

Preparation and Characterization of Polyurethane Flame-Retardant Coatings Using Pyrophosphoric Lactone-Modified Polyesters/Isophorone Diisocyanate–Isocyanurate

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ABSTRACT: Pyrophosphoric lactone-modified polyester containing two phosphorous functional groups in one structural unit of base resin was synthesized to prepare a nontoxic, reactive flame-retardant coatings. Then, the pyrophosphoric lactone-modified polyester was cured at room temperature with isocyanate and isophorone diisocyanate (IPDI)–isocyanurate to get a two-component polyurethane flame-retardant coatings (TAPPU). Comparing the physical properties of the films of TAPPU with the film of nonflame-retardant coatings, no deterioration of physical properties was observed with the incorporation of a flame-retarding component into the resin. Three kinds of flame retarding tests were conducted, including the 45° Meckel burner method, limiting oxygen index method (LOI method), and oxygen combustion method with Cone calorimeter. It was observed that the char lengths were 3.1~4.5 cm and LOI values were 27~30%. These results indicate that the prepared coatings are good flame-retardant ones. It was also found that the flame retardancy of those coatings was increased with the contents of phosphorous. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2316–2327, 2001

Key words: flame-retardant coatings; pyrophosphoric lactone- modified polyesters; isophorone diisocyanate–isocyanurate

INTRODUCTION

The research on flame-retardant materials was spurred by an important finding of flame-retardant materials such as halogenized paraffin and antimony oxide in the course of research on flame-retardant military clothes in the United States during World War II. After that, the find-

ing of a synergism between the halogen compound and antimony oxide makes halogen compounds a typical organic flame-retardant compound.¹

Recently it has become obligatory to use flame-retardant coatings for painting the outside and inside of all kind of buildings, so that research on flame-retardant coatings is now conducted more actively than ever before. Until now the majority of the flame-retardant coatings were halogen-containing compounds, but because of the environmental pollution a regulation to limit the amounts of toxic gas emission, such as halogenized hydrogen and fluorine hydrogen, will be enforced.

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Bhandari and Chandra² incorporated chlorine into castor oil alkyd to make flame-retardant coatings. Haythornthwaite³ tested the burning behavior of the flame-retardant coatings according to flame-retardant functional groups used. Favstritsky and Wang⁴ grafted 16~55% of dibromostyrene onto latex and tested the flame retardancy and physical properties of the product. They found that physical properties and the flame retardancy were both good, so they proposed that the substance could be applicable to a latex treatment agent, adhesive, sealant, and latex coatings. We⁵⁻⁷ have also prepared several flame-retardant coatings by introduction of halogen functional groups into two-component polyurethane coatings. But as mentioned above, the toxic burning gases become a barrier in the development of the flame-retardant coatings.

One of the most promising nontoxic coatings will probably be the one that contains phosphorous in its structure. It is known that the flame-retardant coatings containing phosphorous reveals 2-4 times more flame-retarding effect than that of the one containing bromine or chlorine functional groups.⁸ Ma et al.⁹ prepared a polyurethane flame-retardant coatings with spirocyclic phosphate polyol, and they found that flame retardancy was increased with the content of spirocyclic phosphate polyol. Liu et al.¹⁰ prepared polyurethane coatings containing phosphorous by reaction of bis(4-isocyanatophenoxy) phenyl phosphine oxide with polyol. Weil and McSwigan¹¹ prepared a flame-retardant coatings by blending of phosphoric melamine salt with some resins. Most of the flame-retardant coatings known by now are prepared not by a reaction but by a blending or mixing so that cracks on the film surface due to a phase separation and blooming phenomenon are observed.¹² Though a few reactive flame-retardant coatings containing phosphorous were developed as mentioned above, they contain one phosphorous functional group in their structure unit, so that it is difficult to get a strong flame-retarding effect.

In this study to get a nontoxic reactive flame-retardant coatings containing phosphorous moiety in the structural unit, we synthesized a pyrophosphoric lactone-modified polyester that contains two phosphorous functional groups in its base resin structure unit. Then, the pyrophosphoric lactone-modified polyester was cured at room temperature with isocyanate, isophorone diisocyanate (IPDI)-isocyanurate, to get the two-component polyurethane flame-retardant coatings.

Finally, we examined the physical properties of films of the coatings and flame retardancy of the coatings to validate the possibility as a flame-retardant coatings.

EXPERIMENTAL

Reagents

The reagents used in this study, pyrophosphoric acid (PYPA; Aldrich Chemical Co.), adipic acid (AA; Sigma Chemical Co.), trimethylolpropane (TMP; Tokyo Kasei Kogyo Co.), and 1,4-butanediol (BD; Junsei Chemical Co.) were all reagent grade, and polycaprolactone 0201 [PCP: MW 530, OH No. 212, viscosity (at 55°C) 65 cP, Union Carbide Co.] was a purified one. Desmodur Z-4470 [Z-4470: IPDI-isocyanurate type, solid contents 70.5%, NCO contents 11.8%, viscosity (at 23°C) 1600 ± 700 mPa S, Bayer Leverkusen Co.] was used as isocyanate; TiO₂ (DuPont Co.) as a white pigment; Dow Corning-11 (silicone glycol copolymer, Dow Chemical Co.) as a flowing agent; Byk-320 (Byk-Chemie GmbH Co.) as a dispersant; Tinuvin-384 (benzotriazole derivative, Ciba-Geigy Co.) as a UV absorber; Tinuvin-292 (HALS, Ciba-Geigy Co.) as a UV stabilizer; and di-*n*-butyltindilaurate (DBTDL; reagent grade, Wako Pure Chemical Co.) as a curing catalyst.

