

Preparation and Flame-Retardant Optimization of PU Coatings Using Chlorine-Containing Modified Polyester/IPDI-Isocyanurate

Hyuk-Jae You · Il-Woo Shim · Hye-Jin Jo · Hong-Soo Park[†]
Seung-Jin Kim* · Young-Geun Kim*

Department of Chemical Engineering, Myongji University, Yongin 449-728, Korea

**Korea Institute of Construction Materials, Seoul 137-707, Korea*

(Received September 13, 2004 ; Accepted December 10, 2004)

Abstract : Chlorine-containing modified polyester polyols were synthesized by two-step condensation reactions. Intermediate was synthesized by the esterification of monochloroacetic acid with trimethylolpropane in the first step. Polycondensation of the intermediate (MCAOs), 1,4-butanediol, and trimethylolpropane with adipic acid was carried out. Two-component polyurethane (PU) coatings were prepared by blending MCAOs and IPDI-isocyanurate. These new flame-retardant coatings showed various properties comparable to other non-flame-retardant coatings. They were superior to flammable coatings from the experimental results showing rapid and 10 to 13 hours of pot-life. Coatings with 30wt% monochloroacetic acid was not flammable by the vertical flame retardancy test.

Keywords : chlorine-containing modified polyester, IPDI-isocyanurate, PU coatings, flame retardancy.

1. Introduction

Polyurethane (PU) flame-retardant coatings are generally nonintumescent[1,2]. The combustion property of PU is greatly influenced by the polyol or isocyanate structure. In general, phosphates are introduced to the polyol structure to give flame retardancy. To give flame retardancy to isocyanate, such as diphenyl-methane-4,4'-diisocyanate (MDI) and toluene diisocyanate (TDI), are introduced[3,4].

There are few reports on the synthesis of two-component PU flame-retardant coatings by chemical reaction, not by blending. Presenting the synthesis of flame-retardant two-component PU coatings possessing improved pot-life and yellowness is the goal of this study. First we polycondensed chlorine-containing aliphatic carboxylic acid and polyester to synthesized modified polyester prepolymers. Two-component PU flame-retardant coatings were then prepared by blending these polyester prepolymers with isocyanate, wetting/dispersing agent, and white pigment. Characterizations are presented for the properties of the prepared coatings,

[†] To whom all correspondence should be addressed.
(e-mail : hongsu@mju.ac.kr)

including flame retardancy by vertical and horizontal tests.

2. Experimental

2.1. Materials

Adipic acid (AA) and trimethylolpropane (TMP) were purchased from Hayashi Pure Chemical, and 1,4-butanediol (1,4-BD) and monochloroacetic acid (MCA) were from Tokyo Kasei. Isocyanate prepolymer was Desmodur Z-4470 [isophorone diisocyanate (IPDI)-isocyanurate] from Bayer which has 70% solid, 12% NCO, and 1600mPa·s viscosity at 23°C. Dow Corning Chemicals as a flowing agent, BYK P-104S from BYK-Mallinckrodt as a wetting/dispersing agent, and TiO₂ from British Titan was used as a white pigment.

2.2. Synthesis of Modified Polyester

The synthetic condition of the modified polyester was the same as the B-9 in Table 1. The detailed synthetic condition was described in the previous paper[5].

2.3. Synthesis of Chlorine-Containing Modified Polyester

MCA/TMP intermediate : The reaction conditions for the synthesis of MCA/TMP intermediate are given in Table 1. Reaction products were purified by precipitation with *n*-hexane and the transparent neohexanediol chloroacetate (NHCA), which is a MCA/TMP intermediate, was obtained by vacuum drying at 50°C and 5mmHg.

Chlorine-Containing Modified Polyesters : The polymerization conditions for the synthesis of polyester containing 10wt% MCA are given in row MCAO-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 10wt% MCA (MCAO-10).

Rows MCAO-20 and MCAO-30 in Table 1 are the conditions for the synthesis of polyester containing 20wt% (MCAO-20) and 30wt% (MCAO-30) MCA, respectively.

2.4. Instrumental Analyses

The FTIR spectroscopy was carried out with a Digilab FTS-40 (Bio-Rad) and the ¹H-NMR with a Gemini 200 (Varian). A GPC R-410 (Waters) was used to determine molecular weights and their distributions.

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

Two-component PU coatings were prepared by blending 350g of polyester resin solution with 190g of isocyanate resin curing solution. The resulting mixture of MCAO-10/IPDI, MCAO-20/IPDI, and MCAO-30-/IPDI were named MCPU-10, MCPU-20, and MCPU-30, respectively. The mixture of B-9/IPDI was named BPU-9.

2.6. Physical Properties of Coatings

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).

