Preparation and Physical Properties of Polyurethane Flame Retardant Coatings Using Phosphorus-Containing Lactone Modified Polyesters

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Two-component polyurethane flame retardant coatings were prepared using phosphorus-containing lactone modified polyesters (PLMPs) and polyisocyanate. PLMPs were synthesized by polycondensation of dimethyl phenylphosphonate, a flame retardant component with polycaprolactone, adipic acid, and trimethylolpropane. PLMPs were prepared with dimethyl phenylphosphonate content from 10 to 20 wt%. It was found that various physical properties of these new flame retardant coatings were comparable to non-flame retardant coatings. The flammability of coatings depends strongly on the dimethyl phenylphosphonate content in PLMP. Coatings with 20 wt% dimethyl phenylphosphonate content did not burn in the vertical burning test.

INTRODUCTION

Organic coatings are generally highly combustible materials due to their high carbon and oxygen content. For various applications in the building, electrical, automobile, and other industries, organic coatings increasingly need to meet flame retardancy requirements. Among these, especially severe restrictions on flammability have been imposed on coating materials for building interior applications. The development of flame retardant polyurethane coatings has received significant attention, because polyurethanes are one of the major polymers used in the coating industry. They are preferred for many applications due to their excellent properties, such as good adhesion, abrasion resistance, and weather and chemical resistance.[1,2] Moreover, they can be formulated to have rapid drying time and long pot life.

Some recent studies have reported on reactive type flame retardant polyurethane coatings.[3-7] Bhandari and Chandra proposed flame retardant polyurethane coatings by introducing chlorine compounds into a castor oil alkyd.[3] Haythornthwaite examined the effect of halogen groups used in flame retardant coatings on the flammability of coatings.[4] More recently, we also synthesized and examined the properties of flame retardant two-component polyurethane coatings using various halogen compounds.[5-7] However, one limitation of these halogen-containing flame retardant coatings is the problem of toxic gas generation during combustion of halogen compounds.

Among non-toxic flame retardant coatings, phosphorus-containing coatings are one possible candidate for the replacement of halogen-containing coatings. It also has been generally accepted that phosphorus-containing coatings materials are superior to halogen-containing ones in flame retarding performance.[8] Recently Nippon Kokan Co. reported on the use of ammonium polyphosphate for PVC and melamine coatings.[9] Melamine phosphates were also used for flame retardant coatings by Weil and McSwigan.[10] These phosphorus-containing flame retardant coating materials were prepared by simple blending of phosphorus compounds with base polymers, which resulted in deterioration of the coating surface and blooming of phosphorus compounds.[11]

It is the purpose of this study to synthesize non-toxic reactive polyurethanes and to characterize the physical properties and the flammability of coatings. First, we polycondensed dimethyl phenylphosphonate, adipic acid, trimethylolpropane, and polycaprolactone polyol to obtain phosphorus-containing lactone modified polyester prepolymers. Flame retardant coatings with three-dimensional networks were then prepared by the crosslinking reaction of these prepolymers and hexamethylene diisocyanate (HDI)-Biuret. The prepared coatings were characterized in terms of physical properties, flammability test, and morphology of coated surfaces.

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Table 1—Polymerization Conditions for Lactone Modified Polyester and Phosphorus-Containing Lactone Modified Polyesters

Products	AA[a] g (mol)	TMP[b] g (mol)	PCL[c] g (mol)	DMPP[d] g (mol)	Toluene (g)	Temp. (°C)	Time (h)	Dehydration (mL)	Acid Value	Yield (%)
LMP	196.6(1.35)	177.6(1.32)	174.3(0.33)	—	20	150~190	13	48.0	3.7	92
PLMP-10	155.6(1.07)	176.7(1.31)	173.4(0.33)	50.0(0.27)	20	150~200	14	54.9	4.1	90
PLMP-15	135.0(0.92)	176.2(1.31)	172.9(0.33)	75.0(0.40)	20	150~200	14	58.6	4.3	90
PLMP-20	114.5(0.78)	175.7(1.30)	172.4(0.33)	100.0(0.54)	20	150~200	14	62.5	4.8	87

(a) AA : adipic acid
(b) TMP : trimethylolpropane
(c) PCL : polycaprolactone 0201
(d) DMPP : dimethyl phenylphosphonate

