

Preparation and Characteristics of Two-Component Polyurethane Flame Retardant Coatings Using 2,3-Dibromo Modified Polyesters

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SYNOPSIS

Two-component polyurethane flame retardant coatings were prepared by blending 2,3-dibromo modified polyesters (2,3-DBPOs) and polyisocyanate. 2,3-DBPOs were synthesized by polycondensation of 2,3-dibromopropanoic acid, a flame retardant aliphatic carboxylic acid, with 1,4-butanediol, trimethylolpropane, and adipic acid. The content of 2,3-dibromopropanoic acid was varied at 10, 20, and 30 wt % for the polycondensation reaction. Various physical properties of these new flame retardant coatings were comparable to non-flame-retardant coatings. They showed desirable properties for a flame retardant coating such as rapid drying and 9–12 h of pot life. Coatings with 30 wt % 2,3-dibromopropanoic acid did not burn using the vertical burning test. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Polyurethane coatings are significant products in the coating industry because of their high abrasion resistance, weather resistance, chemical resistance, and excellent electrical properties. They may be classified into two kinds: one component^{1,2} and two component.^{3,4} The one-component coatings includes oil modified, moisture-cured, and heat-cured types. Catalyzed and polyol-cured type coatings belong to the two-component type coatings. Recently, the most popular coating among the two-component type coatings is polyol cured because of its excellent film properties as compared with other kinds of urethane coatings. The reason for the excellent film properties of the polyol-cured type coatings is that the polyol and polyisocyanate easily react with each other to form a 3-dimensional crosslinked structure at room temperature.⁵

In the two-component polyol-cured type coating, the polyols used are broadly classified into three kinds: polyester, polyether, and polyacrylate. The polyester and polyacrylate are often used as a raw

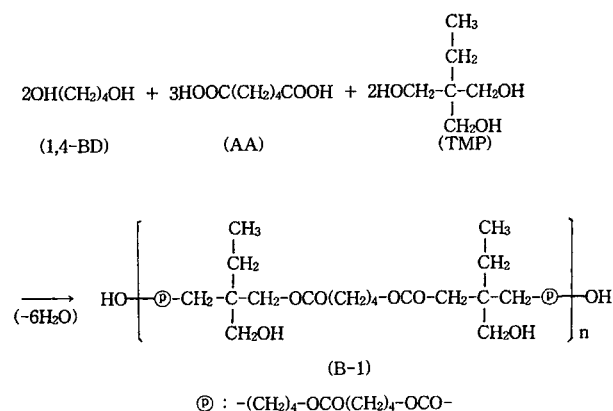
material for coatings, while polyether is used in areas requiring more elasticity.⁶

Because molecular structure, molecular weight, functional groups, and crosslinked density can be easily controlled, it is easy to control the film properties when a polyurethane coating is prepared from polyester and polyisocyanate.

In general, polyurethane flame retardant coatings belong to nonintumescent flame retardant coatings⁷⁻⁹ because of the introduction of an organic reactive flame retardant component. The combustion property of a polyurethane is affected largely by the structure of polyol or polyisocyanate used. There is a trend to use phosphorus-containing polyol¹⁰ and polyaromatic isocyanates,¹¹ such as diphenylmethane-4,4'-diisocyanate or toluene diisocyanate, as components of the polyisocyanates.

Some recent research findings on flame retardant coatings of interest were from Ishizawa and Oshima,¹² who observed viscosity changes of a flame retardant coating with flame retardant functional groups, and from Giudice and Del,¹³ who compared the flame retardancy of coatings prepared by blending alkyd resins of different chlorine contents, Sb₂O₃, and pigment, by using the Bunsen burner flame retardant method. However, there is little literature on the application of two-component reactive polyurethane flame re-

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Scheme 1 Synthesis of B-1.

tardant coatings prepared by chemical reaction, not by blending.

