Synthesis and Characterization Of Waterborne and Phosphorus-Containing Flame Retardant Polyurethane Coatings

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Phosphorus-containing flame retardant water-dispersed polyurethane coatings were produced by incorporating different amounts of a phosphorus compound onto the polyurethane main chain. The novel phosphorus containing compound (phosphorus phenyl dihydroxy) was synthesized in three steps using benzaldehyde, pentaerythritol, phenyl phosphonic dichloride, and acetic acid.

The addition of phosphorus phenyl dihydroxy to the main chain of polyurethane, in which NCO/OH ratio was kept constant at 1.5 and the amount of dimethylolpropionic acid (DMPA) at 3.5 wt%, increased the hardness and abrasion resistance, but only slightly decreased the gloss values of the polyurethane paints. All the samples showed superior impact resistance and flexibility. Moreover, increasing the phosphorus content increased the char yield, and the maximum fire retardancy was reached at 1.5% P content with a limiting oxygen index (LOI) value of 29.

INTRODUCTION

The demand for polyurethanes in the coatings industry is growing rapidly due to their excellent mechanical and elastic properties, high abrasion and chemical resistance, and good hardness values. The increasing public awareness of their potential as fire hazards have stimulated the development of fire retardant polyurethane coating systems.[1-6] As with other polymeric materials, the flame resistance of a polyurethane can be improved by incorporating either reactive[2,5,7-9]or nonreactive fire retardants.[10-12] The former approach is preferable since, in contrast to the nonreactive class of additives, they do not diffuse toward the polymeric surface and remain more effectively resistant to combustion for longer periods. They also tend to change the physical and mechanical properties of the materials to a lesser extent.[3,8,13]

Flame retardants can be classified as organic materials, like phosphorus and halogenated compounds, or inorganic materials like metal oxides, metal hydroxides, and metal borates.[14-19] Even though inorganic flame retardants offer low cost and a lack of toxic by-products, their effectiveness is relatively poor. Thus, high levels of additives are required to reach the desired flame retardant levels, which can cause detrimental effects to other properties of the polymer. Halogenated compounds are known to be effective flame retardants but a high temperature is necessary to initiate the radical-trapping activity. It is suggested by Ravey, et al.[20] that the temperature of a polyurethane flame might not be sufficiently high enough to initiate the radical-trapping based flame poising mechanism. Halogenated compounds also present hazards in the form of toxic gas emissions such as hydrogen halides. Conse-quently, there is a continuing search for flame retardant systems that do not present these disadvantages. Organic phosphorus-containing compounds are be-lieved to be very effective nontoxic flame retardant additives in lowering the pyrolytic decomposition and temperature of the polymer while raising the yield of incombustible char.[3,4,8,21] This is based on the formation of phosphorus acid, which promotes the formation of char to protect the polymer from the flame and heat.[22-24] Another proposed mechanism involves the reaction of

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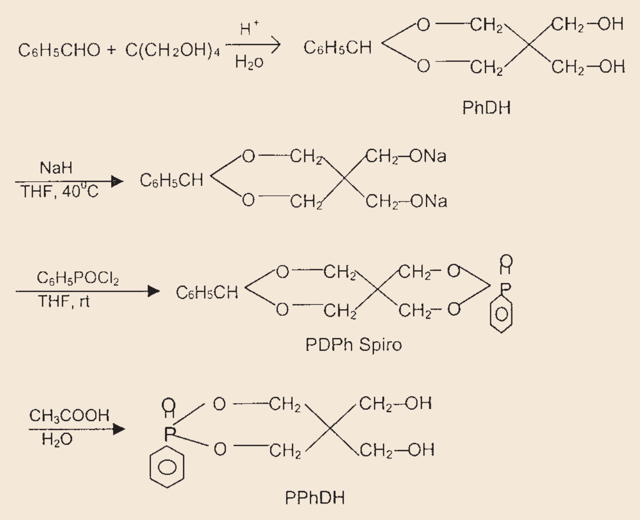

Figure 1—Synthesis scheme of PPhDH.

phosphoric acid with carbodiimide formed during the thermolysis of polyurethane; this reaction leads to crosslinking and char formation.[21] Phosphorus compounds generally lower the initial decomposition temperature of a polyurethane but tend to increase the char formation at a higher temperature. It has been generally accepted that phosphorus-containing coating systems are superior to halogen-containing ones in flame retarding performance, in light stability, and their effect on viscosity and thermal stability.[5,8,25] It is also suggested by Sivriev, et al.[26] that phosphorus-containing compounds, when appropriately chosen, could impart to the polymer other interesting properties, such as physiological activity, extraction capability, and improved adhesion.