2.7. Flame Retardancy Tests

The flame retardancy of prepared two-component PU coatings was examined by the vertical (ASTM D 568-77) and

Table 1. Reaction Conditions and Physical Properties for Modified Polyester, MCA/TMP Intermediate, and Chlorine-Containing Modified Polyesters

Products	Materials						Reactions		Acid value	Dehydration (mL)	Conversion (%)
	1,4-BD ^a g(mol)	AA ^b g(mol)	TMP ^c g(mol)	MCA ^d g(mol)	NHCA ^e g	Toluene g	Temp (°C)	Time (h)			
B-9	54.5(0.61)	151.1(1.04)	81.7(0.61)	—	—	10	140~220	16	4.2	37.1	94
NHCA	—	—	160.8(1.20)	113.4(1.20)	—	10	110~200	10	3.9	22.0	88
MCAO-10	53.5(0.60)	127.7(0.88)	49.2(0.25)	—	56.0	10	110~200	10	4.4	36.2	88
MCAO-20	52.4(0.58)	104.2(0.72)	16.7(0.13)	—	111.9	10	100~205	11	4.9	35.1	87
MCAO-30	51.4(0.57)	80.7(0.56)	77.1(0.58)	—	75.0	10	100~210	12	5.7	34.2	84

^a1,4-BD : 1,4-Butanediol^bAA : Adipic acid^cTMP : Trimethylolpropane^dMCA : Monochloroacetic acid^eNHCA : MCA/TMP intermediate

horizontal (ASTM D 635-88) methods.

3. Results and Discussion

3.1. Identification of Chlorine-Containing Modified Polyester

Glaser[6] and Tehranisa et al.[7] 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 molecular weight and viscosity, and achieved improvements of hardness, adhesion, drying time, and chemical resistance. However, there are few reports on incorporating monobasic acid to polyesters for the purpose of PU coatings.

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

The results of absorption peaks of FTIR spectrum and the chemical shifts of $^1\text{H-NMR}$ spectrum are summarized in Table 2. The observed peaks are coincident with theoretical peaks of NHCA. The observed chlorine contents in NHCA are in good agreement with the calculated results as shown in Table 3. No catalyst is used in the synthesis of MCAO 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 $^1\text{H-NMR}$ spectrum in Table 2 may identify modified chlorine-

containing polyester as the structure of MCAO-10 as shown in Scheme 1. Table 4 lists the molecular weight characteristics of modified chlorine-containing polyesters. The presence of NHCA increases the content of hydroxyl group in MCAO, which reduces the reactivity of MCAO. This is the reason that the molecular weight and the polydispersity tend to decrease with increasing chlorine contents.

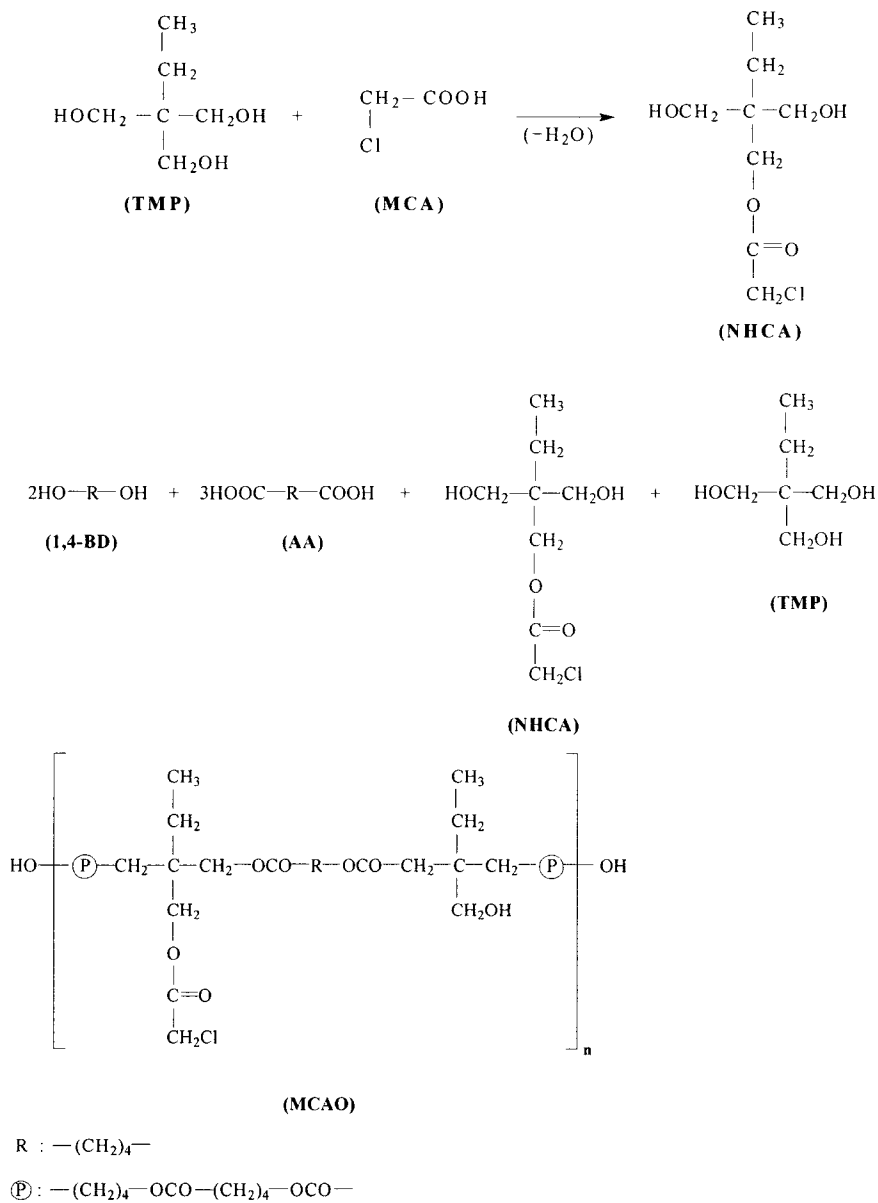
3.2. Property Changes of Flame-Retardant Coatings