Presenting the synthesis of flame retardant two-component polyurethane coatings possessing improved pot life and yellowness was the goal of this study. First we polycondensed bromine-containing aliphatic carboxylic acid and polyester to synthesize modified polyester prepolymers. Two-component polyurethane flame retardant coatings were then prepared by blending these polyester prepolymers with polyisocyanate, wetting/dispersing agent, and white pigment. Characteristic properties of the prepared coatings, including flame retardancy by vertical and horizontal tests, are presented.

EXPERIMENTAL

Materials

Industrial grade 1,4-butanediol (1,4-BD) from Mitsubishi Industry (Japan) was dehydrated with Na_2SO_4 and purified by vacuum distillation at 107–108°C and 4 mmHg.¹⁴ Adipic acid (AA) was purchased from Sigma Chemical, and trimethylolpropane (TMP) and 2,3-dibromopropanoic acid (2,3-DBP) were from Tokyo Kasei. Polyisocyanate was Desmodur L-75, which has 75% solid, 13% NCO, and 2000 ± 500 cps viscosity at 20°C. TiO_2 from British Titan was used as a white pigment, BYK P-104S from BYK-Mallinckrodt as a wetting/dispersing agent, and Dow Corning-11 from Dow Corning Chemicals as a flow agent.

Synthesis of a Modified Polyester (B-1)

A modified polyester, B-1, was synthesized (Scheme 1) with 20 g toluene, 108.9 g 1,4-BD (1.21 mol), 302.2 g AA (2.07 mol), and 163.4 g TMP (1.22 mol). N_2 gas was introduced at 70°C at 30 mL/min, and stir-

ring rate was 250 rpm. Esterification was carried out by raising temperature at a rate of 10°C/h; dehydration started at 150°C and continued to 200°C, and reaction temperature was held at 220°C for 2 h. The end point was decided by acid value measurement. The product was precipitated with 10 × amounts of xylene and the unreacted reactants were removed; then 465 g of polyester prepolymer (B-1, its constituents are 1,4-BD/AA/TMP), a liquid phase colorless viscous OH-containing modified polyester, was obtained by vacuum distillation at 50°C and 5 mmHg.

The IR spectrum¹⁵ of B-1 is shown in Figure 1(a). From the spectrum, OH groups could be identified by the stretching vibration peaks of the OH group and primary alcohol at 3460 and 1060 cm^{-1} , respectively. Also, from the peaks at 2950 and 1470 cm^{-1} corresponding to CH_3 stretching vibration and $\text{-CH}_2\text{-}$ deformation vibration absorption, alkyl groups could be identified.

Figure 2(a) shows the $^1\text{H-NMR}$ ^{16,17} spectrum of the B-1: $\text{CH}_3\text{-C}\equiv$, at δ 0.8 ppm; $\text{-CH}_2\text{-C}\equiv$, at δ 1.2 ppm; $\text{C}\equiv\text{-CH}_2\text{-C}\equiv$, at δ 1.6 ppm; $\text{C}\equiv\text{-CH}_2\text{-CO-}$, at δ 2.3 ppm; and at δ 3.5 and 4.1 ppm multiplet peaks according to $\text{C}\equiv\text{-CH}_2\text{-O}$ and $\text{C}\equiv\text{-CH}_2\text{-OCO-}$ were found. From these peaks, B-1 could be identified.