EXPERIMENTAL

Materials

Dimethyl phenylphosphonate (DMPP) from Nissan Chemical Co., adipic acid (AA), from Sigma Chemical Co., trimethylolpropane (TMP), from Tokyo Kasei Co. and polycaprolactone 0201 (PCL), from Union Carbide Co., molecular weight: 530, hydroxyl number: 212, viscosity at 55°C: 65 cps, specific gravity: 1.072 were used without further purification. Polyisocyanate, Desmodur N-100 (N-100), from Bayer, Co., HDI-Biuret type, solids content: 100%, NCO content: 22.0%, white pigment (RCR-6, TiO_2), from British Titan Products Co., wetting/dispersing agent (BYK P-104S, BYK-Mallinckrodt Co.), and flowing agent (Dow Corning-11, from Dow Chemical Co.) were used as received.

Synthesis of Lactone Modified Polyester

The experimental conditions for the synthesis of lactone modified polyesters (LMP) are listed in *Table* 1. The reactor, stirred at 250 rpm, was purged with nitrogen gas at the rate of 30 mL/min. The esterification was carried out with an increasing temperature at the rate of 10°C/hr. Dehydration occurred from 155° to 190°C. The reaction temperature was maintained at 190°C for nine hours, and the reaction end point was determined by the acid value measurement method. Unreacted residues were removed by the precipitation with excess xylene. Finally, AA/TMP/PCL polyester prepolymer LMP was obtained after a vacuum drying at 40°C.

Table 2—FTIR and ^{1}H-NMR Chemical Shifts of LMP and PLMP-10

Products	FTIR (NaCl, cm^{-1})	^{1}H-NMR (200 MHz, $CDCl_3$, δ in ppm)
LMP	2940 : CH_3	0.9 (C$\underline{H}_3$–C)
	1470 : –CH_2–	1.4 (–C$\underline{H}_2$–C)
	3510 : OH	1.7 (C–C$\underline{H}_2$–C)
	1060 : OH of pri-alcohol	2.3 (C–C$\underline{H}_2$–CO–)
	1740 : C=O	3.6 (C–C$\underline{H}_2$–O–)
	1180 : C–O–	4.1 (C-C$\underline{H}_2$-OCO–)
PLMP-10	1740 : C=O	0.9 (C$\underline{H}_3$–C)
	1170 : C–O–	1.4 (–C$\underline{H}_2$–C)
	3520 : OH	1.7 (C–C$\underline{H}_2$–C)
	1060: OH of pri-alcohol and –O–PO–O– of phosphate	2.4 (C–C$\underline{H}_2$–CO–) 3.6 (C–C$\underline{H}_2$–O–) 4.1 (C–C$\underline{H}_2$–OCO–)
	1460 : –CH_2–	7.5 (–CH=CH– of Ar)
	1610 : C=C of Ar	

Synthesis of Phosphorus-Containing Lactone Modified Polyesters

The reaction conditions for the synthesis of lactone modified polyester containing 10 wt% DMPP are given in row PLMP-10 of *Table* 1. Unreacted residues were removed by distilled water and n-hexane precipitation resulting in a light-brown and transparent polyester prepolymer with 10 wt% DMPP (PLMP-10). Rows PLMP-15 and PLMP-20 in *Table* 1 show the conditions for the synthesis of polyester containing 15 wt% and 20 wt% DMPP, respectively.

Instrumental Analyses

FTIR spectra were obtained with a Digilab FTS-40 from Bio-Rad and ^{1}H-NMR spectra were obtained with a Unity Plus 300 from Varian. Molecular weight and its distribution were determined by gel permeation chromatography (GPC) with a Waters R-410. Polystyrene standard samples were utilized to calibrate the molecular weight. Thermal analyses of coated film were carried out by a DuPont 951 thermogravimetric analyzer. Kinematic viscosity was examined with the method for determining viscosity of transparent liquids with KS M 5000-2121,[12] i.e., Gardner tube method.

