

# Preparation and Physical Properties of Two-Component Polyurethane Flame-Retardant Coatings Using Trichloro Modified Polyesters

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**ABSTRACT:** Trichloro modified polyester polyols were synthesized by two-step condensation reactions. An intermediate compound was synthesized by the esterification of trichloroacetic acid with trimethylolpropane in the first step. In the next step, polycondensation of the intermediate, 1,4-butanediol and trimethylolpropane with adipic acid was carried out. Two-component flame-retardant polyurethane coatings were prepared by blending these modified polyester polyols and polyisocyanate. The physical properties of these new coatings were comparable to non-flame-retardant coatings. They showed a drying time of 3–4 h and a pot life time of 10–13 h, which could belong to the flame-retardant coatings with long pot life times. Coating with 20 wt % trichloroacetic acid showed a self-extinguishing property in the vertical burning test. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 913–920, 1998

**Key words:** polyurethane; flame-retardant coatings; trichloro modified polyesters

## INTRODUCTION

Flame-retardant coatings are noncombustible materials, which prevent or delay flashover from the coating surface of combustibles. Recently, interest has been growing in developing flame-retardant coatings<sup>1,2</sup> of two-component polyurethane because they have many advantages such as good crosshatch adhesion; resistance against abrasion, weathering, and chemicals; and curing at ambient temperature. Ishizawa and Oshima<sup>3</sup> reported that the viscosity was increased when flame-retardant functional groups were introduced to polyurethane flame-retardant paints. Bhandari and Chandra<sup>4</sup> prepared flame-retardant coatings produced by the introduction of the chlorine radical into castor oil alkyd. Also, Park

et al.<sup>5,6</sup> prepared two-component polyurethane flame-retardant coatings by reacting aliphatic polyester polyols, containing a dibromo or dichloro group, with polyisocyanate and obtained good flame retardance and improvement of the physical properties of the coating film. However, there is a dearth of literature on the application of reactive type two-component polyurethane flame-retardant coatings.

It is the purpose of this article to present the synthesis of flame-retardant two-component polyurethane coatings and to characterize the physical properties and the flammability of the prepared coatings. First we polycondensed trichloro group-containing aliphatic carboxylic acid and polyol to synthesize chlorinated modified polyester prepolymers. Two-component polyurethane flame-retardant coatings were then prepared by blending these polyester prepolymers with polyisocyanate, wetting agent, and pigment. The prepared coatings were characterized in terms of physical properties and flammability test results.

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## EXPERIMENTAL

## Materials

Adipic acid (AA) and 1,4-butanediol (1,4-BD) were purchased from Sigma Chemical Inc., and trimethylolpropane (TMP) and trichloroacetic acid (TCA) were from Tokyo Kasei Inc. and used as received. Our polyisocyanate was Desmodur L-75 (L-75, solid content 15%, NCO content 13%, viscosity of 2000 cps at 20°C) from Bayer Leverkusen Co. TiO<sub>2</sub> (British Titan Co.) was used as a white pigment, BYK P-104S (BYK-Mallinckrodt) was a wetting agent, and Dow Corning-11 (Dow Corning Chemicals) was a flowing agent.

## Synthesis of Modified Polyester

The experimental conditions for the synthesis of modified polyesters are listed in Table I (B-5). The reactor was stirred at 250 rpm and purged with nitrogen gas at the rate of 30 mL/min. The esterification was carried out with increasing the temperature at 10°C/h. Dehydration occurred from 150 to 200°C. The reaction temperature was maintained at 220°C for 2 h, and the reaction end point was determined by the acid value measurement method. Unreacted residues were removed by precipitation with excess xylene. Finally AA/1,4-BD/TMP polyester prepolymer (B-5) was obtained after vacuum drying at 50°C. The structure characterization of B-5 was shown in an earlier article.<sup>5</sup>

## Synthesis of Trichloro Modified Polyesters

The experimental conditions for the synthesis of TCA/TMP intermediate are given in Table I (TCA-3). The reaction procedure is the same as that of modified polyester (B-5). The reaction product was purified by precipitation with excess *n*-hexane. Following vacuum drying at 50°C, 453 g of neohexanediol trichloroacetate (TCA-3) was obtained.

The structural formula of TCA-3 and the reaction conditions to synthesize TCA-3 are shown in Scheme 1 and Table I, respectively.

The results of absorption peaks of the FTIR spectrum and the chemical shifts of the <sup>1</sup>H-NMR spectrum are summarized in Table II. The observed peaks are coincident with the theoretical peaks of TCA-3. The observed chlorine contents in TCA-3 well agree with the calculated results as shown in Table III.