Synthesis of Lactone-Modified Polyester

The synthesis conditions for the lactone-modified polyester are listed in Table I(TAP-2). The reactor was purged with N₂ gas with a flow rate of 30 mL/min at 70°C and stirring rate was fixed at 250 rpm. Esterification reaction was carried out with the heating rate of 10°C/h. Dehydration started at 150 and continued to 190°C. The reaction temperature was held constant at 190°C for 5 h and at 200°C for 6 h, then the reaction was ended. The ending point of reaction was determined by the calculation of the amounts of dehydrated water and the measurement of acid value (AV 4.7). The unreacted reactants were removed by excess xylene, and the product, lactone-modified polyester prepolymer (TAP-2), was dried in a vacuum dry oven at 5 mmHg and 40°C. The color of the transparent viscous liquid product was light brown.

Synthesis of Pyrophosphoric Lactone-Modified Polyesters

TBOP Intermediate

The synthesis conditions for TBOP [tetramethylene bis(orthophosphate)] intermediate are listed

Table I Molar Ratios of the Reactants and Reaction Conditions for Lactone-Modified Polyester, TBOP, and Pyrophosphoric Lactone-Modified Polyesters

Products	Reactants						Reactions				
	TMP ^a [g(mol)]	AA ^b [g(mol)]	PCP ^c [g(mol)]	TBOP ^d (g)	PYPA ^e [g(mol)]	BD ^f [g(mol)]	Toluene (g)	Temp. (°C)	Time (h)	Dehydration (mL)	Yield (%)
TAP-2	142.1 (1.05)	157.3 (1.08)	139.4 (0.26)	—	—	—	16	140 ~ 200	13	38.0	86
TBOP	—	—	—	—	500.0 (2.81)	126.4 (1.40)	—	65	2	Phosphoric acid 273.5	53
TAPT-10C	143.4 (1.06)	127.2 (0.87)	140.7 (0.27)	28.1	—	—	16	140 ~ 210	8	39.0	88
TAPT-20C	144.7 (1.07)	97.2 (0.67)	142.0 (0.27)	56.2	—	—	16	140 ~ 200	7	39.8	90
TAPT-30C	146.0 (1.08)	67.1 (0.46)	143.2 (0.27)	84.3	—	—	16	140 ~ 200	7	40.4	90

^a TMP: trimethylolpropane.^b AA: adipic acid.^c PCP: polycaprolactone 0201.^d TBOP: tetramethylene bis(orthophosphate).^e PYPA: pyrophosphoric acid.^f BD: 1,4-butanediol.

in Table I. The TBOP intermediate was prepared as follows: PYPA was poured in a four-necked flask of 1 L, and temperature was raised from 36 to 60°C for 90 min, dropping BD into the flask slowly, then held at 65°C for 2 h to complete the reaction. Then the product was purified with the excess of ethylether to remove phosphoric acid seven times; after that, by vacuum drying at 5 mmHg and 40°C the dark-brown transparent viscous TBOP intermediate was obtained.

Pyrophosphoric Lactone-Modified Polyesters

The synthesis conditions for pyrophosphoric lactone-modified polyester containing 10% PYPA are in Table I (TAPT-10C). The other synthesis conditions were the same as for TAP-2. Unreacted reactants were removed by excess distilled water and methanol. Then, brown transparent viscous TAPT-10C (pyrophosphoric lactone-modified polyester containing 10% PYPA) was obtained. The synthesis conditions for TAPT-20C and TAPT-30C, containing 20 and 30% PYPA, respectively, are listed in Table I (TAPT-20C and TAPT-30C). All other reaction conditions and the purifying procedure were the same as the one for TAPT-10C.

Phosphorous Content and Kinematic Viscosity Measurement

Phosphorous content in TBOP intermediate was measured by the phosphomolybdate method¹³ us-

ing UV spectroscopy as follows: First, 2.5 g of TBOP sample was placed in a Kiedahl flask, and a mixture of 10 mL HNO₃ and 100 mL distilled water was poured into the flask. The flask was heated at 100°C for 30 min to decompose the sample. Then the solution was cooled and the solution filtered. The filtered solution was then diluted with distilled water for a total volume of 500 mL to make the sample solution. An arbitrary volume (*x* mL) of the sample solution was mixed with 20 mL of molybdenum vanadate; then the mixed solution was diluted with distilled water for a total volume of 100 mL. With the diluted solution, the acid equivalent (mL, *V*) was measured using UV spectroscopy at a wavelength of 400 nm.

$$\text{Phosphorous content (\%)} = \frac{V \times 0.1}{2.5g \times x} \times 100$$

The kinematic viscosity of the samples was measured by the Gardner tube method¹⁴ (KS M 5000-2121), which is a method for viscosity measurement of transparent liquids.