Preparation of Polyurethane Coatings

A two-component polyurethane flame retardant coating was obtained from the lactone modified polyester and polyisocyanate. The lactone modified polyester resin solution was prepared by adding 40 g each of butyl acetate, ethyl acetate, cellosolve acetate, and toluene to 110 g of lactone modified polyester synthesized (PLMPs). This mixture was blended with 89 g of TiO_2, 0.5 g of flowing agent (Dow Corning-11), and 0.5 g of wetting/dispersing agent (BYK P-104S). The polyisocyanate resin curing solution was prepared by adding 35 g each of xylene and cellosolve acetate to 80 g of polyisocyanate N-100. The two-component polyurethane coating was prepared by blending 300 g of the lactone modified polyester resin solution and 150 g of the polyisocyanate resin curing solution. Those coatings prepared from PLMP-10/N-100, PLMP-20/N-100, and PLMP-30/N-100 were named PLPUC-10, PLPUC-

20, and PLPUC-30, respectively. The coating prepared from LMP/N-100 was named LPUC for the blank test.

Physical Properties of the Coatings

Three different types of specimens were prepared to examine various properties of coatings. The cold-rolled carbon steel sheet and the tin sheet as substrate materials were prepared according to the method of KS M 5000-1111[13] and that of KS M 5000-1112,[14] respectively. Coatings were painted on each substrate with a thickness of 0.076 mm. Coated samples were dried at 50% relative humidity and 23°C for seven days. The dimension of the glass sheets used were 200 × 150 × 5 mm. The application of the coating onto the glass sheet and drying were performed with the same procedure as the steel sheet and the tin sheet.

Viscosity of solution was measured with a Krebs-Stormer viscometer from Pacific Scientific Co. A fineness gauge from the Precision Gauge and Tool Co. was used to determine fineness of grind. The dry-hard method was used for the measurement of drying time. Pot life was defined as the time at which the viscosity reached the maximum value of 140 kU by the curing reaction. Hardness of samples was determined by the Sward hardness test method. Thermal resistance, flexibility, impact resistance, 60° specular gloss, and abrasion resistance were determined according to KS M 5000-3421,[15] KS M 5000-3331,[16] JIS K 5400,[17] KS M 5000-3312,[18] and FS 141-6152,[19] respectively. A Weather-Ometer using a xenon lamp as a light source (model: Ci 65A, Atlas Electric Devices Co.) was used to determine the accelerated weathering resistance. The measurement of yellowness, lightness index difference, and color difference was performed according to KS M 5000-3221,[20] KS M 5000-3031,[21] and KS A 0063,[22] respectively.

Flame Retardancy Tests

The flame retardancy of prepared two-component polyurethane coatings was examined by the vertical (ASTM D 568-77) and horizontal (ASTM 635-88) methods. Specimens of 5 × 0.5 × 0.1 in. were used in both cases. In the vertical tests, a vertically fixed sample was burned for 10 sec with a one-inch methane flame, and the burning time was measured after the flame was removed. In the horizontal tests, burning times were measured from the one-inch to the four-inch point in horizontal length after ignition under a methane flame.

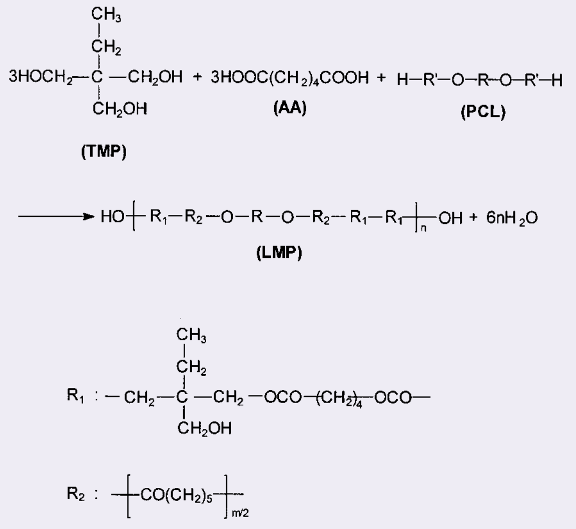
Surface Morphology

A scanning electron microscope (JSM 840, Jeol) was used to observe the morphology of the surface and the cross-section of coated films. Before observation, samples were coated with gold film with an ion coater E 5000 from Polaron Equipment Co.

