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Synthesis and Flame-Retardant Improvement of PU Coatings Containing Trichloro Modified Polyester/IPDI-Isocyanurate

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Abstract : Two-component polyurethane (PU) flame-retardant coatings were prepared by blending trichloro modified polyesters (TCMPs) and isophorone diisocyanate-isocyanurate. TCMPs were synthesized by polycondensation of trichlorobenzoic acid (TCBA), a flame-retardant component, with adipic acid, 1,4-butanediol, and trimethylolpropane. The content of TCBA was varied in 10, 20, and 30 wt% for the reaction. Theses new flame-retardant coatings showed various properties comparable to other non-flame-retardant coatings. Moreover, we carried out the combustion test and the flammability test for our flame-retardant coatings. The results of vertical burning test for the coatings containing more than 20 wt% of TCBA were determined as no burn. The results of flammability test for the coatings with 20 wt% and 30 wt% of TCBA contents indicated the limiting oxygen index (LOI) values of 26% and 29% respectively, which implied relatively good flame retardancy.

Keywords : trichloro modified polyester, IPDI-isocyanurate, PU coatings, combustion, flammability, vertical burning test, LOI method.

1. Introduction

Flame-retardant coatings are noncombustible materials, which prevent or delay flash over from the coating surface of combustibles. Recently, interest has been growing in developing flame-retardant coatings[1-3] of two-component polyurethane (PU), because they have many advantages such as good cross-hatch adhesion, resistance against abrasion, weathering, and chemicals, and curing at ambient temperature.

It is the purpose of this article to present the synthesis of flame-retardant two-component PU coatings and to characterize the physical properties and the flammability of the prepared coatings. First we polycondensed trichloro group-containing

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aromatic carboxylic acid and polyol to synthesize chlorinated modified polyester prepolymers. Two-component PU flame-retardant coatings were then prepared by blending these polyester prepolymers with isocyanate, wetting agent and pigment. The prepared coatings were characterized in terms of physical properties [4], combustion [5], and flammability [6] test results.

2. Experimental

2.1. Materials

Trimethylolpropane (TMP) and trichlorobenzoic acid (TCBA) were purchased from Tokyo Kasei Inc., and adipic acid (AA) and 1,4-butanediol (1,4-BD) were from Sigma Chemical Inc. and used as received. Our isocyanate was isophorone diisocyanate (IPDI) -isocyanurate (Desmodur Z-4470, solid content 70%, NCO content 12%, Viscosity of 1600 mPa·s at 23℃) from Bayer Leverkusen Co. TiO_2 (Britisch 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.

2.2. Synthesis of Trichloro Modified Polyesters

TCBA/TMP Intermediate : The reaction conditions for the synthesis of TCBA/TMP intermediate are given in Table 1. The reaction procedure is the same as that of modified polyester (B-10). Reaction products were purified by precipitation with excess n-hexane and the transparent TCBA-adduct, which is a TCBA/TMP intermediate, was obtained by vacuum drying at 50℃ and 7 mmHg.

Trichloro Modified Polyesters : The polymerization conditions for the synthesis of polyester containing 10 wt% TCBA are given in row TCMP-10 of Table 1. Unreacted 1,4-BD and AA were removed by distilled water and the remaining TMP was then removed by n-hexane precipitation resulting in a transparent polyester prepolymer with 10 wt% TCBA (TCMP-10). Rows TCMP-20 and TCMP-30 in Table 1 are the conditions for the synthesis of polyester containing 20 wt% (TCMP-20) and 30 wt% (TCMP-30) TCBA, respectively.

2.3. 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.

2.4. Preparation of Two-Component PU Flame-Retardant Coatings

The modified polyester produced (110g) was mixed with 40 g each of cellosolve acetate, ethyl acetate, butyl acetate, and toluene. To prepare polyester resin solution, TiO_2 88g white pigment, 0.4g dispersant BYK P-104S, and 0.5g flowing agent Dow Coring-11 were blended with the mixture. Isocyanate resin curing solution was prepared by adding 25g each of cellosolve acetate and xylene to 150g of IPDI-isocyanurate.