Instrumental Analysis

For infrared analysis, Fourier transform infrared (FTIR) (FTS-40, Bio-Rad Co.) was used, and the ¹H-NMR spectrometer (Unity-300, Varian Co.) was used for NMR analysis with CDCl₃/tetramethylsilane (TMS) solvent. Molecular weight and

Table II Test Methods and Conditions of Physical Properties

Types of Tests	Instruments and Spec
Viscosity (KU)	Krebs-Stormer viscometer Pacific Scientific Co., serial 80328 KS M 5000-2122
Fineness of grind	Braive Instruments Co., type 2020 KS M 5000-2141
Drying time	Set-to-touch, dry-hard, dry-through method KS M 5000-2512
Pot-life	Krebs-Stormer viscometer JIS K 5400(4.9)
Hardness	Yasuda Seiki Seisakusho, serial 4664 JIS K 5400(8.4.1)
Flexibility	Mandrel : Pacific Scientific Co., Conical KS M 5000-3331
Impact resistance	Dupont impact tester, type 552 Ureshima Seisakusho JIS K 5400(8.3.2)
60° Specular gloss	Glossmeter Pacific Scientific Co., Glossgard II KS M 5000-3312
Cross-hatch adhesion	Cross-cut test ISO 2409
Abrasion resistance	Abrasion tester Toyo Seiki Seisakusho, Taber FS 141C-6192.1
Contrast ratio	KS M 5000-3111 Electric furnace, Hae Dong Instrumental Co., HD-010, 450°F/h
Thermal resistance	
Gloss retention	Glossmeter, Pacific Scientific Co., Glossgard II
Yellowness index difference	Spectro color meter, Data Color Ind. Co., ACS-5
Lightness index difference	Spectro color meter, Data Color Ind. Co., ACS-5
Color difference	Spectro color meter, Data Color Ind. Co., ACS-5

molecular weight distribution were measured by the GPC (R-410, Waters Co.) with four columns of Shodex KF-802, KF-803, KF-804, and KF-805 in series, and the sample concentration was 1.0% and sample weight was 10 mg. Thermogravimetric analysis (TGA) was carried out with TGA-50H (Shimadzu, Japan) in the air environment.

Preparation of the Flame-Retardant Coatings

A modified polyester resin solution was prepared as follows: First, dilute 100 g of TAPT (synthesized before) with 25.4 g of ethyl cellosolve, *n*-butyl acetate, and ethyl acetate, respectively, then blend it with 90 g of TiO₂, 3.0 g of Byk-320, 1.0 g of Dow Corning-11, 1.0 g of Tinuvin-384, 0.5 g of Tinuvin-292, and 0.5 g of DBTDL, respectively. The isocyanate curing solution was prepared by mixing of 136.1 g of Desmodur Z-4470, 15 g of ethyl cellosolve, and 15 g of xylene.

Two-component polyurethane flame-retardant coatings were prepared by a blend of 272.7 g of the prepared modified polyester resin solution and 166.1 g of isocyanate curing solution. The two-component polyurethane flame-retardant coatings prepared from TAPT-10C/Z-4470, TAPT-20C/Z-4470, and TAPT-30C/Z-4470 were designated as TAPPU-10C, TAPPU-20C, and TAPPU-30C, respectively. And the product of a blank experiment with TAP-2/Z-4470 was designated as TAPU-2.

Test of Physical Properties of Coatings

Three kinds of substrate materials were used to evaluate the physical properties of coatings. Specimens were made as follows: When using cold-rolled carbon steel sheet (KS D 3512) as the substrate, the specimen was made according to KS M 5000-1111 standard; for a tin sheet (KS D 3516),

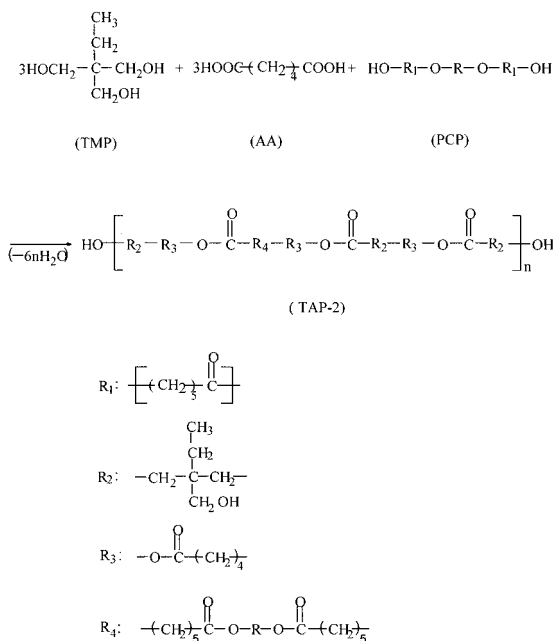
according to KS M 5000-1112; and for a glass sheet, according to KS M 5000-1121. Film thicknesses were controlled to be 0.076 mm with Doctor film applicator. Physical properties of coatings were evaluated with various test methods as listed in Table II.

Flame Retardancy Test

To see the flame retardancy of the flame-retardant coatings three kinds of flame retardancy tests were carried out. The 45° Meckel burner method¹⁵ was used according to JIS Z-2150. Flame retardancy test conditions for various textiles were as follows: Textiles used were refined acrylic textile [100%, Ne 2/36, Hanil Co., ROK], nylon taffeta [70D/24F, Dongyang Nylon Co., ROK], and polyester taffeta [75D/24F, Samyoung Textile Co., ROK]; wet pick-up¹⁶ condition was 80% acrylic textile, 60% nylon taffeta, and 60% polyester taffeta; and curing took place at 100°C for 5 min. The flame retardancy test by the limiting oxygen index method (LOI method)¹⁷ was carried out with a flammability tester [ON-1, Suga Co., Japan], and the flame retardancy test by oxygen combustion method¹⁸ was carried out with Cone calorimeter (Fire Testing Technology Co., UK).