RESULTS AND DISCUSSION

Identification of Lactone Modified Polyester

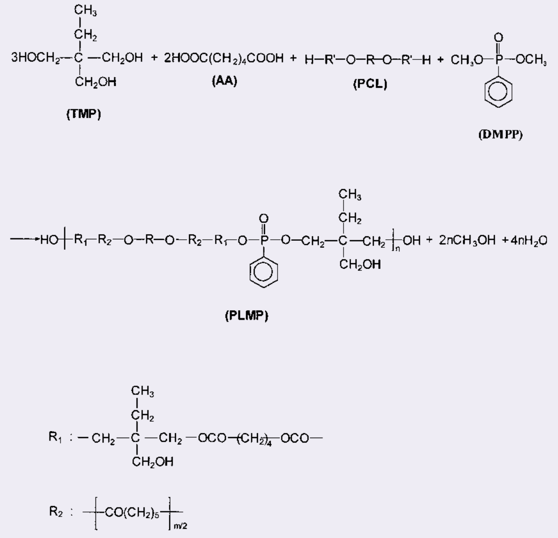
It has been known that the properties of polyurethane coatings strongly depend on the chemical structure of polyols.[1] The polyester polyols have advantages[2] in the properties of abrasion, hardness, and softness, while polycaprolactone polyols have merits[23] in heat resistance, corrosion and oil resistance, impact, and flexibility. We used polycaprolactone-modified polyester polyols in this experiment to obtain balanced final properties of coatings.



Scheme 1—Synthesis of LMP.

Based on our previous experimental method of polyester polyol synthesis,[6] lactone-modified polyester polyols were obtained using PCL as a diol, TMP as a triol, and AA as a dibasic acid. The molar ratio of each reactant in *Table* 1 was determined by the calculated OH values and OH contents.[6] The expected reaction mechanism of these lactone modified polyester prepolymers (LMP) is shown in *Scheme* 1.

The results of absorption peaks of FTIR spectra and the chemical shift of ^{1}H-NMR spectra of synthesized



Scheme 2—Synthesis of PLMP.

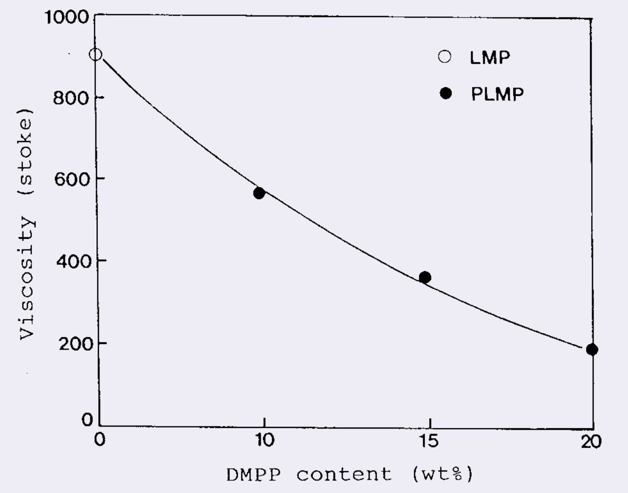


Figure 1—Relationship between viscosity and DMPP contents of lactone modified polyester.

Table 3—GPC Data for LMP, PLMP-10, and PLMP-20

Type	M_n	M_w	M_z	M_w/M_n
LMP	8750	35100	138600	4.01
PLMP-10	5510	17800	71400	3.23
PLMP-20	3460	7200	12900	2.08

LMP are summarized in *Table* 2. The observed peaks are qualitatively in agreement with those expected from *Scheme* 1. The molecular weight of LMP shown in *Table* 3 is relatively high. This can be attributed to not only the optimum reaction conditions but also the high molecular weight of PCL used as diol in condensation reaction.

Identification of Phosphous-Containing Lactone Modified Polyesters

Serini et al. synthesized branched polyphosphonate using dialkyl phosphonate and diol.[24] Based on this transesterification reaction, phosphorus-containing lactone modified polyester was synthesized using PCL as a diol, TMP as a triol, AA and phosphorus-containing DMPP as an acid. The expected reaction scheme is shown in *Scheme* 2 and the detailed reaction conditions are listed in *Table* 1.