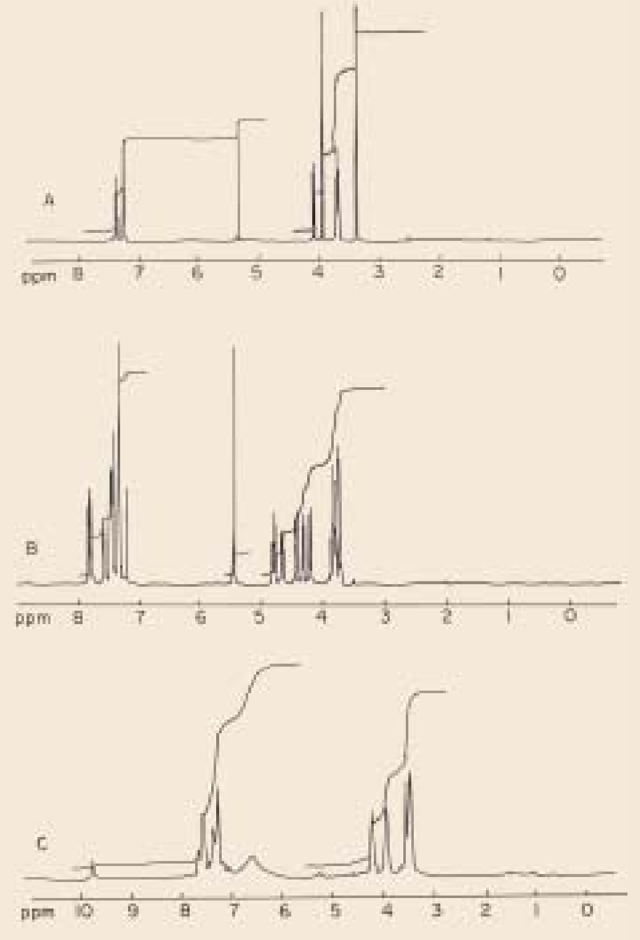

Figure 2—^{1}H-NMR spectrum of (A) PhDH, (B) PDPh Spiro, and (C) PPhDH.

There are many phosphorus-containing flame retardants for polyurethane systems[3-5,9,20,26-29] but few of them are industrially applicable. This is mainly because most of the presently available flame retardant polyurethane systems in the literature are achieved by phosphorus compounds of levels 5% or more to reach certain LOI values, but the raw materials necessary for the synthesis of these compounds are not readily available, are expensive, and are too difficult to produce. Therefore, in this investigation, we have attempted to synthesize a new reactive phosphorus compound to improve the flame retardancy of a water-dispersed polyurethane resin in the hope that we might achieve high LOI at low levels of phosphorus compound. Consequently, there would be less influence upon the excellent physical and mechanical properties of the polyurethane itself. It would also be more economical than those currently obtained by high levels of additives. An important advantage of the flame retardancy mechanism is that the presence of both phosphorus and nitrogen in the synthesized polymer leads to some synergism.[5,30-32] Considering this, we used melamine as a crosslinker to support the flame retardant activity of the phosphorus compound.

In this research, we prepared and characterized flame retardant aqueous polyurethanes with phosphorus on a polymer main chain. Novel reactive phosphorus compound was synthesized and then introduced onto the polyurethane main chain. By changing the feed ratio of polyester and phosphorus compound, polyurethanes with different phosphorus contents (1-2.5%) were prepared. In most of the coatings applications, where solvent resistance and improved mechanical properties are important, additional crosslinking can be achieved by using a polyisocyanate, or crosslinker which is reactive with an active hydrogen.[33-36] However, using a high level of polyisocyanate is restricted by the high viscosity which makes the process difficult and leads to poor coalescence of the dispersion.[33] To overcome these problems and to obtain polyurethanes with high mechanical properties, both polyisocyanate Desmodur N3300 (aliphatic polyisocyanate) and crosslinker (melamine) were used in this study. The physical, mechanical, as well as the thermal properties of all the samples were investigated. The flame retardant properties of the samples were determined by using the LOI test method.