RESULTS AND DISCUSSION

The physical properties of the film of polyol-curing type polyurethane coatings depend on the mo-



Scheme 1 Synthesis of TAP-2.

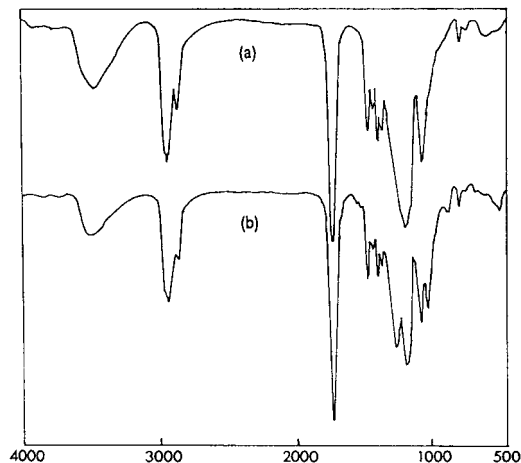


Figure 1 FTIR spectra of (a) TAP-2 and (b) TAPT-10C.

lecular structure of isocyanate and polyol; they also depend on the content of functional groups. The polyol used in this study to prepare polyurethane flame-retardant coatings was the one containing phosphorous, which has good mechanical strength and flame retarding effect; the isocyanate used was IPDI trimer,¹⁹ which has good thermal stability, low vapor pressure, low toxicity, and relatively high stability.

Identification of the Synthesized Lactone-Modified Polyester

In this study the lactone-modified polyester containing hydroxyl group was synthesized by the methods done by Shoemaker²⁰ to prepare polyester for coatings with isophthalic acid/AA/neopentyl glycol/TMP, and done in our lab⁶ to prepare modified polyester containing hydroxyl group with BD/TMP/AA. In this study to synthesize the lactone-modified polyester containing hydroxyl group, we chose PCP as diol, TMP as triol, and AA as dibasic acid. And lactone-modified polyester TAP-2 was synthesized like Scheme 1, with the calculated amounts of reactants²¹ keeping the content of hydroxyl group constant at 6.5%.

Figure 1(a) shows the FTIR spectrum of TAP-2. We could verify the existence of ester by C=O stretch vibration at 1740 cm⁻¹ and C—O— stretch vibration at 1170 cm⁻¹, and could verify hydroxyl group by OH stretch vibration at 3510 cm⁻¹ and the stretch vibration of alcohol at 1060 cm⁻¹. The ¹H-NMR spectrum of TAP-2 is shown in Figure 2(a). We could identify TAP-2 by peaks at δ 0.9 ppm for CH₃—C, δ 1.4 ppm for —CH₂—C,

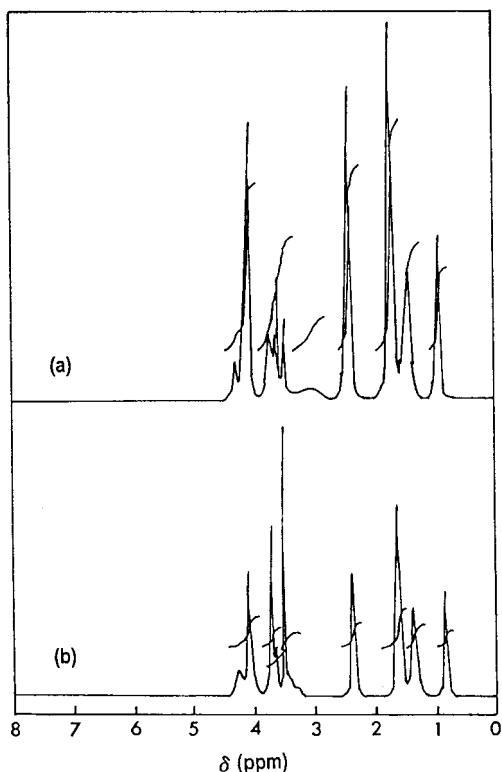


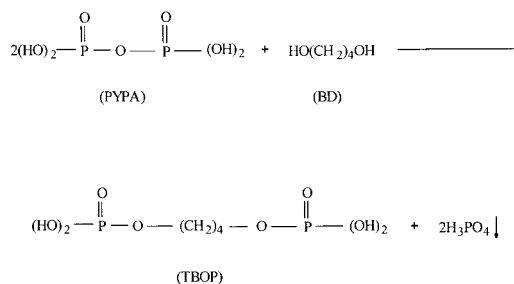
Figure 2 $^1\text{H-NMR}$ spectra of (a) TAP-2 and (b) TAPT-10C.

δ 1.7 ppm for $\text{C-CH}_2\text{-C}$, δ 2.4 ppm for $\text{C-CH}_2\text{-CO-}$, δ 3.6 ppm for $\text{C-CH}_2\text{-O-}$, and δ 4.1 ppm for $\text{C-CH}_2\text{-OCO-}$, respectively. Table III shows the gel permeation chromatography (GPC) measurement results of TAP-2. The polydispersity index value was 4.08, and it is larger than general polydispersity index values. It is supposed some side reactions were taking place because of the polyol monomer TMP, which has three functional groups.

Table III Molecular Weight Characteristics for TAP-2 and TAPT Resins Synthesized^a

Resin Names	M_n	M_w	M_z	M_w/M_n
TAP-2	2600	10600	37500	4.08
TAPT-10C	2900	14000	49300	4.83
TAPT-30C	3300	26100	149100	7.91

^a Measured from GPC run on μ -Stragel columns with tetrahydrofuran (THF) as eluent.