Two-component PU Coatings were prepared by blending 359g of polyester resin and 200g of isocyanate resin curing solution at the time of film formation. Resulting blends of TCMP-10/IPDI, TCMP-20/IPDI, and TCMP-30/IPDI were named TCPU-10, TCPU-20, TCPU-30, respectively. The blend of B-10/IPDI was named BPU-10.

2.5. 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 0.076mm. Coated samples were dried at 50% relative humidity

and 23℃ for 7 days. Tin sheets (KS D 3516) were prepared according to the KS M 5000-1112 manual. After polishing and cleaning, 0.076mm 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, 200×150×5mm glass sheets were coated with the same products as the tin sheets.

Methods for Property Examination : The Krebs-Stormer viscometer 80328 from Pacific Scientific Co. was used to determine viscosity. Fineness of grind was estimated with a fineness gauge from Precisions Gauge & Tool. Measurement of drying time was carried out by the dry-hard method. Pot-life was measured based upon the degree of curing at which the viscosity reachs maximum, 140 KU. Hardness was determined by 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 spectrocolorimeter (model SZ-∑80) from Nippon Denshoku Kogyo was used to determine yellowness. Lightness index differences were measured according to the KS M 5000-3031 manual.

2.6. Flame Retardancy Tests

In order to test flame retardancy of flame-retardant coatings, TCPU, the combustibility and flammability of the specimens coated by the coatings were measured. The combustibility was measured by a vertical test (ASTM D568-77) and a horizontal test (ASTM D635-88)[7], and the flammability (ASTM D568-77, with A-type specimen) was measured by the limiting oxygen index method (LOI method) using a combustion tester (ON-1, Yoyo Rika Co.).