The characterization of the synthesized prepolymer (PLMP-10) using ^{1}H-NMR and FTIR is shown in *Table* 2. The data of PLMP-20, not shown here, also showed similar peaks as PLMP-10. *Table* 3 lists the molecular weight of PLMP-10 and PLMP-20. Clearly, the increased phosphorus content results in a decrease of the molecular weight and the polydispersity.

Rheological Behavior of Phosphorus-Containing Lactone Modified Polyesters

In polyurethane coatings, the viscosity of polyols plays an important role not only in the rheological properties of paints but also in the physical properties of coatings. If the viscosity of modified polyester is too low, coatings can spot easily and can have poor leveling. High viscosity may result in low solid content and poor solvation.[25]

A typical rheological behavior of modified polyester polyols is shown in *Figure* 1. The kinematic viscosity of LMP shows 910 strokes, but for PLMPs it decreases when the DMPP content is increased. It reduced to the lowest viscosity of 190 strokes in case of PLMP-20. This low viscosity will lead to high-solid contents in final

Table 4—Physical Properties of Two-Component Polyurethane Flame Retardant Coatings

	Sample Names			
Test Types	LPUC[a]	PLPUC-10[b]	PLPUC-15[c]	PLPUC-20[d]
Viscosity (kU)	84	81	70	64
Fineness of grind	7^+	7^+	7^+	7^+
Pot life (h)	20	12	8	6
Drying time	4	2	1	1
Hardness (7 days)	35	43	48	55
Thermal resistance (60° gloss retention, %)	98.5	96.7	95.3	94.0
Flexibility (1/8 in.)	good	good	good	good
Impact resistance (1000g/50cm)				
Direct	good	good	good	good
Reverse	good	good	good	good
60° specular gloss	94	92	91	90
Abrasion resistance (mg loss/100 cycles)	2.38	2.40	2.46	2.55
Hydrocarbon resistance (20 days)	good	good	good	good
Accelerated weathering resistance (100% gloss retention)	93	94	95	95
Yellowness index (ΔN)	0.006	0.005	0.003	0.003
Lightness index difference (ΔL)	2.45	2.01	1.68	1.07
Color difference (ΔE)	2.20	2.14	1.90	1.88

(a) LPUC : LMP/N-100
(b) PLPUC-10 : PLMP-10/N-100
(c) PLPUC-15 : PLMP-15/N-100
(d) PLPUC-20 : PLMP-20/N-100

paint formulation and will reduce volatile organic compounds (VOC). The presence of DMPP in PLMP results in a higher molar ratio of OH/COOH, which is believed to reduce reactivity during condensation reaction.[26] Consequently this reduced reactivity leads to lower molecular weight and viscosity of prepolymers.

Thermal Behavior of Phosphorus-Containing Lactone Modified Polyesters

Although thermal stability of polyester and halogen-containing modified polyesters has been studied in earlier works,[6,27] no result has been reported for phosphorus-modified polyesters. The thermal stability of PLMPs was monitored by TGA as shown in *Figure* 2. The temperature range showing the initial weight loss was detected between 270°-510°C for LMP, 180°-500°C for PLMP-10, and 130°-500°C for PLMP-20. Comparing the thermogram of LMP, it is clear that the presence of DMPP in PLMP results in poor thermal stability at high temperature. This observation is in agreement with the fact that the addition of phosphorus compound into polyurethane lowers initial thermal decomposition temperature and also promotes char formation at high temperature.[8]

Physical Properties of Coatings

The PLMPs were blended with polyisocyanate (N-100) and cured at room temperature to prepare films of flame retardant coatings. The detailed physical properties of coated films are summarized in *Table* 4. The introduction of the phosphorus moiety into the backbone of polyurethane (PLPUCs) was found to enhance the coated film properties including rheology, hardness, and weathering resistance. The other properties such as fineness of grinding, flexibility, impact strength, and oil resistance were found to be similar in comparison with non-flame retardant coatings (LPUC). However, the addition of the phosphorus moiety showed a somewhat negative effect in heat resistance, gloss, and abrasion resistance. Moreover, it reduced pot life and drying time of coatings. It indicates that in the case of phosphorus containing coatings, the phosphorus moiety acts as an acid catalyst during film formation.