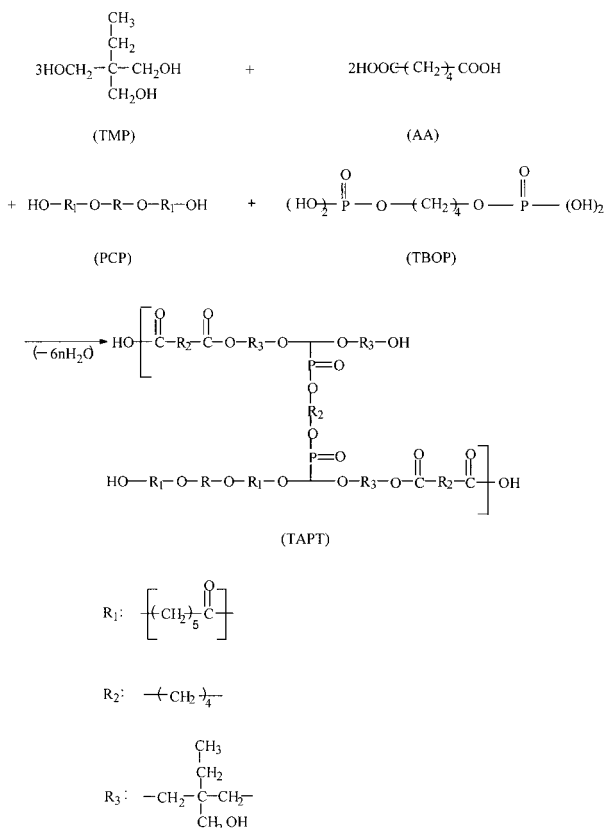


Scheme 2 Synthesis of TBOP.

Identification of Synthesized Pyrophosphoric Lactone-modified Polyesters

The reaction intermediate TBOP was synthesized first to synthesize lactone-modified polyesters changing the content of PYPA.

Scheme 2 shows the synthesis reaction equation of TBOP. TBOP is a well-known substance^{22,23} so that the identifying step by analytical instruments was omitted. The content of phosphorous in TBOP measured according to the method mentioned in the section on phosphorous content above was 23.9%. Comparing the value with a theoretically calculated value of 24.8%, there was not much difference in those values. From this result, we could suppose that the TBOP was synthesized well. The synthesis reaction mechanism of TAPT is shown in Scheme 3. We could infer that the reaction was proceeded by cross-linking of the main reactant TBOP containing four functional groups and the others as shown in Scheme 3. Figure 1(b) shows the FTIR spectrum of TAPT-10C. We could verify the existence of ester by C=O stretch vibration at 1740 cm^{-1} and C-O- stretch vibration at 1170 cm^{-1} , and could verify hydroxyl group by OH stretch vibration at 3490 cm^{-1} and the stretch vibration of alcohol at 1060 cm^{-1} . And the newly introduced phosphorous into TAPT-10C could be identified by the P-O-C stretch vibration at 1020 cm^{-1} and the P=O stretch vibration at 1240 cm^{-1} . FTIR peaks for TAPT-30C were similar to the one for TAPT-10C, so we omitted their interpretation. The $^1\text{H-NMR}$ spectrum of TAPT-10C is shown in Figure 2(b). We could identify TAPTs by peaks at δ 0.9 ppm for $\text{CH}_3\text{-C}$, δ 1.4 ppm for $\text{-CH}_2\text{-C}$, δ 1.6 ppm for $\text{C-CH}_2\text{-C}$, δ 2.3 ppm for $\text{C-CH}_2\text{-CO-}$, δ 3.5 ppm for $\text{C-CH}_2\text{-O-}$, and δ 4.0 ppm for $\text{C-CH}_2\text{-OCO-}$ as shown in Scheme 3. The $^1\text{H-NMR}$ spectrum of TAPT-30C was similar to the one for TAPT-10C, so we omitted its interpretation. Table III shows the GPC



Scheme 3 Synthesis of TAPT.

measurement results of TAPT-10C and TAPT-30C. It was found that molecular weights increased with the content of PYPA. It is supposed that TBOP acted as a catalyst²⁴ because of its high reactivity coming from four hydroxyl groups it has.

Kinematic Viscosity

Figure 3 shows the kinematic viscosity of lactone-modified polyester changing the content of PYPA, that is, changing the content of acid. When acid content was 30 wt % the kinematic viscosity was decreased down to 110 stoke, while the kinematic viscosity of TAP-2 was 1310 stoke. Typical viscosity range of 100% solid polyester polyols for coatings is 100~600 stoke in general. The kinematic viscosity of the lactone-modified polyesters (TAPTs) synthesized in this study was decreased with the content of acid. This opens the possibility of use of high content of solid components; therefore, it becomes possible to apply this technique to high solid coatings, that is, to environment-friendly coatings.

Thermal Stability

It is known that the flame-retarding action of phosphorous are caused not only by the formation of a char layer by dehydrating carbonation and an effect of radical separation but also by the expansion of the char by the expansion a thick porous char layers produced.²⁵ Because of this action of phosphorous, it becomes possible to achieve high flame retardancy for organic compounds containing oxygen, and moreover, it is possible to get the advantage of afterglow prevention by phosphorous.