**Table I** Reaction Conditions and Yields for Modified Polyester, TCA/TMP Intermediate, and Chlorine-Containing Modified Polyesters

Products	Materials					Reactions					Yield (%)
	AA g (mol)	1,4-BD g (mol)	TMP g (mol)	TCA g (mol)	TCA-3 g (g)	Toluene (g)	Temp. (°C)	Time (h)	Acid Value	Dehydration (mL)	
B-5	302.2 (2.07)	108.9 (1.21)	163.4 (1.22)	—	—	20	150–220	14	3.9	74.0	92
TCA-3	—	—	241.2 (1.80)	294.3 (1.80)	—	20	100–190	10	4.5	32.4	90
TCAO-10	259.7 (1.78)	104.0 (1.16)	120.1 (0.9)	—	85.8	20	100–180	11	4.3	69.5	88
TCAO-20	217.2 (1.49)	99.0 (1.10)	76.9 (0.57)	—	171.6	20	100–180	11	4.8	63.8	87
TCAO-30	174.6 (1.20)	94.0 (1.04)	33.6 (0.25)	—	257.3	20	100–160	11	5.0	59.4	84

AA, adipic acid; 1,4-BD, 1,4-butanediol; TMP, trimethylolpropane; TCA, trichloroacetic acid; TCA-3, TCA/TMP intermediate.



**Table IV** Molecular Weight Distribution Data for B-5, TCAO-10, and TCAO-30 Determined by GPC

Type	$M_n$	$M_w$	$M_z$	$M_w/M_n$
B-5	1080	2060	3260	1.91
TCAO-10	960	1390	1750	1.45
TCAO-30	870	1150	1540	1.32

flask method.<sup>6</sup> The kinematic viscosity of the modified polyester was evaluated by the Gardner tube method according to KS M 5000-2121.

### Instrumental Analyses

The FTIR spectroscopy was carried out with a Digilab FTS-40 (Bio-Rad) and the <sup>1</sup>H-NMR with a Gemini 200 (Varian). A GPC R-410 (Waters) was used to determine molecular weights and their distributions. The thermal properties were analyzed with a TG-DTA 92 (Setaram).

### Preparation of Two-Component Polyurethane Flame-Retardant Coatings

To prepare polyester resin solution, 109.6 g of the trichloro modified polyester was mixed with 39.5 g each of cellosolve acetate, butyl acetate, and toluene. This mixture was blended with additives: 88 g of the white pigment TiO<sub>2</sub>, 0.3 g of the wetting agent BYK P-104S, and 0.4 g of the flowing agent Dow Corning-11. 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 solution with 178.2 g of polyisocyanate resin curing solution. The resulting mixtures of TCAO-10/L-75, TCAO-20/L-75, and TCAO-30/L-75 were named TCPU-10, TCPU-20, and TCPU-30, respectively. The mixture of B-5/L-75 was named BPU-5.

### Physical Properties of Coatings

Three different kinds of substrate materials—cold rolled carbon steel, tin, and glass—were used for the preparation of coating specimens (KS M 5000-1111, 1112). Coatings were painted on each substrate with a thickness of 0.076 mm. Coated samples were dried at 50% relative humidity at 23°C for 7 days.

A Krebs–Stormer viscometer 80328 (Pacific Scientific Co.) was used to determine viscosity. The fineness of grind was estimated with a fineness gauge (Precisions Gauge & Tool). The drying time was measured by the dry-hard method. The pot life was measured based on the degree of cure at which the viscosity reaches the maximum value of 140 kU. The physical properties of the coatings were examined in terms of hardness, flexibility, impact resistance, and abrasion resistance. In addition, a weatherability test of the coatings was performed with a Xenon Weather-O-Meter (Atlas Electric Device) and a Spectro color meter (Nippon Denshoku Kogyo).

### Flame Retardancy Tests

The flame retardancy of prepared two-component polyurethane coatings was examined by the vertical (ASTM D 568-77) and horizontal (ASTM D 635-88) methods.

