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Synthesis and Physical Properties of Two-Component Polyurethane Coatings Containing Alkyd and Polyester Polyols

Hong-Soo Park*, Young-Je Jeon, and Seong-Kil Kim

Department of Chemical Engineering, Myong Ji University, Yongin 449-728, Korea

Doo-Whan Kang

Department of Polymer Science and Engineering, Dan Kook University, Seoul 140-714, Korea

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Abstract: Modified polyesters containing alkyd and polyester polyols were synthesized. Alkyd modified polyesters (THAOs) were synthesized from the polycondensation of 1,4-butanediol, adipic acid, and the esterification adduct (THA-TMP) of 3,5,5-trimethylhexanoic acid (THA) and trimethylolpropane (TMP). The THA contents of the adduct were 10, 20, and 30 wt%. Two-component polyurethane coatings were prepared by blending THAOs with Desmodur IL, the polyisocyanate component. The two-component polyurethane coatings had shorter drying times and longer pot-life as the THA content increased, as can be expected from the characteristics of alkyd component. This shows that the two-component polyurethane coatings can be used as rapid drying coatings.

Introduction

The two-component polyurethane coatings[1-3] are classified into catalyst-cured and polyol-cured types. Among them, the polyol-cured type have been of more interest, because the polyols and polyisocyanates can easily be reacted at room temperature to produce three dimensional crosslinked structures, which have better physical properties than any other kinds of polyurethane coatings.[4]

Recently, Xiao *et al.*[5] prepared two-component polyol-cured type polyurethane coating by reacting a polyacrylate polyol with Desmodur N-100 as the polyisocyanate component, and Park *et al.*[6,7] prepared two-component polyurethane flame retardant coatings by reacting aliphatic polyester polyols containing bromine or chlorine with Desmodur L-75, and obtained good flame retardance and improvement of the physical properties of the coating film. Also, Park *et al.*[8] reported on the preparation of a new type of modified polyester of lower viscosity by adding varied amounts of benzoic acid in the preparation of the polyester polyol component, and suggested that the solids content may be increased by using the modified polyester polyol component.

Therefore, the physical properties of the coating film may be greatly enhanced, if a two-component polyurethane coatings employing polyester polyol and alkyd polyol can be synthesized. The two-component polyurethanes are expected to exhibit the advantages[9,10] of each component, i.e. polyester and alkyd. Enhancements of the crosshatch adhesion, hardness, abrasion resistance, and softness due to the polyester polyol component and enhancement of the hardness, gloss, rapid drying, mechanical properties, and fineness of grind due to the alkyd polyol component is expected.

In this study, alkyd modified polyesters were synthesized by the polycondensation of 1,4-butanediol, trimethylolpropane, adipic acid, and the intermediate obtained by the esterification of 3,5,5-trimethylhexanoic acid and trimethylolpropane. The contents of 3,5,5-trimethylhexanoic acid in the intermediate were 10, 20, or 30 wt%. Two-component polyurethane coatings were prepared by blending the synthesized alkyd modified polyester, Desmodur IL, and other chemicals, and the physical properties of the coatings were evaluated.

Experimental

Materials. Trimethylolpropane (TMP, Tokyo Kasei Co.), 3,5,5-trimethylhexanoic acid (THA, Sam Jung Chemical Co.), adipic acid (AA, Sigma Chemical Co.), and 1,4-butanediol (BD, Sigma Chemical Co.) were all first grade chemicals and were used without further purification. Polyisocyanate, Desmodur IL (IL, Bayer Leverkusen Co., solids content: 51%, NCO content: 8%, viscosity at 23 ℃: 1600 cps), white pigment (RCR-6, TiO_2, Britisch Titan Products Co.), flowing agent (Dow Corning-11, Dow Chemical Co.), and wetting/dispersing agent (Byk P-104S, Byk-Mallinckrodt Co.) were used as received.