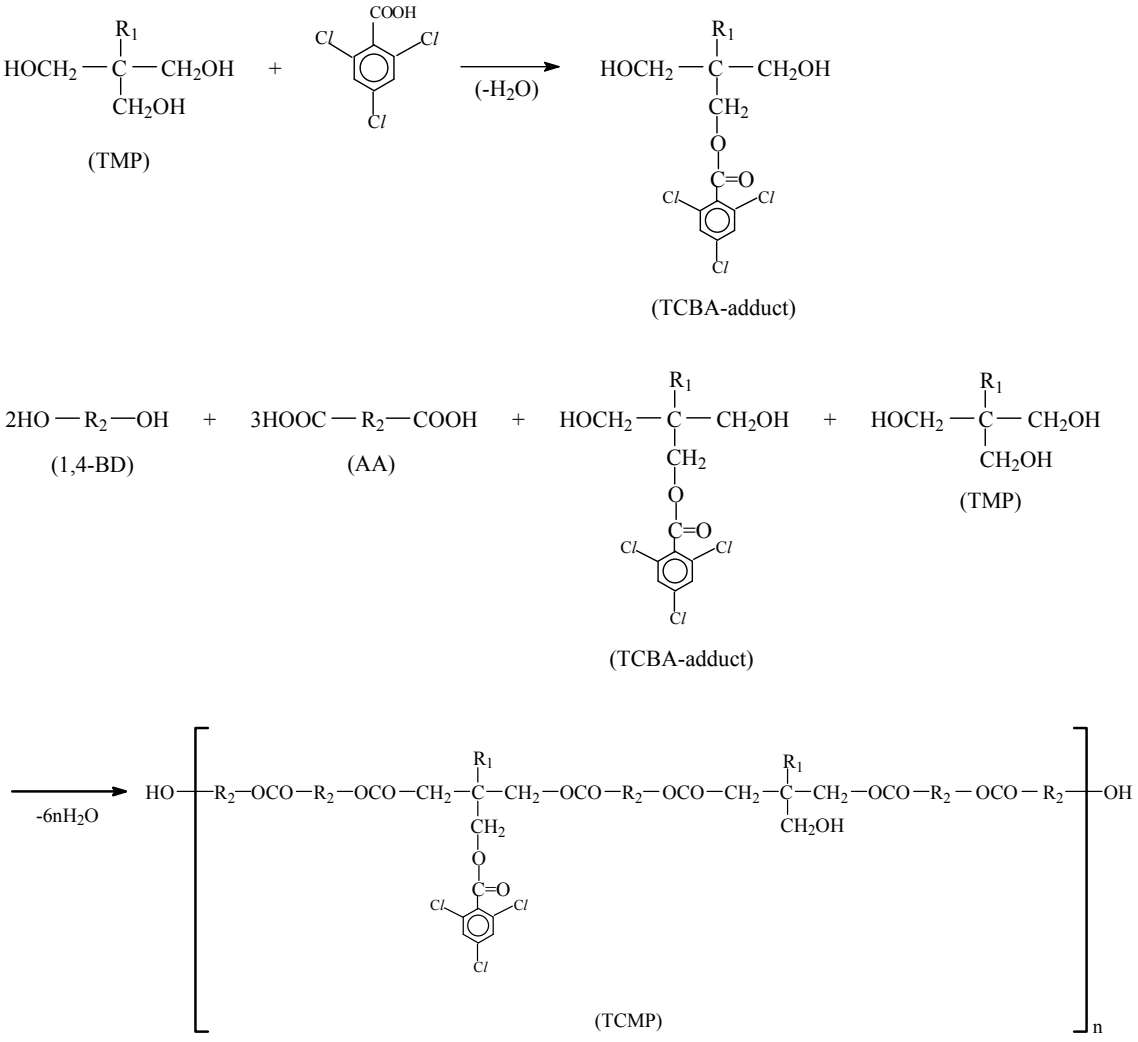
3. Results and Discussion

3.1. Identification of Trichloro Modified Polyesters

Formerly, Kashyap et al. [8] prepared fast-drying and chemicals-resistant coatings by using benzoic modified polyester resins. Recently, Shin et al. [9] prepared a modified polyester by using 3,5,5-trimethylhexanoic and used it to prepare polyurethane coatings.

We here carried out polycondensation of AA, TMP, and 1,4-BD by introducing monobasic acid, TCBA, to improve polymer properties and flame retardancy. We carried out two-step synthetic method. First, an intermediate, TCBA-adduct was synthesized by the esterification of TMP and TCBA to eliminate unreacted free acid. Next the TCBA-adduct was used in the polycondensation reaction with 1,4-BD, AA, and TMP. The chemical structure and the reaction condition for the synthesis of TCBA-adduct are shown Fig. 1 and Table 1.

The results of absorption peaks of FTIR spectrum and the chemical shifts of 1H-NMR spectrum are summarized in Table 2. The observed peaks are coincident with theoretical peaks of TCBA-adduct. The observed chlorine contents in TCBA-adduct are in good agreement with the calculated result as shown in Table 3. No catalyst is used in the synthesis of TCMP because the existence of catalyst tends to reduce pot-life when it is blended with isocyanate. Sufficient dehydration occurred during the reaction and the acid value was maintained below 5. The results of FTIR spectrum and 1H-NMR spectrum in Table 2 may identify modified chlorine-containing polyester as the structure of TCMP-10 as shown in Fig. 1. Table 4



R1 : -CH2-CH3
R2 : -(CH2)4-

Fig. 1. Synthesis of TCBA-adduct and TCMP.

