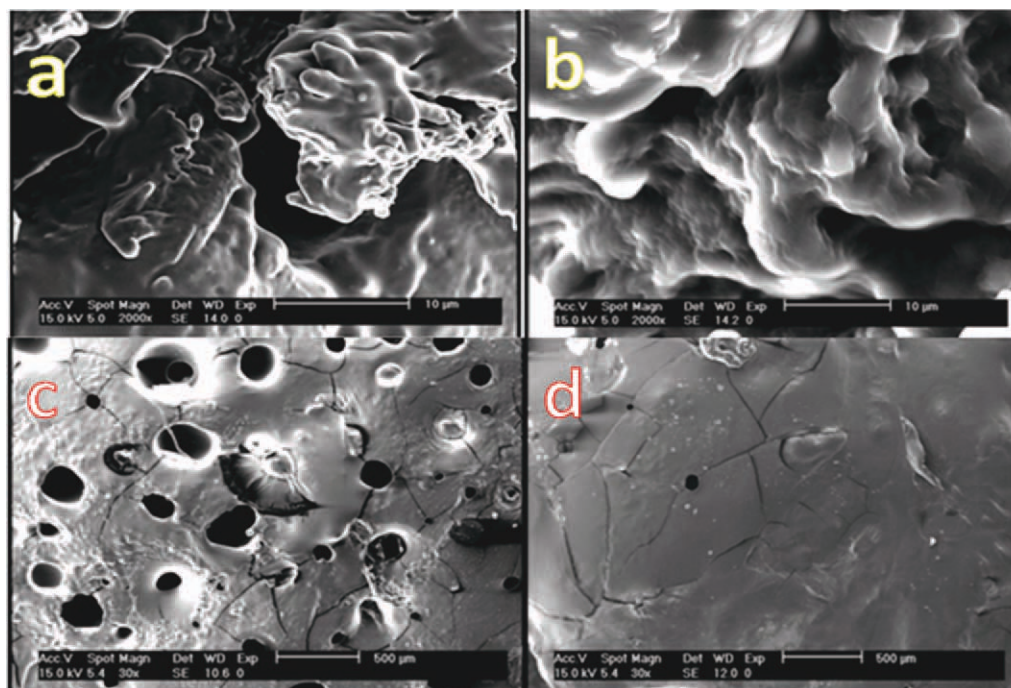


Figure 8. SEM microphotograph of (a) internal structure of sample PUPh2.5, (b) internal structure of sample PUB2.5, (c) surface of sample PUPh2.5, and (d) surface of sample PUB2.5. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Consequently, a larger bubble (which is formed by volatile degradation products) is produced and the size of holes of PUPh2.5 is greater than those of PUB2.5.

CONCLUSIONS

In this study, three flame retardant polyurethane composites and nanocomposites were synthesized. Results of LOI tests and ignitability test show that POPO, nanoclay, TCP, and HBCD increase the flame retardancy of polyurethane. Moreover, flame retardant property of polyurethane is improved with increasing the amount of flame retardant additives as well as the amount of nanoclay. Polyurethanes containing 2.5 and 5 wt % of POPO, TCP, and HBCD show self-extinguishing property. Nanoclay increases thermal stability and char residue of polyurethane. Consequently, flame retardant property of polyurethane is improved. The results of TGA test show that char residue content increases in the order nanoclay > POPO > TCP > HBCD. POPO has an important role in char residue of polyurethane due to aromatic ring in its structure. TEM micrographs show that PUN2.5 is exfoliated well in comparison to PUN5. The results of TGA test indicate that POPO follows intumescent mechanism, whereas HBCD follows nonintumescent mechanism as confirmed by the SEM micrographs.

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