EXPERIMENTAL

Materials

Pentaerythritol, benzaldehyde, isophorone diisocyanate (Merck Co.), sodium hydride (Acros Organics), dimethylol propionic acid (Aldrich A.G.), melamine (Sigma), and Desmodur N3300 (Bayer Co.) were used as received. Tetrahydrofuran (THF) was dried with sodium. Triethylamine (TEA), methyl ethyl ketoxime (MEKO), and dimethyl formamide (DMF) were dried over molecular sieves prior to use.

Synthesis of Monobenzalpentaerythritol (PhDH)

Pentaerythritol (1.32 moles) and water (1.3 L) were introduced into a three-liter four-necked flask. The flask was equipped with a graduated dropping funnel containing 147 g (1.38 moles) of benzaldehyde. The mixture was continuously stirred by a magnetic stirrer.

The mixture in the flask was heated until all the solid had dissolved and was then cooled to room temperature. Concentrated hydrochloric acid (6.6 ml) and benzaldehyde (30 ml) were added to the mixture. After the formation of monobenzalpentaerythritol had started, dropwise addition of the remaining benzaldehyde was begun. When the addition of benzaldehyde from the dropping funnel was completed, the mixture was stirred for an additional three hours. The precipitate was collected on and washed with ice-cold water which had been made slightly alkaline by the addition of sodium carbonate. The collected solid was heated to 100°C in water for 10 min and filtered at this temperature. The solid was washed with hot alkaline water. The aqueous filtrate was cooled in an ice bath and the crystals were collected and dried. The melting point of the resulting product was 132°C.

Synthesis of Phosphorus Diphenyl Spiro (PDPh Spiro)

Monobenzalpentaerythritol (0.05 moles) was dissolved in 150 mL dry THF in a 500-mL flask equipped with nitrogen inlet, dropping funnel, and magnetic stirrer. Then 5 g NaH (60%) was added and the reaction mixture was stirred for an hour at room temperature and another 40 min at 40°C. After the formation of sodium salt of monobenzalpentaerythritol, the system was cooled to room temperature and 10 g (0.05 moles) of phenyl phosphonic dichloride was added through the dropping funnel. The mixture was stirred for one hour at 40°C followed by overnight stirring at room temperature. Then, the mixture was poured into a one-liter flask, containing 150 mL of ice-cold water which had been made slightly alkaline with KOH. The mixture was extracted two times with ethyl acetate and the organic part of this extraction was dried with $MgSO_4$. Then the solvent was evaporated and the product with the melting point of 198°C was obtained.

Synthesis of Phosphorus Phenyl Di-Hydroxyl Spiro (PPhDH)

Phosphorus diphenyl spiro (0.01 moles) was introduced into a 250-mL flask including 25 mL of acetic acid (75% v/v) and heated for two hours at 70°C while being stirred. After removing the solvent, the desired product with the melting point of 140°C was obtained.

Figure 1 summarizes the routes for the synthesis of the active flame retardant compound.

Aqueous Polyurethane Dispersion Synthesis

Polyurethane resin was synthesized using the prepolymer method. The molar ratio of isocyanate groups to hydroxyl groups was kept constant at 1.5. The reaction procedure is as follows.