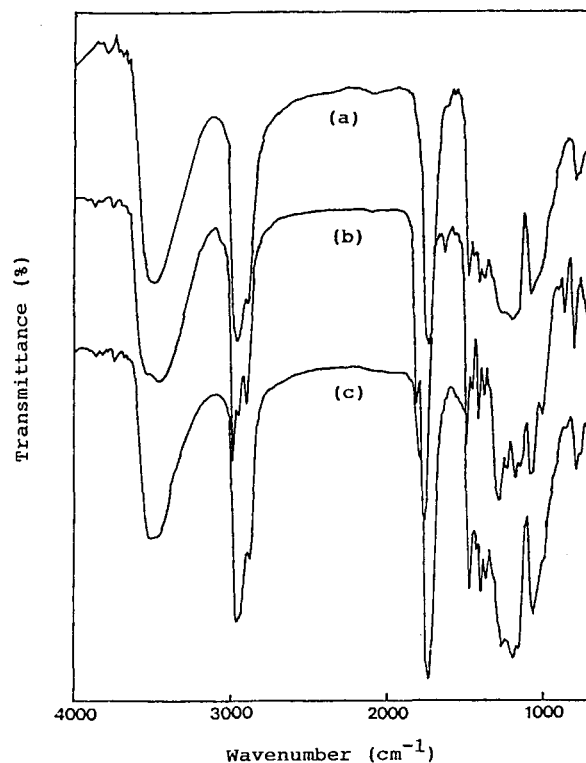


Figure 1 FTIR spectra of (a) B-1, (b) NDDP, and (c) 2,3-DBPO-10.

Table I Reaction Conditions and Yields for Modified Polyester, 2,3-DBP/TMP Intermediate, and Bromine-Containing Modified Polyesters

Products	Materials					Reactions				Dehydration (mL)	Yield (%)
	1,4-BD g (mol)	AA g (mol)	TMP g (mol)	2,3-DBP g (mol)	NDDP (g)	Toluene (g)	Temp (°C)	Time (h)	Acid Value		
B-1	108.9 (1.21)	302.2 (2.07)	163.4 (1.22)	—	—	20	150-220	14	4.0	74.2	93
NDDP	—	—	120.6 (0.90)	208.8 (0.90)	—	12	120-200	9	4.8	16.0	91
2,3-DBPO-10	41.1 (0.46)	104.6 (0.72)	51.6 (0.39)	—	30.1	40	115-210	13	4.5	26.5	90
2,3-DBPO-20	38.6 (0.43)	88.3 (0.60)	37.8 (0.28)	—	60.2	40	115-210	13	4.8	24.0	89
2,3-DBPO-30	36.2 (0.40)	72.0 (0.49)	24.0 (0.18)	—	90.3	40	115-210	13	5.0	21.9	86

1,4-BD, 1,4-butanediol; AA, adipic acid; TMP, trimethylolpropane; 2,3-DBP, 2,3-dibromopropionic acid; NDDP, 2,3-DBP/TMP intermediate.

From these peaks it was proved that NDDP was synthesized by esterification of TMP and 2,3-DBP.

Figure 2(b) shows the $^1\text{H-NMR}$ spectrum^{16,17} of NDDP. The peaks are as follows: δ 0.8 ppm (triplet, 3H, $\text{CH}_3-\text{C}\equiv$); δ 1.5 ppm (triplet, 2H, $\equiv\text{C}-\text{CH}_2-\text{C}\equiv$); δ 3.4 ppm (multiplet, 6H, $\equiv\text{C}-\text{CH}_2-\text{O}$ and $\text{R}-\text{OH}$); δ 3.5 ppm (doublet, 2H, $\equiv\text{C}-\text{CH}_2-\text{Br}$); δ 3.9 ppm (doublet, 2H, $\equiv\text{C}-\text{CH}_2-\text{OCO}-$); and δ 4.3 ppm (singlet, 1H, $\equiv\text{C}-\text{CHBr}-\text{C}\equiv$). From these peaks, the NDDP structural identification was possible.

Table II shows the measured Br content of NDDP. The measured Br content was almost the same as the calculated one.

From the results mentioned above it was proved that NDDP was synthesized successfully.

2,3-Dibromo Modified Polyesters

A modified polyester containing 10 wt % 2,3-DBP, 2,3-DBPO-10, was synthesized with 40 g toluene, 104.6 g AA (0.72 mol), 41.1 g 1,4-BD (0.46 mol), 51.6 g TMP (0.39 mol), and 30.1 g NDDP. The reaction product was precipitated into plenty of distilled water to remove unreacted 1,4-BD and AA, and it was purified further by precipitation with *n*-hexane to remove unreacted TMP. Through these sequential operations a modified polyester (2,3-DBPO-10) was obtained that was liquid phase, viscous, light brown colored, and contained 10 wt % 2,3-DBP.