### Observation with SEM

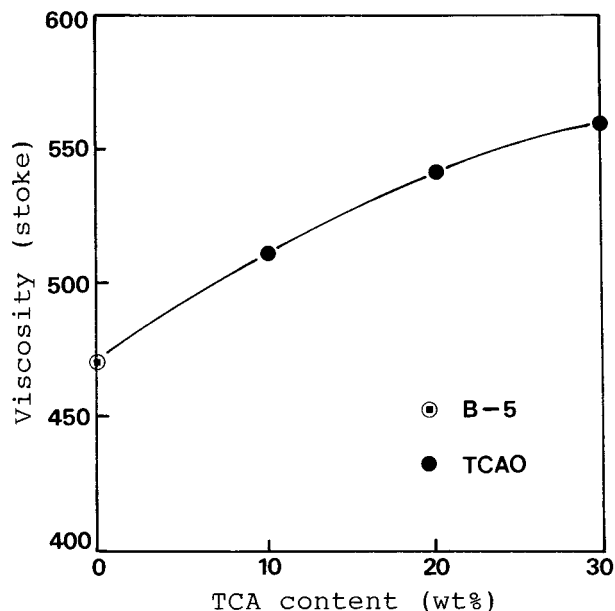
A scanning electron microscope (JSM 840, Jeol, Japan) was used to observe the surface and longitudinal structure after coating the samples with gold film with an ion coater E 5000 from Polaron Equipment Co.

## RESULTS AND DISCUSSION

It is generally known that the properties of polyesters for polyurethane coatings may have the following ranges: molecular weight, 400–6000; OH value, 210–220; and acid value 1–5.<sup>8</sup> To meet the above properties in the preparation of OH-containing modified polyester, the ratio of 1,4-BD, TMP, and AA chosen as diol, triol, and dibasic acid, respectively, was adjusted. The detailed preparation procedure can be found elsewhere.<sup>5,6</sup>

### Identification of Trichloro Modified Polyesters

David<sup>9</sup> and Tehranisa et al.<sup>10</sup> improved the coating properties of alkyd and heat-cured oil-free polyesters by incorporating monobasic acids such as fatty acid, tall oil acid, and benzoic acid. They lowered the average functionality to adjust the molecular weight and viscosity and achieved improvements of hardness, adhesion, drying time, and chemical resistance. However, there are few



**Figure 1** Effect of trichloroacetic acid contents on viscosity in modified polyester.

reports on incorporating monobasic acid to polyesters for the purpose of polyurethane coatings.

We carried out polycondensation of AA, TMP, and 1,4-BD by introducing the monobasic acid TCA to improve polymer properties and flame retardancy. First, an intermediate, TCA-3, was synthesized by the esterification of TCA and TMP to remove unreacted free acid and to maintain the proper molecular structure of the polymer. The modified polyesters were then synthesized by using TCA-3, AA, 1,4-BD, and TMP. The reaction conditions and mechanism are shown in Table I and Scheme 1. In addition, the synthesis of the modified polyesters was confirmed from the results of Tables I-IV.

#### Effects of TCA Content on Kinematic Viscosity

In polyurethane coatings, the viscosity of polyols (i.e., trichloro modified polyesters in this study) plays an important role not only in the rheological properties of paints but also in the physical properties of coatings. If the viscosity of a 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.<sup>11</sup>

Figure 1 shows the effect of TCA contents on the kinematic viscosity of modified polyesters. B-5 showed 470 stokes (S) consistently, but the kinematic viscosity of TCAO increased as TCA content

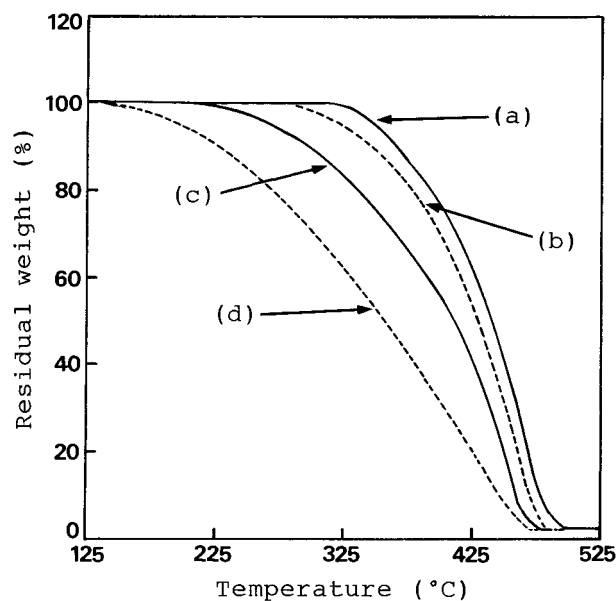
increased. TCA (30 wt %) recorded the highest viscosity of 560 S. The usual kinematic viscosity of polyester coatings with 100% solid is in the range of 100–600 S.<sup>12</sup>