Hydroxyl terminated 2000 molecular weight polyester and hydrophilic monomer (DMPA), which was

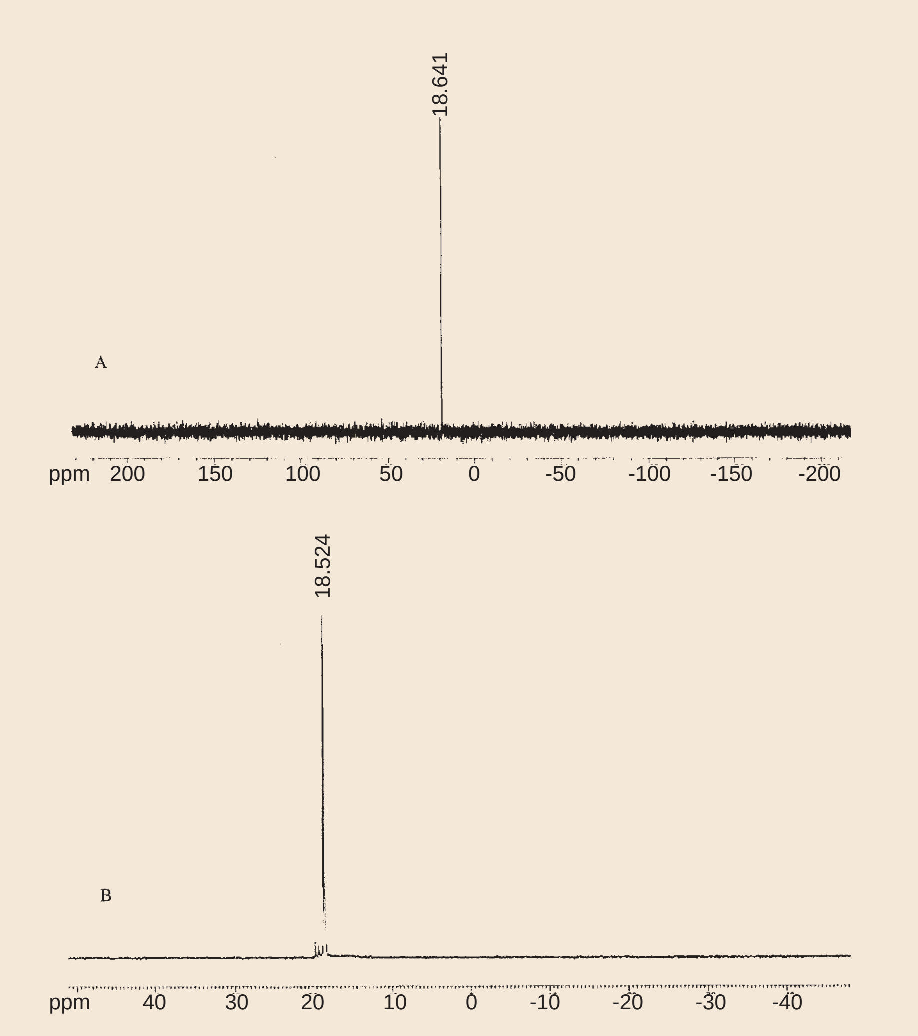

Figure 3—^{31}P-NMR spectrum of (A) PDPh Spiro and (B) PPhDH.

dissolved in DMF, were charged into a 500-mL four-neck round bottom flask equipped with a nitrogen inlet, mechanical stirrer, and condenser. The mixture was heated to 80ºC for 30 min. Then isophorone diisocyanate (IPDI)-Desmodur N3300 mixture and a tin catalyst dibutyltindilaurate were added and the mixture was stirred at that temperature for approximately four hours. The completion of the reaction was controlled by determining the unreacted NCO groups, using the dibutylamine back titration method. After cooling the mixture to 50°C, NCO end groups of the prepolymer were blocked with methylethylketoxime (MEKO) by stirring the solution for two hours. Then, carboxylic acid groups of DMPA were neutralized with triethylamine (TEA) for a period of 30 min. A dispersion step was carried out by adding demineralized water dropwise while stirring. To stabilize the dispersion, stabilizing agents, D-OP25 and D-25S, and the trace amount of ammonia were added to water. Melamine was then added and the system was stirred for an additional two hours.

Preparation of Flame Retardant Water-Dispersed Polyurethanes

A phosphorus compound (PPhDH) was used as a reactant monomer and added to the reaction vessel with polyester and DMPA at the beginning of the reaction. Since it has hydroxyl functional groups, the amount of polyester added was decreased as the phosphorus content was increased so that the NCO / OH molar ratio of 1.5 was kept constant. The same procedure was followed for the rest of the process to obtain polyurethane resins with 1% P (PU-P1), 1.5% P (PU-P1.5), 2% P (PU-P2), and 2.5% P (PU-P2.5).