A modified polyester containing 20 wt % 2,3-DBP, 2,3-DBPO-20, was synthesized with 40 g toluene, 88.3 g AA (0.60 mol), 38.6 g 1,4-BD (0.43 mol), 37.8 g TMP (0.28 mol), and 60.2 g NDDP. Synthesis and purification procedures were the same as for 2,3-DBPO-10.

Finally, a modified polyester containing 30 wt % 2,3-DBP, 2,3-DBPO-30, was synthesized with 40 g toluene, 72.0 g AA (0.49 mol), 36.2 g 1,4-BD (0.4 mol), 24.0 g TMP (0.18 mol), and 90.3 g NDDP. Again synthesis and purification procedures were the same as for 2,3-DBPO-10.

2,3-DBPOs were synthesized by reacting NDDP intermediate, AA, 1,4-BD, and TMP. 2,3-DBPOs in the following text stands for 2,3-DBPO-10, 2,3-DBPO-20, and 2,3-DBPO-30 according to the content (10, 20, 30 wt %) of the 2,3-DBP used. Synthesis reaction conditions and yields of the 2,3-DBPOs are summarized in Table I, and its structural formula is shown in the Scheme 2. In Table I, moles of reactants were calculated by the same method used in B-1 synthesis. In the synthesis of the 2,3-DBPOs, no catalyst was used because the catalyst could damage the pot life of the blend of 2,3-DBPOs and polyisocyanate as a coating. In the reaction, dehy-

Table II Bromine Content for NDDP

Type	Molecular Formula	MW	Br Content ^a	
			Calcd	Obsd
NDDP	C ₉ H ₁₆ O ₄ Br ₂	348	45.98	45.66

^a Measured by reforming combustion flask method at 25°C.

dration was complete and observed acid value was below 5. From these results, it was found that even without catalyst, the reaction went well.

Figure 1(c) shows the IR spectrum¹⁵ of 2,3-DBPO-10. Ester groups in the 2,3-DBPO-10 could be identified by the C=O stretching vibration peak at 1740 cm⁻¹ and the C—O— stretching vibration peak at 1170 cm⁻¹. The OH group could also be identified by the OH group stretching vibration peak at 3500 cm⁻¹ and the primary alcohol stretching vibration peak at 1060 cm⁻¹. The IR spectrum for 2,3-DBPO-30 was the same as that of 2,3-DBPO-10.

Figure 2(c) shows the ¹H-NMR spectrum^{16,17} of the 2,3-DBPO-10 as follows: δ 0.8 ppm (CH₃—C≡); δ 1.5 ppm (—CH₂—C≡); δ 2.3 ppm (≡C—CH₂—CO—); δ 3.5 ppm (≡C—CH₂—O—); and δ 4.0 ppm (≡C—CH₂—OCO—). From these peaks, the structure of 2,3-DBPO-10 could be identified. The measured spectrum for 2,3-DBPO-30 was the same as that of 2,3-DBPO-10.

Figure 3 shows results of GPC measurement: for 2,3-DBPO-10: \bar{M}_n , 880; \bar{M}_w , 1560; \bar{M}_z , 3350; \bar{M}_w/\bar{M}_n , 1.95; for 2,3-DBPO-30: \bar{M}_n , 690; \bar{M}_w , 1400; \bar{M}_z , 3440; \bar{M}_w/\bar{M}_n , 2.04. The average molecular weight decreased with Br content but polydispersity slowly increased with Br content.

Bromine Contents and Kinematic Viscosity

Bromine content in the modified polyester was measured by the reforming combustion flask method.¹⁸ A sample of 6 mL NDDP, intermediate for modified polyester, was mixed with 0.5 mL of 28% H₂O₂ and 5 mL of distilled water, and then the mixture was burned on a Pt wire located in a flask filled with O₂ gas. Then the burned gas was perfectly distilled in H₂O₂ solution, held still for 30 min, and then was titrated by 0.005N Hg(NO₃)₂ factored with diphenylcarbazone indicator.