Table 1. Molar Ratios of the Reactants and Reaction Conditions for Modified Polyester, TCBA/TMP Intermediate, and Trichloro Modified Polyesters

Products	Reactants						Reaction		Acid value	Dehydration (mL)	Yield (%)
	1,4-BD[a] g(mol)	AA[b] g(mol)	TMP[c] g(mol)	TCBA[d] g(mol)	TCBA-adduct[e] g	Toluene g	Temp (℃)	Time (h)			
B-10	54.5 (0.61)	151.1 (1.04)	81.7 (0.61)	—	—	10	130~220	16	3.5	37.0	94
TCBA -adduct	—	—	100.5 (0.75)	169.2 (0.75)	—	10	130~180	12	3.8	13.3	93
TCMP-10	51.4 (0.57)	130.7 (0.90)	64.2 (0.72)	—	38.0	10	130~180	12	4.0	34.0	90
TCMP-20	48.4 (0.54)	110.3 (0.76)	46.6 (0.35)	—	76.0	10	120~175	11	3.0	31.0	89
TCMP-30	45.4 (0.51)	89.8 (0.62)	29.1 (0.22)	—	113.9	10	120~175	11	2.5	27.9	87

a1,4-BD : 1,4-Butanediol
bAA : Adipic acid
cTMP : Trimethylolpropane
dTCBA : Trichlorobenzoic acid
eTCBA-adduct : TCBA/TMP intermediate

Table 2. FTIR and 1H-NMR Chemical Shifts of TCBA-adduct and TCMP-10

Products	FTIR (KBr, cm^{-1})	1H-NMR (200MHz, $CDCl_3$, ∂ in ppm)
TCBA-adduct	2980 : CH_3	0.9 (CH_3-C)
	3380 : OH	1.6 (C-CH_2-C)
	1470 : -CH_2-	3.4 (R-OH)
	1750 : C=O	3.7 (C-CH_2-O-)
	1580 : C=O of Ar	4.4 (C-CH_2-OCO-)
	1060 : OH of pri-alcohol	7.4~7.7 (-CH=CH of Ar)
TCMP-10	2970 : CH_3	0.9 (CH_3-C)
	3520 : OH	1.5 (-CH_2-C)
	1470 : -CH_2-	1.7 (C-CH_2-C)
	1740 : C=O	2.4 (C-CH_2-CO-)
	1180 : C-O-	3.6 (C-CH_2-O-)
	1060 : OH of pri-alcohol	4.2 (C-CH_2-OCO-)
		7.4~7.7 (-CH=CH of Ar)

Table 3. Chlorine Content for TCBA-adduct a Measured by reforming combustion flask method at 25℃.

Type	Molecular formula	Mw	*Cl* content[a]	
			Calcd	Observed
TCBA–adduct	$C_{13}H_{16}O_4Cl_3$	342.5	31.09	30.09

Table 4. Molecular Weight Distribution Data for B-10 and TCMPs Determined by GPC

Type	$\overline{M_n}$	$\overline{M_w}$	$\overline{M_z}$	$\overline{M_w}/\overline{M_n}$
B-10	3070	5250	8010	1.71
TCMP-10	2850	4500	6970	1.58
TCMP-20	2560	3580	5300	1.40
TCMP-30	2310	2890	4410	1.25

lists the molecular weight characteristics of modified chlorine-containing polyesters. The presence of TCBA-adduct increases the content of hydroxyl group in TCMP, which reduces the reactivity of TCMP. This is the reason that the molecular weight and the polydispersity tend to decrease with increasing chlorine contents.

3.2. Physical Properties of Flame-Retardant Coatings

The synthesized trichloro modified polyesters were blended with IPDI-isocyanurate to prepare flame-retardant coatings. Table 5 summarizes the physical properties of coated films depending on the TCBA content. Viscosity, fineness of grind, hardness, 60°specular gloss, and accelerated weathering resistance of flame-retardant TCPUs were comparable to those of non-flame-retardant coatings BPU-10. TCPUs showed better pot-life and cross-hatch adhesion but drying time, flexibility, impact resistance, abrasion resistance, yellowness index, and lightness index difference than BPU-10. The pot-life of TCPUs was 13~19 h, which belong to the long pot-life coatings.

3.3. Combustion and Flammability of Coatings

Flame-retardant coatings should have slow combustion and self-extinguishing properties. Decomposition gases of flame-retardant coatings suppress flaming combustion and thus stop nonflaming combustion [10,11]. Chlorine compounds usually have low flammability in the gaseous state. The presence of chlorine affects the chemical reactions during combustion, and thus suppresses the access of oxygen and heat transfer by generating chlorine-containing heavy gases.