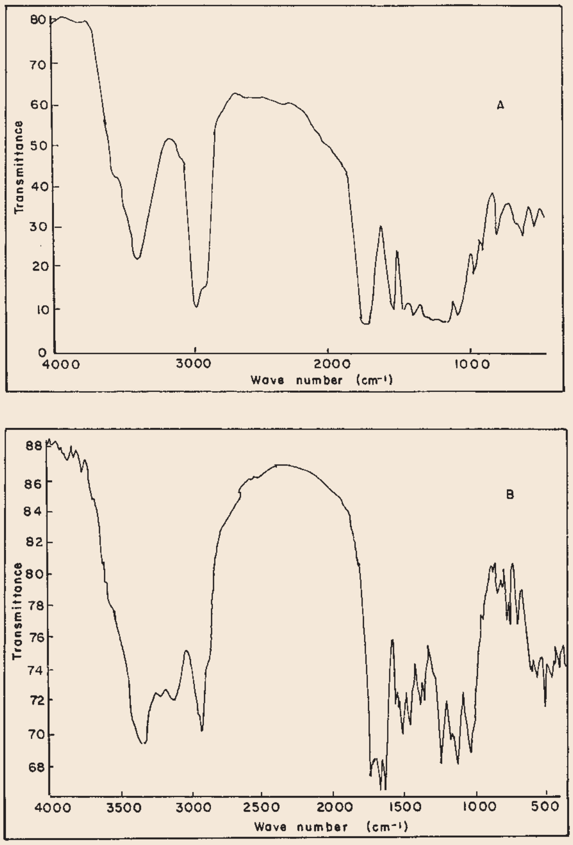

Figure 4—IR spectrum of (A) water-dispersed polyurethane and (B) water-dispersed flame retardant polyurethane.

Instrumental Analysis

CHARACTERIZATION METHODS: A Bruker Avance 400 MHz Ultra Shield Digital NMR spectrometer was used to obtain ^{1}H-NMR spectra to characterize the flame retardant compound with $CDCl_3$ as a solvent. ^{31}P-NMR spectra were obtained by using the same instrument as the proton NMR spectra, but at a frequency of 100 MHz. A Hitachi 270-30 model FTIR spectrophotometer was used to characterize polyurethane resins by forming solution cast films on KBr pellets. The pellets were predried in an oven at 125ºC.

THERMAL TESTS: Differential scanning calorimetry (DSC) thermograms were obtained by a Perkin-Elmer (DSC-4) at a heating rate of 10°C / min in nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed using a 910 DuPont thermal analyser at a heating rate of 10°C / min in nitrogen atmosphere.

FLAMMABILITY TEST: LOI values of the polymers were measured on a Stanton Redcroft flame meter and the minimum concentration of oxygen in a flowing mixture of oxygen and nitrogen that will just support flaming combustion was measured according to ASTM D 2863.

PHYSICAL AND MECHANICAL TESTS:

Preparation of Test Panels—50 µm wet film thickness was applied on the test panels using a film casting knife (Braive-Instruments). After standing at room temperature for one day to allow evaporation of the water, the test panels were heated in an oven at 130°C for one-half hour for curing.

Impact Resistance—The impact resistance of the cured resins was measured with a Gardner impact tester (Model: 5510). A standard weight (1+0.9 kg) was dropped on a film-coated metal plate from various distances and the impact value was recorded from a distance at which failure occurred by cracking according to ASTM D 2794.

Mandrel Bending—A conical mandrel bending tester (Braive-Instruments No. 1510) was used. The coated metal panels were fastened and bent approximately 135º to observe the resistance of the coating to cracking along the increasing radius of the conical mandrel (ASTM D 522).

Gloss Measurement—A Braive-Instruments glossmeter was used to measure the intensity of light reflected from the coated plates following ASTM D 523.

Pendulum Hardness—The hardness of the cured resins was measured by using a Braive-Instruments Persoz Pendulum (No. 3034) and the data were reported as the number of swings (ASTM D 4366).