Br (%)

$$= \frac{\text{consumed Hg(NO}_3)_2 \text{ (mL)} \times \text{factor} \times 0.3995}{\text{amounts of sample (mL)}}$$

× 100.

The viscosity was estimated by the Gardner tube method according to the KS M 5000-2121 manual.

Instrumental Analyses

An FTIR was carried out with a Digilab FTS-40 from Bio-Rad and ¹H-NMR with a Gemini 200 from Varian. A GPC R-410 from Waters was used to determine molecular weights and their distribution. Thermal analyses were carried out with a TG-DTA 92 from Setaram, France.

Preparation of Two-Component Polyurethane Flame Retardant Coatings

The modified polyester produced (109.6 g) was mixed with 39.5 g each of cellosolve acetate, butyl acetate, ethyl acetate, and toluene. To prepare polyester resin solution, TiO₂ 88 g white pigment, 0.3 g wetting/dispersing agent BYK P-104S, and 0.4 g flowing agent Dow Corning-11 were blended with the mixture. Polyisocyanate resin curing solution was prepared by adding 21.2 g each of cellosolve acetate and xylene to 135.8 g of polyisocyanate L-75.

Two-component polyurethane coatings were prepared by blending 356.3 g of polyester resin and 178.2 g of polyisocyanate resin curing solution at the time of film formation. Resulting blends of 2,3-DBPO-10/L-75, 2,3-DBPO-20/L-75, and 2,3-DBPO-30/L-75 were named 2,3-DPU-10, 2,3-DPU-20, and 2,3-DPU-30, respectively. The blend of B-1/L-75 was named BPU-1.

Tests of General Properties for Flame Retardant Coatings

Preparation of Specimens

Three types of specimens were prepared. When cold rolled carbon steel sheets (KS D 3512) were used, steel sheets were prepared according to the KS M 5000-1111 manual and coatings were painted with a thickness of 0.076 mm. Coated samples were dried at 50% relative humidity and 23°C for 7 days. Tin sheets (KS D 3516) were prepared according to the KS M 5000-1112 manual. After polishing and cleaning, 0.076-mm coatings were made by a Doctor film applicator and dried at the same conditions as cold rolled carbon steel sheets. When glass sheets were used, 200 × 150 × 5 mm glass sheets were coated with the same procedure as the tin sheets.

Methods for Property Examination

The Krebs–Stormer viscometer 80328 from Pacific Scientific Co. was used to determine viscosity. Fine-

ness of grind was estimated with a fineness gauge from Precisions Gauge & Tool. Measurement of drying time was carried out by the set-to-touch method and dry-hard method. Pot life was measured based upon the degree of curing at which the viscosity reaches maximum, 140 kU.

Hardness was determined by the pencil hardness method and the Sward hardness method. Flexibility was measured according to the KS M 5000-3331 manual for the tin sheets. Impact resistance was determined according to JIS K 5400 for the cold rolled carbon steel sheets. KS M 5000-3312 was followed to determine 60° specular gloss and FS 141-6152 to determine abrasion resistance. Cross adhesion tests were carried out to determine the strength of adhesion of the tin sheets.

A xenon Weather-ometer (model Ci65A) from Atlas Electric Devices was used to examine the accelerated weathering resistance and a spectrophotometer (model SZ-Σ80) from Nippon Den-shoku Kogyo was used to determine yellowness. Lightness index differences were measured according to the KS M 5000-3031 manual. In addition salt spray exposure tests and immersion resistance tests were carried out.

Flame Retardancy Tests

Flame retardancy of prepared two-component polyurethane coatings were examined by the vertical (ASTM D 568-77) and horizontal (ASTM D 635-88) methods. Specimens 5 × 0.5 × 0.1 in. were used for the both cases. In the vertical tests, a vertically fixed sample was burned for 10 s with a 1-in. methane flame, and the burning time was measured after the flame was removed. In the horizontal tests, burning times were measured from the 1-in. point to the 4-in. point in horizontal length after ignition under a methane flame.