Figure 4 shows the results of thermal analysis of TAPTs containing phosphorous. TAPT-10C and TAPT-30C containing 10 and 30% PYPA, respectively showed 36.90 and 79.24% weight losses respectively at 400°C, and residues were 10.20 and 18.76% at 600°C. TAPT-10C decomposed suddenly at 400°C and TAPT-30C showed large weight loss at 330°C. It was found that the decomposition temperature was decreased with the increase of phosphorous content. With the increase of phosphorous content, decomposition temperature was lowered and the amount of final char was increased rapidly.

Park²⁶ proposed a char area theory, which explains the thermal characteristics of coatings containing phosphorous. According to the theory, by the introduction of phosphorous into polyurethane, the decomposition starting temperature is lowered and the formation of char is accelerated at high temperature. Lawton and Setzer²⁷ discovered that the compounds containing halogen or phosphorous, added before melting to spin polyethylene terephthalate (PET) textile, revealed a

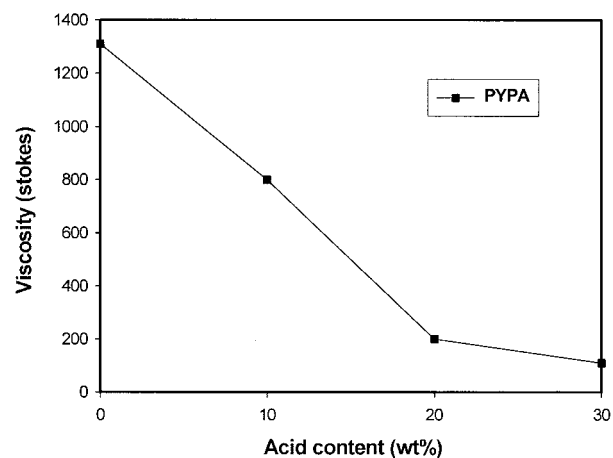


Figure 3 Effect of acid content on viscosity in lactone-modified polyester.

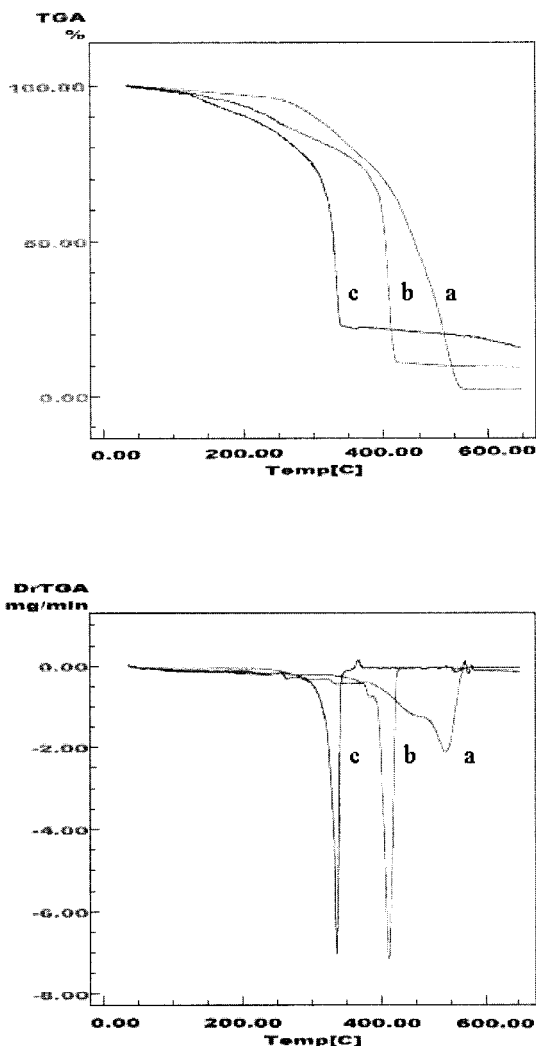


Figure 4 Thermal analysis data of (a) TAP-2, (b) TAPT-10C, and (c) TAPT-30C.

flame-retarding property. Koch et al.²⁸ reported that the thermal decomposition of PET textile containing phosphorous took place at lower temperature than that of not containing phosphorous. Thus, the result obtained in this study, that is, the coatings' decomposition temperature was lowered with the increase of phosphorous content, agreed well with the results mentioned above.

Physical Properties of Flame-Retardant Coatings

The measured physical properties of the flame-retardant polyurethane coatings are listed in Table IV. Contrast ratios were excellent in spite of the content of pigment was 31.9%. The values for fineness of grind were good as 7⁺. And viscosities were 66~69 KU (60~80 KU: good), which means

good workability. Drying times tested by three kinds of methods were all within 1 h (within 4 h: good), which means that these coatings are rapid drying one. Pot-lives were good as 7~11 h (more than 4 h: good). Recently, it is required for coatings to dry fast, that is, long pot-life and short drying time. Since the flame-retardant coatings containing phosphorous prepared in this study have the properties mentioned above, so it was proved an ideal coatings. The values for pencil hardness were HB~H, and it was a little bit soft than usual coatings. The values for impact resistance were better on a direct surface than reverse one, and the values for flexibility were excellent for all the coatings. The value for 60° specula gloss is generally increased with the content of resin and decreased with the content of pigment. The values for 60° specula gloss were increased with the contents of phosphorous. Cross-hatch adhesion was excellent, and abrasion resistance was medium. On the thermal resistance properties, gloss retention was good; yellow index difference was a little bad; and lightness index difference and color difference were both good. From the results of physical properties' test, the physical properties of the film of the prepared flame-retardant coatings containing phosphorous were never inferior to those of the nonflame-retardant coatings, TAPU-2.