Abrasion Resistance—The resistance of the resins to abrasion produced by sand falling onto coated test panels from a height of 80 cm were measured following ASTM D 968-81. The amount of abrasive per unit film thickness was reported as the abrasion of the resin on the panel.

RESULTS AND DISCUSSION

Synthesis of Phosphorus-Containing Flame Retardant

Figure 1 illustrates the synthesis routes for the active flame retardant compound (PPhDH). A monobenzalpentaerythritol (PhDH) was first synthesized and its structure was confirmed using ^{1}H-NMR (*Figure* 2A). The peaks appearing at $\delta = 3.30$ ppm and at $\delta = 3.90$ ppm as singlets correspond to two protons of $C\underline{H}_2$–OH. The other two methylene groups attached to oxygen atoms ($C\underline{H}_2$–O) gave two doublets at $\delta = 3.60$ ppm and $\delta = 4.15$ ppm, and the hydroxyl group protons (CH_2–O$\underline{H}$) were observed at $\delta = 3.70$ ppm as a singlet. The methine proton of C_6H_5-C$\underline{H}$ was characterized at $\delta = 5.30$ ppm as a singlet and aromatic group protons between $\delta = 7.20$-7.50 ppm ($C_6\underline{H}_5$–CH) as a multiplet.

In the ^{1}H-NMR spectrum of phosphorus diphenyl spiro (PDPh spiro) given in *Figure* 2B, methylene protons near the benzaldehyde group ($C_6H_5CHOC\underline{H}_2$) were observed at δ=3.70, 3.80, 3.82, and 4.18 ppm. Other methylene protons of $OPOC\underline{H}_2$ gave peaks at $\delta = 4.30$, 4.40, 4.61, and 4.78 ppm. The splittings of the peaks are due to the axial and equatorial protons which are affected by the presence of both benzaldehyde and phosphorus groups. The peak at $\delta = 5.30$ ppm corresponds to the C_6H_5–C$\underline{H}$ proton and the multiple peaks at 7.20-7.80 ppm refer to the $C_6\underline{H}_5$ protons. In the ^{31}P–NMR spectrum (*Figure* 3), the single sharp peak at 18.98 ppm confirms both the purity and phosphonate structure of the resulting PDPh spiro compound.

The characteristic peaks in the ^{1}H-NMR spectrum (*Figure* 2C) which determined the chemical structure of PPhDH are described as follows: $\delta = 3.45$ and 3.50 ppm ($C\underline{H}_2$–OH), $\delta = 3.90$ and 4.20 ppm ($C\underline{H}_2$–O), $\delta = 6.50$ ppm (CH_2–O$\underline{H}$) and $\delta = 7$-7.8 ppm (aromatic protons). Furthermore, the peak at $\delta = 18.54$ ppm in the ^{31}P-NMR spectrum shown in *Figure* 3 confirms the phosphonate structure of the resulting compound.

Synthesis of Water-Dispersed Polyurethanes

Waterborne polyurethanes can be crosslinked with a variety of reactants to improve mechanical properties. In this study, polyisocyanate (Desmodur N3300) and melamine were used as crosslinking agents. The optimum amount of polyisocyanate was found to be 5% of the total isocyanate needed since gelation occurred beyond 10%.

The structure of the polyurethane resin was verified by the IR spectroscopy given in *Figure* 4. The spectrum showed strong absorption bands at 3400 cm^{-1} corresponding to urethane N–H stretching, and at 1730 cm^{-1} referring to the C=O group in urethane. The asymmetric stretching, and symmetric stretching absorption bands for C–H in CH_2 groups were observed at 2940 and 2855 cm^{-1}, respectively. The absorption band around 1600 cm^{-1} was assigned to the aromatic groups and C–O–C stretching in hard segment (O=C–O–C) was detected at 1082 cm^{-1} in the spectrum. In the IR spectrum of flame retardant polyurethane resin (*Figure* 4B), in addition to the absorption bands corresponding to the polyurethane resin previously described, P=O, P–Ph, and P–O–C stretching bands were observed around 1250, 1438, and 1030 cm^{-1}, respectively. The O–P–O deformation was also detected at 790 cm^{-1} in the spectrum.