RESULTS AND DISCUSSION

Identification of Synthesized Modified Polyester

The physical properties of polyurethane coatings depend upon the properties of the polyol used, that is, content of functional groups, molecular weight distribution, and molecular structure of the polyol.¹⁹ Among the polyols that are often used as two-component polyol hardening-type coatings, polyester was chosen. Polyester for polyurethane coatings must have low molecular weight and many OH-functional groups. In general, a modified polyester whose OH content is 6.5% is suitable for coatings.⁶

In this study, a modified polyester containing OH groups was synthesized with 1,4-BD as a diol, TMP as a triol, and AA as a dibasic acid using the synthesis method of Rybny et al.²⁰ (in the synthesis of polyester for coatings with 1,6-hexanediol, ethylene glycol, and AA). B-1 was synthesized with the appropriate moles of reactants that were calculated by using the following equations, keeping the OH content and OH value at 6.5% and 215, respectively.

OH content

$$(\%) = \frac{(e_b - e_a) \times 17}{\text{theoretical amounts of product}} \times 100,$$

$$\text{OH value} = \frac{(e_b - e_a) \times 56100}{\text{theoretical amounts of product}} + \text{AV},$$

where e_a are the initial equivalents of OH of the reactant, e_b are the initial equivalents of COOH of the reactant, and AV is the acid value.

Changes of Kinematic Viscosity of 2,3-Dibromo Modified Polyesters According to 2,3-DBP Content

In general, when a polyurethane is prepared and used as a coating, the more the OH group content in the polyol of the coating, the harder the film. This phenomenon is due to the increase of crosslinking density.²¹ If the viscosity of the modified polyester is too low, workability is lowered; for example, when painting with a brush the film surface is not smooth and leveling²² is difficult. On the contrary, if the viscosity is too high, some disadvantages are apparent: the solid component must be lowered and, because of the decrease in solubility, a polar solvent such as cellosolve acetate is necessary instead of toluene. Therefore, the viscosity of the synthesized modified polyester in this study was preadjusted to meet the coating properties by fixing the ratio of TMP to 1,4-BD at 1 : 1.

Dynamic viscosity change of the 2,3-dibromo modified polyester with the 2,3-DBP content is plotted in Figure 4. While the dynamic viscosity of the B-1 was 470 Stokes (S), the dynamic viscosity of the 2,3-DBPO increased with the content of 2,3-DBP: it increased to 590 S at 30 wt % of 2,3-DBP content. The dynamic viscosity of a coating is usually 100–600 S when its polyester constituent is 100% solid state²³; therefore, the dynamic viscosity of the 2,3-DBPO meets the required range, but it is a little bit high.

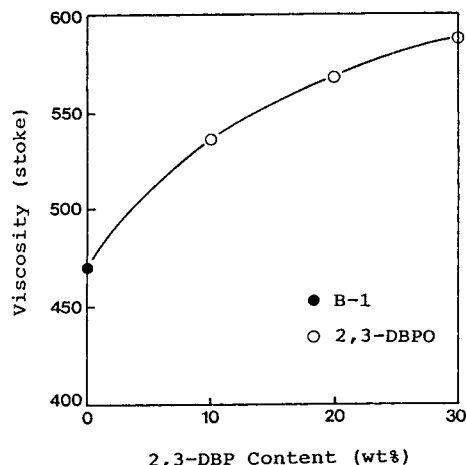


Figure 4 Effect of 2,3-dibromopropanoic acid contents of viscosity in modified polyester.

Thermal Behaviors of 2,3-Dibromo Modified Polyester

Polymers with halogen show mainly exothermic thermal decomposition.²⁴ There are several mechanisms proposed for the thermal decomposition of polyester. Yokouchi and Nakamura²⁵ proposed that thermal decomposition of end groups took place first of all. Pohl²⁶ proposed that decomposition reaction took place by fission of a polyester chain. Zimmerman and Kim²⁷ observed that carboxylic end group content was increased by thermal decomposition. Schwenker and Beck²⁸ carried out DTA analysis of undrawn polyethylene terephthalate and showed an endothermic peak at 447°C, corresponding to thermal decomposition.