The synthesized monochloro modified polyesters were blended with IPDI-isocyanurate to prepare flame-retardant coatings. Table 5 summarizes the physical properties of coated films depending on the MCA content. Viscosity, fineness of grind, hardness, flexibility, and accelerated weather resistance of flame-retardant MCPUs were comparable to those of non-flame-retardant coatings BPU-9. MCPUs showed better cross-hatch adhesion, drying time and pot-life but impact resistance, abrasion resistance, yellowness index and lightness index difference than BPU-9. The pot-life of MCPUs was 10~13h, which belong to the long pot-life coatings. Here the reason for longer pot-life of MCPUs for higher MCA contents, is that the molar content of OH in polyol was increased and thus reactivity was lowered as MCA content increased[8].

3.3. Flame Retardancy of Coatings

Flame-retardant coatings should have the characteristics of show combustion and self-extinguishing properties. 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[9].

Table 6 shows the results of flame-retardant tests with the synthesized coatings.



Scheme 1. Structure of NHCA and MCAO.

Table 2. FTIR and $^1\text{H-NMR}$ Chemical Shifts of NHCA and MCAO-10

Products	FTIR (NaCl, cm^{-1})	$^1\text{H-NMR}$ (200MHz, CDCl_3 , δ in ppm)
NHCA	3420 : OH 1290 : OH of pri-alcohol 1060 : OH of pri-alcohol 1740 : C=O 2970 : CH_3 1470 : $-\text{CH}_2-$	0.9 (t, 3H, CH_3-C) 1.5 (m, 2H, $\text{C}-\text{CH}_2-\text{C}$) 3.1 (s, 2H, R-OH) 3.5 (m, 4H, $\text{C}-\text{CH}_2-\text{O}-$) 3.7 (d, 2H, $\text{C}-\text{CH}_2-\text{OCO}-$) 4.2 (t, 2H, $\text{C}-\text{CH}_2-\text{O}-$)
MCAO-10	1730 : C=O 1180 : C-O- 3520 : OH 1060 : OH of pri-alcohol 2960 : $-\text{CH}_2-$ 1470 : $-\text{CH}_2-$	0.9 (CH_3-C) 1.5 ($-\text{CH}_2-\text{C}$) 1.7 ($\text{C}-\text{CH}_2-\text{C}$) 2.4 ($\text{C}-\text{CH}_2-\text{CO}-$) 3.6 ($\text{C}-\text{CH}_2-\text{O}-$) 4.1 ($\text{C}-\text{CH}_2-\text{OCO}-$)

Table 3. Chlorine Content for NHCA

Type	Molecular formula	MW	Cl content ^a	
			Calcd	Observed
NHCA	$\text{C}_8\text{H}_{15}\text{O}_4\text{Cl}$	210.5	16.86	16.84

^aMeasured by reforming combustion flask method at 25°C

Table 4. Molecular Weight Distribution Data for B-9 and MCAOs Determined by GPC

Type	M_n	M_w	M_z	M_w/M_n
B-9	1550	3070	4850	1.98
MCAO-10	1260	2180	3990	1.73
MCAO-20	1150	1730	3160	1.50
MCAO-30	1000	1440	2890	1.44

In the vertical test, BPU-9, MCPU-10, and MCPU-20 took 102, 145, and 188 sec for a complete combustion, respectively. Samples MCPU-30 revealed a self-extinguishing characteristic. In the horizontal test with MCPUs, the burning of BPU-9 lasted 180 sec, but MCPUs were soon extinguished after ignition. Results in Table 6 suggest 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[10] of flame-retardant coatings.