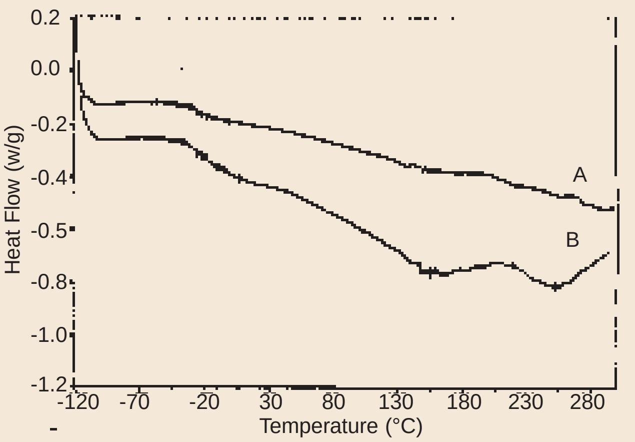

Figure 5—DSC thermogram of (A) PU and (B) PU–P1.

Thermal Analysis and Flame Retardant Properties

The thermal properties of polyurethane and flame retardant polyurethane resins were investigated by DSC and TGA in nitrogen. As seen in the DSC thermograms of PU and PU with 1% phosphorus content (PU-P1) given in *Figure* 5, the glass transition temperatures of the soft segments of the resins were detected around –22°C. This value is higher than the T_g of the polyester itself, which is –48°C, indicating the compatability between

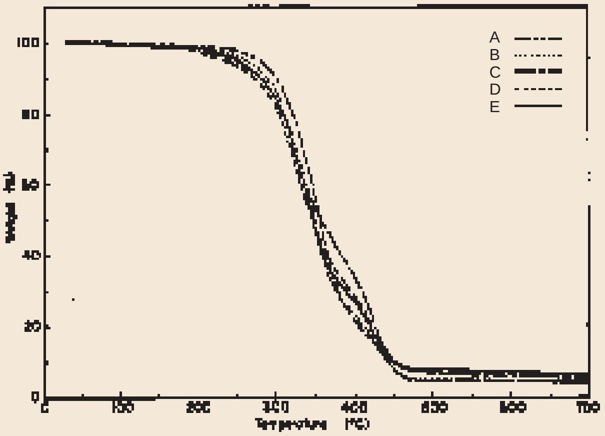

Figure 6—TGA thermograms of (A) PU, (B) PU-P, (C) PU–P1.5, (D) PU–P2, and (E) PU–P2.5.

Table 1—Char Yields and LOI Values of Polyurethane Resins

Sample	Char Yield at 600°C (wt%)	LOI
PU	4.613	24
PU–P1	4.832	28
PU–P1.5	5.606	29
PU–P2	6.574	28
PU–P2.5	7.275	27

Table 2—Physical and Mechanical Properties of Polyurethanes

Sample	Phosphorus Content (wt%)	Impact Resistance (J)	Hardness (Persoz)	Gloss			Mandrel Bend	Abrasion (kg/m)
				85°	60°	20°		
PU	0	>19	22	85	95	78	Pass	16.7
PU–P1	1	>19	29	87	97	71	Pass	25
PU–P1.5	1.5	>19	34	73	91	65	Pass	43
PU–P2	2	>19	41	77	90	63	Pass	46.6
PU–P2.5	2.5	>19	45	88	86	63	Pass	50

the soft and hard segment of the polyurethane resin. Since the amount of phosphorus compound in the total amount of the resin is very low, its effect on the T_g of the soft segment can be neglected. In the DSC thermogram of the flame retardant polyurethane resins, in addition to the T_g of the soft segments of polyurethane, endotherm was detected around 150°C. This temperature might be related to the dissociation due to a long-range ordering of the hard segment domains. Finally, an endotherm occurring above 200°C was assigned to the melting of the hard-segment microcrystalline structure.[37,38] TGA results of the polyurethanes (*Figure* 6) indicated that the thermal stability, in terms of two major weight losses, of each polyurethane sample is similar in nitrogen atmosphere and that the thermal degradation is a two-step process. The first major weight loss occurs around 350°C, due to the depolymerization of polyurethane to the primary degradation products which are diol and diisocyanate. The second loss occurs around 430°C and probably corresponds to the decomposition of carbodiimide or these primary degradation products. Moreover, the thermal stability, in terms of initial decomposition temperature, decreased when the phosphorus compound was incorporated into the polyurethane main chain. This observation is consistent with the other works in literature that the thermal decomposition of phosphorus-containing polyurethane takes place more easily than that of pure polyurethane.[3,8,9]

It is also seen in *Table* 1 that the polyurethane resins containing flame retardant compound have a higher char yield at 600°C than the polyurethane resin itself. The char formation also increases with increasing phosphorus content in the polymer.