Figure 5 shows the DTA curves of our products. B-1 has an endothermic thermal decomposition peak at 460°C, and 2,3-DBPO-10 and -30 had endothermic thermal decomposition and exothermic thermal decomposition peaks caused by Br at 325–420°C and 305–350°C, respectively. NDDP, which contains the largest amounts of Br among the products, shows a larger exothermic thermal decomposition peak than those of the 2,3-DBPO-10 or -30 at 305–335°C. This phenomenon agrees with the above-mentioned observation that polymers containing halogen show exothermic thermal decomposition in DTA peaks.

Figure 6 shows TGA curves of products. The B-1 began to decompose about 325°C and showed about 96% weight loss at about 485°C; but 2,3-DBPO-10, 2,3-DBPO-30, and NDDP showed the first step weight losses at 285–480°C, 265–450°C, and 225–400°C, respectively. From the TGA results, the thermal stability of the modified polyesters containing Br exhibited higher decomposition rates at

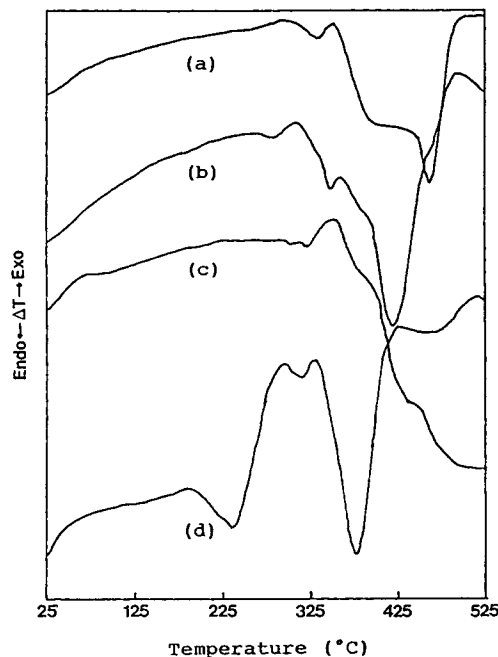


Figure 5 DTA thermograms of (a) B-1, (b) 2,3-DBPO-10, (c) 2,3-DBPO-30, and (d) NDDP (scan rate 25°C/min).

high temperature. This phenomenon is consistent with the theory²⁹ that a halogenated compound decomposes easier at high temperature. Papa and Proops³⁰ reported that when Br was included in an aliphatic compound having a small number of carbon atoms, the thermal stability deteriorated and thermal decomposition could take place easily.

Consequently, NDDP, which contains the highest amount of Br, showed the worst thermal stability, and among the 2,3-DBPOs 2,3-DBPO-30, which

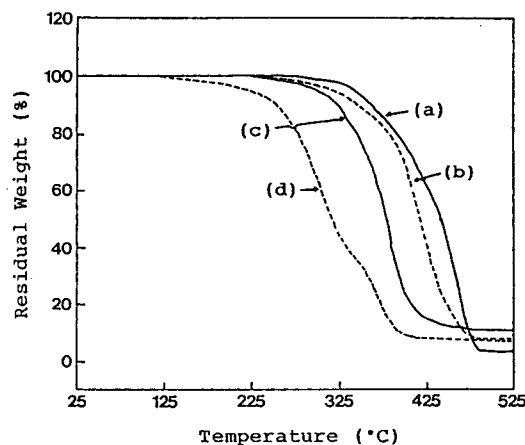


Figure 6 TGA thermograms of (a) B-1, (b) 2,3-DBPO-10, (c) 2,3-DBPO-30, and (d) NDDP with heating of 25°C/min in air.