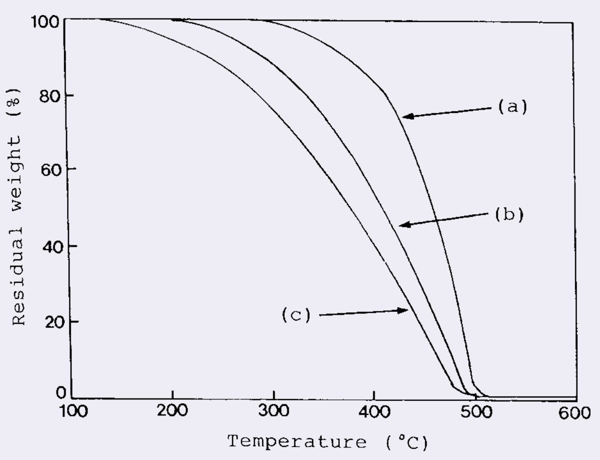


Figure 2—TGA thermograms of (a) LMP, (b) PLMP-10, (c) PLMP-20 with the heating of 10°C/min in N_2 gas.

Flame Retardancy of Coatings

Flame retardant coatings are noncombustible materials, which prevent or delay flash over from the coating surface of combustibles. It is known that a halogen-containing flame retardant acts by interfering with the radical chain mechanism taking place in the flaming gas,[5] while the phosphorus-containing flame retardant mainly influences the reactions taking place in the condensed solid during combustion.[8] The phosphorus compound reacts by hydrogen and oxygen abstracted from the substrate during combustion to form phosphoric acid, metaphosphoric acid, polyphosphoric acid, and finally to form an oxidized barrier layer. It is known that this protective layer interrupts that supply of heat and oxygen.[28]

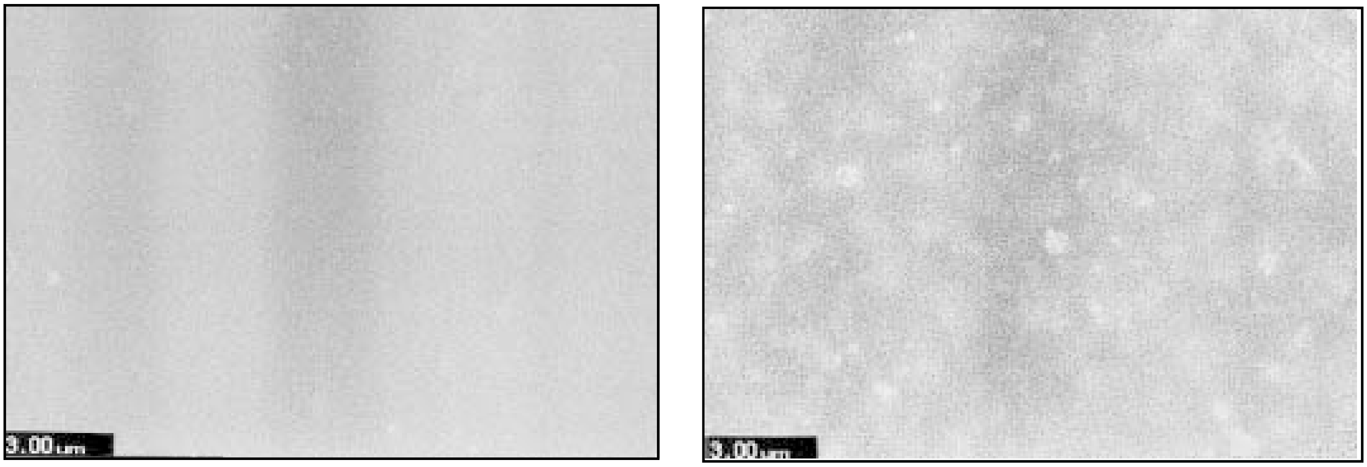


Figure 3—Scanning electron micrographs of the surface of two-component polyurethane flame retardant coatings (a) LPUC (x 30,000), (b) PLPUC-20 (x 30,000).