The effect of this phosphorus compound on the flammability of polyurethane was investigated using the LOI test method. It was found that the flame retardancy of polyurethane increased with increasing phosphorus content from the LOI of 24 to 29 and reached its maximum value at 1.5% P. Further addition of phosphorus decreases the flame resistance of polyurethane as indicated in *Table* 1. This result suggests that there is not a proportional increase in flame resistance with increased phosphorus content, and similar behavior was also observed in other studies.[11,28,38] The reason for decreasing flame retardancy after reaching a maximum with 1.5% P content may arise from the fact that during combustion, degradation products of polyurethane, which is mostly polyester, lead to the formation of foam that reduces the heat transfer to the unburned polymer. However, as the incorporation of phosphorus compound into the polyurethane increases, the amount of polyester decreases, which leads to the foam reduction during combustion. Since phosphorus is known to be more effective between 1-2%,[11,39] it may compensate for the effect of foam reduction on flammability in this range. However, after reaching a maximum point on LOI with 1.5% P, the reduction in foam production due to the decrease in polyester content starts to have a predominant effect on flammability since further addition of phosphorus has only a small effect on the LOI value.

Physical and Mechanical Tests

IMPACT RESISTANCE TEST: No crack formation was observed on the surface of either type of resin up to 19 J energy, which refers to the highest energy level that can be measured on a Gardner impact tester. This result may arise from the formation of crosslinks which enhance the mechanical properties of the resin.

MANDREL BENDING TEST: All samples passed the mandrel bending test without any crack on the resin surface. Thus, it can be concluded that the incorporation of phosphorus compound does not lead to an observable decrease in the flexibility of polyurethane resin, even though increasing the phosphorus compound in the resin decreases the amount of soft segment.

GLOSS TEST: The gloss values of all samples are given in *Table* 2 for metal plates at angles of 20°, 60°, and 85°.

The results of the gloss test indicated that there is a slight decrease in the gloss property of the polyurethane when incorporating phosphorus content that affects the chain conformation of polyurethane, but, in general, all samples showed good gloss properties at all angles. In addition, it can be concluded from the results that the ability of the resins to reflect light at an angle of 60° is better than that at angles of 20° and 85°, which was expected.

PENDULUM HARDNESS TEST: The variation of hardness values of polyurethane resins with various phosphorus content is shown in *Table* 2. The incorporation of a flame retardant agent increased the hardness of the polyurethane resin, which must be due to the decrease in polyester content with increasing flame retardant material.

ABRASION RESISTANCE TEST: The phosphorus compound increased the resistance of polyurethane resins against abrasion as seen in *Table* 2.

CONCLUSIONS

The synthesis of reactive phosphorus-containing flame retardant compound and its incorporation into the polyurethane was successfully achieved and their chemical structures were confirmed by ^{1}H-NMR, ^{31}P–NMR, and IR. TGA analysis revealed that the thermal stability of a polyurethane resin, in terms of initial decomposition temperature, decreased when phosphorus phenyl dihydroxyl (PPhDH) was incorporated into the polyurethane main chain, and the char yield increased proportionally with the phosphorus content confirming the char promoting effect of the phosphorus compounds. DSC experiments showed that the flame retardant compound did not affect the T_g value of the polyurethane soft segments. Most of the physical properties of the flame retardant resins were comparable to those of a non-flame retardant resin. The LOI values indicated that the flame resistance of polyurethane was improved even by a small addition of PPhDH and was increased linearly with an increasing phosphorus content up to 1.5% P. Further addition of the flame retardant compound decreased the flame retardancy.

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