Table 5. Physical Properties of Two-Component PU Flame-Retardant Coatings

Test types	BPU-9	MCPU-10	MCPU-20	MCPU-30
Viscosity(KU)	56	57	59	60
Fineness of grind	7 ⁺	7 ⁺	7 ⁺	7 ⁺
Pot-life (h)	8	10	11	13
Dring time, D. H(h)	3	2	2	2
Pencil hardness (7days)	2H	H	H	H
Flexibility (1/8")	good	good	good	good
Impact resistance 1000g/50cm direct reverse	good good	good good	good good	poor poor
60° Specular gloss	99.3	100.8	100.5	99.4
Cross-hatch adhesion (%)	30	100	100	100
Abrasion resistance (mg loss/100 cycles)	2.1	2.5	5.7	12.8
Accelerated weathering resistance (% gloss retention)	100	98	97	95
Yellowness index (ΔN)	0.0806	0.1277	0.1603	0.2194
Lightness index difference (ΔL)	1.59	1.90	2.67	5.40

Table 6. Flame Retardancy Tests of Synthesized Coatings

Testing methods	BPU-9 (s)	MCPU-10 (s)	MCPU-20 (s)	MCPU-30 (s)
Vertical	102 ^a	145	188	SE ^b
Horizontal	180	SE	SE	SE

^aThe average value obtained from the result of five independent test

^bSE : It denotes self-extinguishing property.

4. Conclusions

Two-component PU coatings were prepared by blending isocyanate and these monochloro aliphatic modified polyester. Various physical properties of new flame-retardant coatings (MCPUs) were comparable to non-flammable -retardant coating. MCPUs showed drying time of 2 h and pot-life time of 10 to 13 h. In vertical burning test, coating with 20wt% monochloroacetic acid proved to be a good flame-retardant coatings with 188 sec of burning time.

Acknowledgements

This work was supported by the RRC program of Most and Gyeonggi-do.

References

1. P. Nowak, D. Robert, and W. Coggio, Pressure-Sensitive Adhesive Composition Containing a Nonhalogen and Nonintumescent Flame-Retardant Agent and Tapes Therefrom, Eur. Pat. Appl.,

- 775736A2 (1997).
2. E. D. Weil and S. V. Levchik, Commercial Flame Retardancy of Polyurethanes, *J. Fire Sciences*, **22**(3), 183 (2004).
 3. Y. Wang and J. W. Nowicki, Flame-Retardant Polyurethane Adhesive Composition, PCT Int. Appl., 026874A1 (2002).
 4. S. Duquesne, M. Le Bras, S. Bourbigot, R. Delobel, H. Vezin, G. Camino, B. Eling, C. Lindsay, and T. Roels, Expandable Graphite : A Fire Retardant Additive for Polyurethane Coatings, *Fire and Materials*, **27**(3), 103 (2003).
 5. H. S. Park, H. S. Hahm, and E. K. Park, Preparation and Characteristics of Two-Component Polyurethane Flame-Retardant Coatings Using 2,3-Dibromo Modified Polyesters, *J. Appl. Polym. Sci.*, **61**, 421 (1996).
 6. D. W. Glaser, Alkyd Resin Calculation Factors, *Official Digest*, **33**(436), 642 (1961).
 7. M. Tehranisa, R. A. Ryntz, H. X. Xiao, P. I. Kordomenos, and K. C. Frisch, Urethane Acrylic Interpenetrating Polymer Networks for Coating Applications, *J. Coat. Technol.*, **59**(746), 43 (1987).
 8. H. F. Mark, N. M. Bikales, C. G. Overberger, G. Menges, and J. I. Kroschwitz, "Encyclopedia of Polymer Science and Engineering", Vol. 1, p. 656, Wiley, New York (1985).
 9. H. Homstrand, P. Andersson, and O. Gustafsson, Chlorine Isotope Analysis of Submicromole Organochlorine Samples by Sealed Tube Combustion and Thermal Ionization Mass Spectrometry, *Analytical Chemistry*, **76**(8), 2336 (2004).
 10. H. Peerlings, W. Brauer, H. G. Wussow, J. Winkler, and H. G. Hoppe, Thermoplastically Processable Polyurethanes (TPU) with Self-Extinguishing Properties, Their Preparation and Use, U.S. Pat. Appl. Publ., 039147A1 (2004).