Table 6 shows the results of flame-retardant tests with the synthesized coatings. In vertical test, BPU-10, TCPU-5, TCPU-10, and TCPU-15 took 101, 130, 151, and 218s, respectively, for the complete combustion. Flame of TCPU-20 was extinguished right after ignition. In horizontal test with TCPUs, flames were soon extinguished after ignition.

Table 5. Physical Properties of TCMP/IPDI PU Flame-Retardant Coatings

Test types	BPU-10	TCPU-10	TCPU-20	TCPU-30
Viscosity (KU)	61	59	58	56
Fineness of grind	7 +	7 +	7 +	7 +
Drying time (h)	3	4	6	8
Pot-life (h)	8	13	15	19
Sward hardness (7days)	50	48	42	38
Flexibility (1/8 inch)	good	good	good	poor
Impact resistance (1000g/500cm) Direct Reverse	 good good	 good good	 poor poor	 poor poor
60°Specular gloss	98.5	99.0	100.7	100.9
Cross-hatch adhesion (%)	30	88	90	91
Abrasion resistance (mg loss/100 cycles)	2.0	3.2	5.8	9.9
Accelerated weathering resistance (% gloss retention)	100	98	96	95
Yellowness index (ΔN)	0.075	0.187	0.315	0.406
Lightness index differenc(ΔL)	1.55	3.07	4.92	6.20

Table 6. Flame Retardancy Test of the Synthesized Coatings

Testing methods	BPU-10 (s)	TCPU-5[a] (s)	TCPU-10 (s)	TCPU-15[a] (s)	TCPU-20 (s)	TCPU-30 (s)
Vertical Horizontal	101[b] 190	130 240	151 SE	218 SE	SE[c] SE	SE SE

aThe blends of TCMP-5/IPDI and TCMP-15/IPDI were named TCPU-5 and TCPU-15, respectively.
bThe average value obtained from the result of five independent tests.
cSE : It denotes self-extinguishing property.

Fig. 2 shows the distribution of LOI values of TCPU with various TCBA content. The LOI value of a non-flame-retardant coating, BPU-10, was 17%, whereas the LOI values of flame-retardant coatings, TCPUs, were increased with increasing TCBA content, becoming 29% at 30% TCBA.

Results in Table 6 and Fig. 2 suggest that flame retardancy increases as chlorine content increases. This may be because chlorine-containing gases such as HCl generated from thermal decomposition block the access of

oxygen and consequently suppress the flammable combustion of PU coatings.

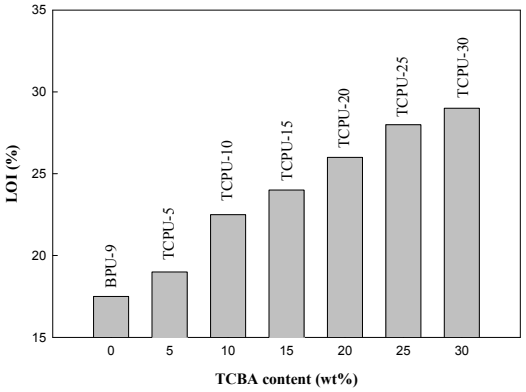


Fig. 2. Relationship between LOI and trichlorobenzoic acid contents of trichloro modified polyester in the two-component polyurethane flame-retardant coatings.

4. Conclusions

Two-component PU flame-retardant coatings were prepared by blending isocyanate and chlorine-containing modified polyesters (TCMPs) synthesized in our lab. Some physical properties such as viscosity, fineness of grind, hardness, 60° specular gloss, and accelerated weathering resistance were comparable to those of non-flame-retardant coatings. Meanwhile, a substantial loss of drying time, flexibility, impact resistance, abrasion resistance, yellowness index, and lightness index difference was observed. From the tests on the combustibility and flammability of the prepared flame-retardant coatings, it proved that the coatings possess excellent flame retardancy.

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