Comparison of Flame Retardancy of Coatings

The flame-retardant coatings does not burn explosively and stop burning spontaneously by removing flame, that is, self-extinguishing coatings. In a flame-retardant coatings, halogen acts as a flame-retarding component through the prevention of the flaming combustion of decomposition gases¹⁴, and nontoxic phosphorous acts as a flame-retardant component through the prevention of the nonflaming combustion of decomposition residues.²⁹ During the burning, furthermore, phosphorous compound is converted to phosphoric acid, meta-phosphoric acid, and poly-meta-phosphoric acid. And these acids layer produced on the film of coatings block heat and oxygen flow, and by this mechanism phosphorous acts as a flame-retarding component.³⁰ Consequently, phosphorous compound can reveal its outstanding flame-retarding actions at even low its content through the two actions mentioned above.³¹

Flame retardancy results tested with 45° Meckel burner method are listed in Tables V–VII. Char lengths of acrylic fabrics treated with 20

Table IV Physical Properties of Flame-Retardant Polyurethane Coatings

Test Types	Sample Names			
	TAPU-2	TAPPU-10C	TAPPU-20C	TAPPU-30C
Contrast ratio	97.2	98.3	98.9	98.5
Fineness of grind	7	7 ⁺	7 ⁺	7 ⁺
Viscosity (KU)	74	69	67	66
Drying time (min)				
Set-to-touch	30	20	15	11
Dry-hard	150	45	41	36
Dry-through	180	59	51	47
Pot-life (h)	32	11	9	7
Pencil hardness (7 days) ^a	H	HB	F	H
Impact resistance (500 g)				
Direct (50 cm)	5	5	4	3
Reverse (50 cm)	5	5	3	2
Flexibility ($\frac{1}{8}$ inch)	5	5	5	5
60° Specular gloss	87	88	91	93
Cross-hatch adhesion (%)	100	100	100	100
Abrasion resistance (mg loss/200 cycles)	0.28	0.30	0.37	0.39
Thermal resistance				
Gloss retention (%)	100	98	99	99
Yellow index difference (δN)	0.6	0.7	0.6	0.6
Lightness index difference (δL)	0.44	0.46	0.45	0.43
Color difference (δE)	1.7	0.9	1.0	1.2

^a Hardness order: H > F > HB.

and 30 wt % TAPPU were both below 4.5 cm; afterflamings were both below 1 s; and afterglows were both below 1 s. These results show that the flame-retardant coatings treated on acrylic fabrics are equivalent to first grade and are good flame-retardant coatings for acrylic fabrics. Results for nylon taffeta and polyester taffeta were

similar to the results for acrylic fabrics, and this means that the flame-retardant coatings used are also good flame-retardant coatings for nylon taffeta and polyester taffeta.

Figure 5 shows LOI (%) values according to the content of PYPA. Flame retarding effect was increased with the content of PYPA; the LOI value

Table V Flame Retardancy of Acrylic Fabrics Treated with Synthesized Flame-Retardant Coatings

Exp.	Concentration (wt %)	45° Meckel Burner Method		
		Char Length (cm)	Afterflaming ^a (s)	Afterglow ^b (s)
Untreated	—	BEL ^c	—	—
TAPPU	10	18.5	23.0	1.0
	20	4.5	0	0
	30	3.9	0	0

^a Burning time of sample with spark was measured from end time of heating flame.

^b Indicates combusting state without spark from end time of heating; it was determined by observation after 1 min from the end time of heating.

^c Burned entire length.

Table VI Flame Retardancy of Nylon Taffeta Treated with Synthesized Flame-Retardant Coatings

Exp.	Concentration (wt %)	45° Meckel Burner Method		
		Char Length (cm)	Afterflaming (s)	Afterglow (s)
B-1 ^a	—	8.9	0	0
B-2 ^b	—	BEL	—	—
TAPPU	10	3.9	0	0
	20	3.3	0	0
	30	3.2	0	0

^a Original fiber not treated with flame-retardant coating and resin.

^b Fiber treated with resin only.

was increased to 30% when PYP A content was 30wt%. Considering the LOI values of a typical nonflame-retardant coatings are around 17%, we could find out that the flame retardancy was much improved.

There is no criterion to test the flame retardancy with Cone calorimeter, but through the comparison of results obtained we could evaluate the flame retardancy of the flame-retardant coatings. Casu et al.³² already used heat release rate (RHR) to compare the flame retardancy of nylon 66 and nylon 6 treated with melamine cyanurate, respectively. Table VIII lists testing conditions and peak-RHR (peak-heat release rate), ave-RHR (average-heat release rate), and ave-EHC (average effective heat of combustion) measured. The peak-RHR values, maximum heat produced by burning, were decreased with

the increase of phosphorous content; and the same trends are also shown in the ave-EHC values (average heat required to burn) and the ave-RHR values.

Figure 6 shows heat release rate according to burning time. The peak-RHR values were decreased with the increase of phosphorous contents, and with the increase of phosphorous contents the positions of peak-RHR were shifted to the right and the peak-RHR values were lowered. Figure 7 shows the effective heat of combustion according to burning time. Initial effective heat of combustion peaks were lowered with the increase of phosphorous content, and burning times became longer with the increase of phosphorous content. These results are similar to the results obtained by TGA analysis. Through the burning tests using Cone calorimeter, it was found out

Table VII Flame Retardancy of Polyester Taffeta Treated with Synthesized Flame-Retardant Coatings

Exp.	Concentration (wt %)	45° Meckel Burner Method		
		Char Length (cm)	Afterflaming (s)	Afterglow (s)
B-1 ^a	—	7.9	2	0
B-2 ^b	—	BEL	—	—
TAPPU	10	3.6	0	0
	20	3.4	0	0
	30	3.1	0	0

^a Original fiber not treated with flame-retardant coating and resin.