#### Thermal Behavior of Trichloro Modified Polyesters

It has been reported that thermal degradation of polyester is initiated either from chain ends or by the chain scission mechanism<sup>13</sup> and that the number of carboxyl end groups is increased.<sup>14</sup> Figure 2 compares the thermal stabilities of four modified polyesters. Degradation of B-5 begins at 325°C and shows a 96% weight loss at 495°C. TGA profiles of TCAO-10, TCAO-30, and TCA-3 show a weight loss at 265–485, 215–480, and 140–460°C, respectively. The thermal stability of trichloro modified polyesters was greatly influenced by the amount of chlorine, implying that the degradation rate at high temperature increased with chlorine content in the modified polyesters. This tendency agrees well with the previous investigation of low thermal stability of halogen-containing materials.<sup>15</sup>

#### Physical Properties of Flame-Retardant Coatings

Trichloro modified polyesters (TCAO) were blended with polyisocyanate (L-75) to prepare flame-retardant coatings. The physical properties of the coat-



**Figure 2** TGA thermograms of (a) B-5, (b) TCAO-10, (c) TCAO-30, and (d) TCA-3 with the heating of 10°C/min in N<sub>2</sub> gas.

**Table V Physical Properties of Two-Component Polyurethane Flame-Retardant Coatings**

Test Types	Sample Names			
	BPU-5	TCPU-10	TCPU-20	TCPU-30
Viscosity (kU)	55	57	58	59
Fineness of grind	7 <sup>+</sup>	7 <sup>+</sup>	7 <sup>+</sup>	7 <sup>+</sup>
Pot life (h)	8	10	12	13
Drying time (h)	3	3	3	4
Hardness (7 days)	50	44	43	42
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	99.0	100.9	101.2	101.9
Crosshatch adhesion (%)	30	100	100	100
Abrasion resistance (mg loss/100 cycles)	2.0	1.4	4.6	5.7
Accelerated weathering resistance (% gloss retention)	100	98	81	70
Yellowness index ( $\Delta N$ )	0.0774	0.1866	0.2350	0.3147
Lightness index difference ( $\Delta L$ )	1.58	3.05	4.87	7.59

ings are summarized in Table V. Viscosity, fineness of grind, hardness, flexibility, and abrasion resistance of flame-retardant coatings were comparable to those of non-flame-retardant coatings (BPU-5). The flame-retardant coatings show better adhesion characteristics, but less impact resistance, accelerated weathering resistance, yellowness index, and lightness index difference than BPU-5. The pot life and drying time of TCAOs was 10–13 and 3–4 h, respectively. As the ratio of OH/COOH functional groups in the monomer increases, the rate of curing reaction in the coatings decreases and this also has an effect on this long pot life.

### Flame Retardancy of Coatings

The results of the flammability test are listed in Table VI. In the vertical test, BPU-5 and TCPU-15 took 102 and 245 s for a complete combustion, respectively. Samples TCPU-20 and

TCPU-30 revealed a self-extinguishing characteristic. In the horizontal test, BPU-5 and TCPU-5 took 185 and 238 s, respectively, for complete combustion. Sample TCPUs extinguished right after ignition. The results in Table VI imply that flame retardancy increases as chlorine content increases. We believe that the chlorine-containing gases generated from thermal decomposition keep oxygen from being supplied, and this results in the self-extinguishing property<sup>16</sup> of flame-retardant coatings.

### Morphology

Kordomenos et al.<sup>17</sup> observed by SEM that cracks occurred on the film surface of two-component polyurethane coatings due to phase separation. Tehranisa et al.<sup>10</sup> reported that no phase separation occurred in two-component coatings composed of acrylic resin and polyisocyanate.

**Table VI Flame Retardancy Tests of Synthesized Coatings**

Testing Methods	BPU-5 (s)	TCPU-5 <sup>a</sup> (s)	TCPU-10 (s)	TCPU-15 <sup>a</sup> (s)	TCPU-20 (s)	TCPU-30 (s)
Vertical	102 <sup>b</sup>	139	160	245	SE	SE
Horizontal	185	238	SE	SE	SE	SE

SE, self-extinguishing property.

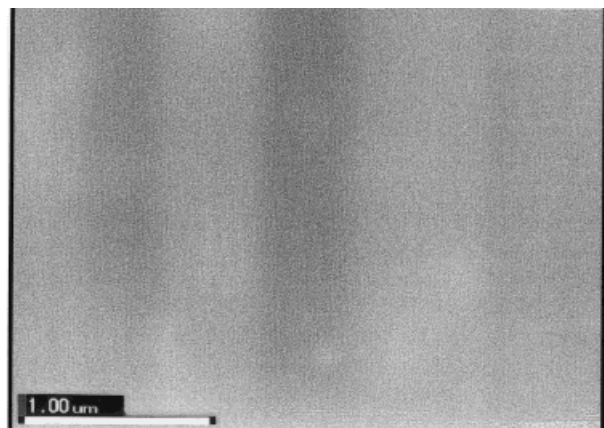
<sup>a</sup> The blends of TCAO-5/L-75 and TCAO-15/L-75 were named TCPU-5 and TCPU-15, respectively.