Table III Physical Properties of Two-Component Polyurethane Flame Retardant Coatings

Test Types	Sample Names			
	BPU-1	2,3-DPU-10	2,3-DPU-20	2,3-DPU-30
Viscosity (kU)	56	54	56	62
Fineness of grind	7 ⁺	7 ⁺	7 ⁺	7 ⁺
Pot life (h)	8	9	11	12
Drying time				
Set-to-touch (min)	9	7	6	5
Dry-hard (h)	4	3	2	2
Pencil hardness (7 days)	2H	2H	2H	3H
Sward hardness (7 days)	50	48	48	48
Flexibility ($\frac{1}{8}$ in.)	Good	Good	Good	Good
Impact resistance (1000 g/50 cm)				
Direct	Good	Good	Good	Good
Reverse	Good	Good	Good	Good
60° specular gloss	97.0	99.5	100.0	100.0
Crosshatch adhesion (%)	30	98	99	100
Abrasion resistance (mg loss/100 cycles)	0.05	0.07	0.05	0.01
Accelerated weathering resistance (% gloss retention)	98	96	95	93
Yellowness index (ΔN)	0.0674	0.0676	0.0731	0.1032
Light index difference (ΔL)	1.58	1.99	2.53	5.17

contains the most Br, showed lower thermal stability than the others.

Property Changes of Flame Retardant Coatings

The synthesized 2,3-dibromo modified polyesters were blended with polyisocyanate L-75 to prepare relatively flame retardant coatings. Table III summarizes the physical properties of coated films depending on the 2,3-DBP content. Viscosity, fineness of grind, hardness, impact resistance, flexibility, and accelerated weather resistance of flame retardant 2,3-DPUs were comparable to those of non-flame-retardant BPU-1. 2,3-DPUs showed better adhesion and shorter drying time but more yellowness and lightness index difference than BPU-1. The pot life of 2,3-DPUs was 9–12 h, which is a desirable drying property. Rust resistance also proved to be good through the salt spray exposure test and immersion resistance.

Flame Retardancy of Coatings

Flame retardant coatings should have nonexplosive combustion and self-extinguishing properties. Decomposition gases of flame retardant coatings suppress flaming combustion and thus stop nonflaming combustion.³¹ Flame retardancy usually results from the existence of phosphate, antimony, bromine, or chlorine.^{32,33} Bromine compounds usually have low flammability in the gaseous state. The presence of bromine affects the chemical reactions during combustion, and thus suppresses the access of oxygen and heat transfer by generating bromine-containing heavy gases. Aliphatic bromine chemicals usually have better flame retardancy than aromatics because aromatic bromine compounds have higher dissociation energy, producing gases with low flammability.³⁴

Table IV shows the results of flame retardant tests with the synthesized coatings. In the vertical test, BPU-1, 2,3-DPU-10, and 2,3-DPU-20 took 105,

Table IV Flame Retardancy Tests of Synthesized Coatings

Testing Methods	Samples			
	BPU-1 (s)	2,3-DPU-10 (s)	2,3-DPU-20 (s)	2,3-DPU-30
Vertical test	105	155	230	—
Horizontal test	186	—	—	—

155, and 230 s, respectively, for complete combustion. The flame of 2,3-DPU-30 was extinguished right after ignition. In the horizontal test with 2,3-DPUs the flame soon extinguished after ignition. Results in Table IV suggest that flame retardancy increases as bromine content increases. This may be because bromine-containing gases such as HBr generated from thermal decomposition block the access of oxygen and consequently suppress the flammable combustion of polyurethane coatings.

In these tests, our two-component polyurethane coatings did not show any loss of significant coating properties, even though high bromine content reduces flexibility, mechanical properties, or heat resistance³⁴ in general.

CONCLUSIONS

Two-component polyurethane flame retardant coatings were prepared by blending polyisocyanate and 2,3-dibromo modified polyesters (2,3-DPUs) which were synthesized in our lab. The kinematic viscosity and the rate of thermal decomposition of modified polyesters increased as the bromine content increased. They showed rapid drying and 9–12 h of pot life. Most of the physical properties of the flame retardant coating were comparable to those of non-flame-retardant coatings. The coatings with 30 wt % 2,3-dibromopropanoic acid was self-extinguishing in the vertical burning test.

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