^b Fiber treated with resin only.

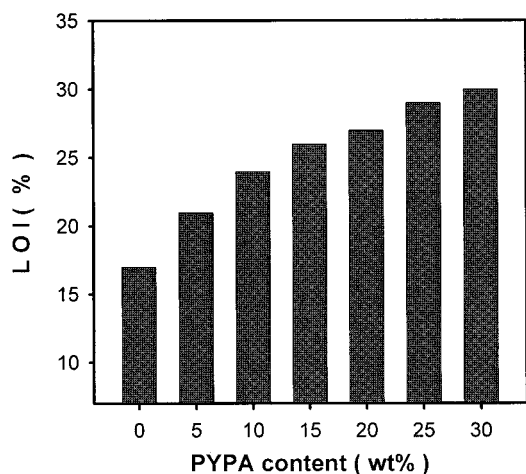


Figure 5 Relationship between LOI and pyrophosphoric acid content of lactone-modified polyester in the two-component polyurethane flame-retardant coatings.

that the flame retardancy was increased with the contents of phosphorous.

CONCLUSIONS

In order to prepare the polyurethane flame-retardant coatings containing phosphorous, first the flame-retardant resin, pyrophosphoric lactone-modified polyesters (TARTs), was synthesized. And it was blended with IPDI-isocyanurate (isocyanate curing agent) and cured at room temperature to prepare the polyurethane flame-retardant coatings (TAPT/IPDI = TAPPU). Then film specimens of TAPPUs were prepared to test physical properties and flame retardancy. The results are as follows: The optimum copolymerization conditions for TAPTs were 140–210°C and reac-

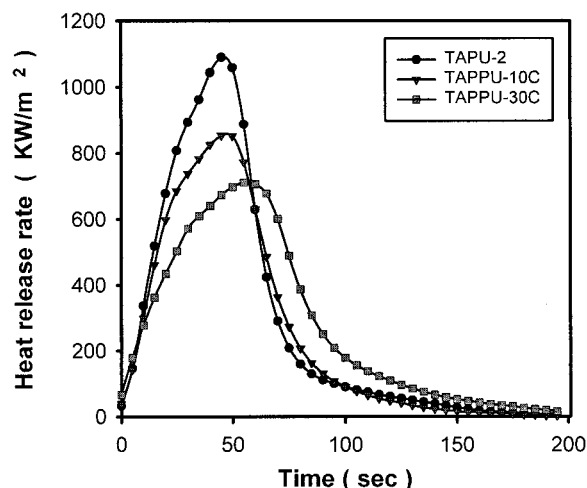


Figure 6 Detailed results for heat release rate of TAPU-2, TAPPU-10C, and TAPPU-30C.

tion time of 7–8 h. Yields were 88–90%; number average molecular weight (M_n) were 2900–3300; and the values for polydispersity index were 4.83–7.91. From the comparison of the physical properties of the film of TAPPU and nonflame-retardant coatings (TAPU-2), we could find out that physical properties of the film of TAPPU did not become deteriorated comparing with those of TAPU-2, and the physical properties were generally good. Among the three kinds of flame retarding tests conducted, from the 45° Meckel burner method the char lengths were 3.1–4.5 cm, and from the LOI method LOI values were 27–30%, and these results shows that the flame-retardant coatings prepared are good flame-retardant ones. Finally, from the oxygen combustion method using Cone calorimeter it was found out that the flame retardancy of the flame-retardant coatings was increased with the contents of phosphorous.

Table VIII Data of Fire Test Result Obtained from Cone Calorimeter

Item	TAPU-2	TAPPU-10C	TAPPU-30C
Specimen thickness (mm)	2.0	2.0	2.0
Heat flux (kW/m ²)	50	50	50
Exhaust duct flow rate (m ³ /s)	0.024	0.024	0.024
Peak-heat release rate (kW/m ²)	1090	854	711
Average-heat release rate (kW/m ²)	420	361	318
Average-heat combustion (MJ/m ²)	26.2	26.0	22.4

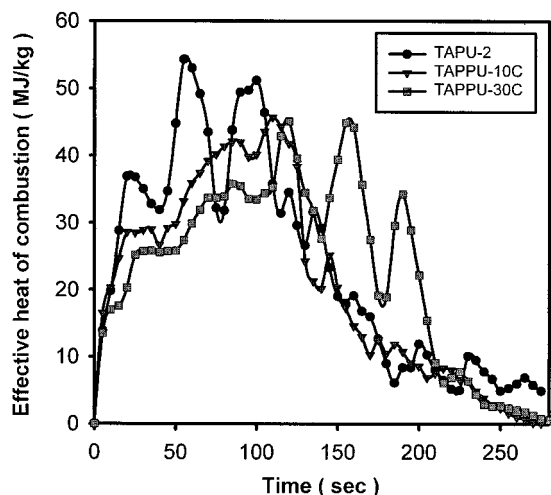


Figure 7 Detailed results for effective heat of combustion of TAPU-2, TAPPU-10C, and TAPPU-30C.

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