<sup>b</sup> The average value obtained from the result of five independent tests.

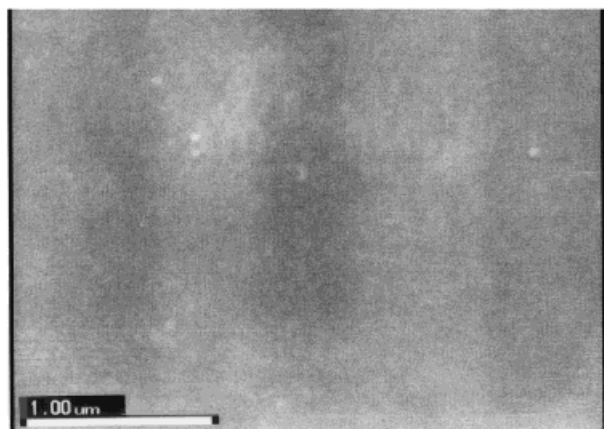
Figure 3 and 4 are the SEM results on the surface and longitudinal side of the films coated with flame-retardant coatings produced in this research. Figure 3 shows that BPU-5 and TCPU-30 have no cracks due to phase separation and no pinholes, craters, crawling, orange peel, and mooning except a few fisheyes.<sup>18</sup> Wavy dispersed shapes are shown on the longitudinal side structure (Fig. 4) whereas the spherical white particles<sup>18</sup> inside the film are those of pigment.

## CONCLUSIONS

Trichloro modified polyesters were synthesized by polycondensation of AA, 1,4-BD, TMP, and TCA.

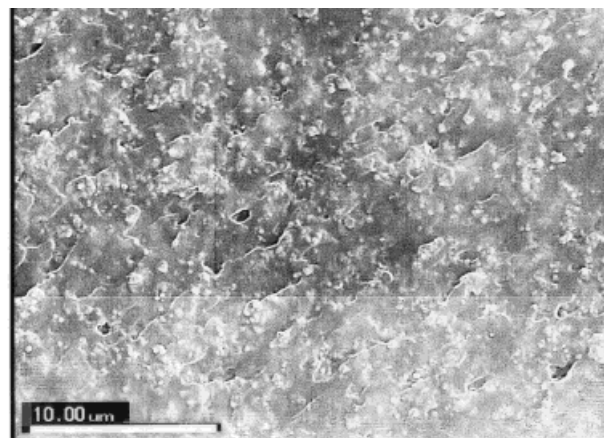


(a)

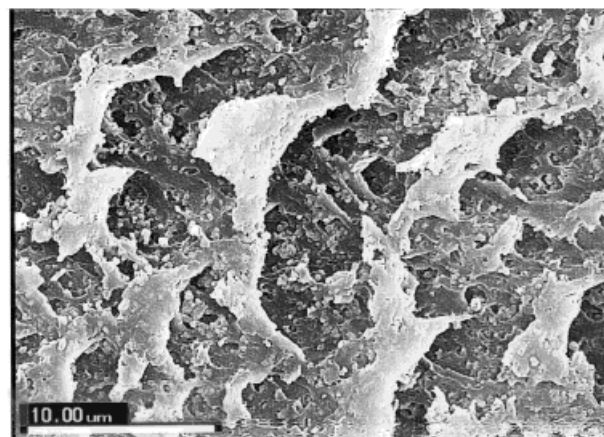


(b)

**Figure 3** Scanning electron micrographs of the surface of two-component polyurethane flame-retardant coatings: (a) BPU-5 and (b) TCPU-30. [Original magnifications]  $\times 30,000$ .



(a)



(b)

**Figure 4** Scanning electron micrographs of the longitudinal structure of two-component polyurethane flame-retardant coatings: (a) BPU-5 and (b) TCPU-30. [Original magnifications]  $\times 3000$ .

Two-component polyurethane coatings were prepared by blending polyisocyanate and these trichloro modified polyesters. The kinematic viscosity increased with increasing chlorine content. The prepared coatings showed drying times of 3–4 h and pot life times of 10–13 h. Most of the physical properties of the flame-retardant coatings were comparable to those of non-flame-retardant coatings. The coatings with 20 wt % TCA had a self-extinguishing property.

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