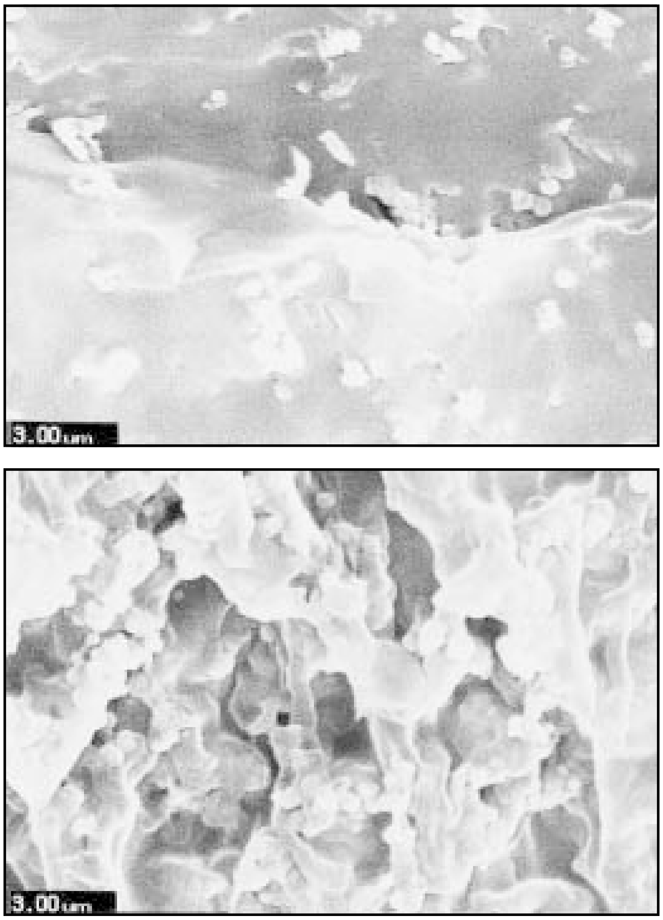


Figure 4—Scanning electron micrographs of the longitudinal structure of two-component polyurethane flame retardant coatings (a) LPUC (x 10,000), (b) PLPUC-20 (x 10,000).

The results of the flammability test are presented in *Table* 5. In the vertical burning test, the burning time for complete combustion of coated films prepared from LPUC, PLPUC-10, PLPUC-15 recorded 97, 180, and 301 sec, respectively. The sample PLPUC-20 revealed self-extinguishing characteristics. In the horizontal burning test, LPUC took 178 sec for a complete combustion, while the PLPUCs extinguished right after ignition. It is clear that flame retardancy of coatings is enhanced as phosphorus content increases. These are the expected results in view of the flame retarding mechanisms of phosphorus compounds.

Morphology of Coatings

The formation of cracks developed on the film surface of two-component polyurethane coatings due to phase separation has been reported by Kordomenos et al.[11] But Tehranisa et al.[1] reported that no phase separation occurred in two-component coatings composed of acrylic resin and polyisocyanate. *Figures* 3 and 4 are the scanning electron micrographs showing the surface and cross-section of the films coated with flame retardant coatings prepared in this study. *Figure* 3 reveals that LPUC and PLPUC-20 do not have any cracks due to phase separation. The wavy dispersed shapes are shown on the cross-section, whereas the spherical white particles[29] inside the film are those of the pigment (*Figure* 4).

Table 5—Flame Retardancy Tests of Synthesized Coatings

Testing Methods	LPUC (s)	PLPUC-10 (s)	PLPUC-15 (s)	PLPUC-20 (s)
Vertical	97[a]	180	301	SE[b]
Horizontal	178	SE	SE	SE

(a) The average value obtained from the result of five independent tests.
(b) SE : It denotes a self-extinguishing property.

CONCLUSIONS

Phosphorus-containing lactone modified polyesters were synthesized by polycondensation of dimethyl phenylphosphonate, adipic acid, trimethylolpropane, and polycaprolactone 0201. Two-component polyurethane coatings were prepared by blending polyisocyanate and these phosphorus-containing lactone modified polyesters. The kinematic viscosity was found to decrease when phosphorus content was increased. This low viscosity of lactone modified polyesters will lead to high-solid contents in final paint formation. Most of the physical properties of the flame retardant coatings were comparable to those of non-flame retardant coatings. The coatings with 20 wt% dimethyl phenylphosphonate revealed self-extinguishing characteristics.

ACKNOWLEDGEMENT

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