Synthesis of Alkyd Modified Polyester. THA/TMP Intermediate : A 4-necked 300 mL flask equipped with an agitator, reflux condenser fitted with a drying tube, thermometer, and a nitrogen inlet tube was charged with 8 g of toluene, 117 g (0.74 mol) of THA, 99.3 g (0.74 mol) of TMP, and 0.4 g of phosphoric acid as catalyst. The reaction proceeded under stirring at 250 rpm at 60 ℃ under 30 mL/min. nitrogen purge. The esterification was promoted by increasing the heating rate to 10 ℃/h, and dehydration commenced at 142 ℃ and continued up to 200 ℃. After aging for 5 hours at 200 ℃, the reaction was terminated. The unreacted materials, THA and TMP were completely removed by washing the reaction product with *n*-hexane and distilled water. 205 g of the THA/TMP intermediate (THA-adduct-4), a bright brown transparent liquid, was obtained by vacuum distillation under 2 mmHg at 50 ℃. Typical reaction conditions and the results are summarized in Table I.

Preparation of Alkyd Modified Polyester of Various THA Contents : A 4-necked 500 mL flask with the same equipments as above was charged with 10 g of toluene, 129.7 g (0.89 mol) of AA, 52 g (0.58 mol) of BD, 59.6 g(0.44mol) of TMP, and 43.5 g of THA-adduct-4. Reaction proceeded following the same procedure as in the preparation of THA/TMP intermediate. The product was precipitated by pouring the reactants into excess methanol. After removing the unreacted, AA, BD, and TMP, 228 g of the bright brown transparent alkyd modified polyester prepolymer containing 10 wt% of THA (THAO-10B) was obtained. Alkyd modified polyester prepolymers containing 20 wt% of THA (THAO-20B) and 30 wt% of THA (THAO-30B) were prepared similarly. The reaction conditions and the results are summarized in Table II.

Preparation of Two-Component Polyurethane Coatings. A two-component polyurethane coating can be prepared from the alkyd modified polyester and polyisocyanate components. The alkyd modified polyester component, a resinous solution, was prepared by adding 39.5 g of ethyl acetate, butyl acetate, and toluene to 109.6 g of THAOs, the alkyd modified polyester synthesized above, and blending with 88 g of white pigment TiO_2, 0.4 g of flowing agent (Dow Corning-11), and 0.3 g of wetting/dispersing agent (Byk P-104S). The polyisocyanate component, a resinous curing solution, was prepared by adding 8.6 g each of xylene and cellosolve acetate to 220.3 g of polyiso-

Table I. Reaction Conditions and Yields for THA/TMP Intermediates

Products	Materials			Reactions			Acid value	Dehydration(mL)
	THA[a] g(mol)	TMP[b] g(mol)	Cat.[c] (g)	Toluene (g)	Temp. (℃)	Time (h)		
THA-adduct-1	117.0(0.74)	99.3(0.74)	-	8	140~200	11	7.3	12.5
THA-adduct-2	117.0(0.74)	99.3(0.74)	-	8	140~220	16	5.7	12.6
THA-adduct-3	117.0(0.74)	99.3(0.74)	PTS 0.4	8	140~200	11	5.0	13.1
THA-adduct-4	117.0(0.74)	99.3(0.74)	H_3PO_4 0.4	8	140~200	11	3.4	13.0

[a]THA : 3,5,5-trimethylhexanoic acid. [b]TMP : trimethylolpropane. [c]PTS : para-toluene sulfonic acid.

Table II. Polymerization Conditions and Yields for THAO-10, THAO-20, and THAO-30

Products	Materials				Reactions			Acid value	Dehydration(mL)
	AA[a] (g)	BD[b] (g)	TMP[c] (g)	THA-adduct[d] -4(g)	Toluene (g)	Temp. (°C)	Time (h)		
THAO-10A	129.7	52.0	59.6	43.5	10	144~200	8	6.6	35.2
THAO-10B	129.7	52.0	59.6	43.5	10	144~200	12	2.9	34.0
THAO-10C	129.7	52.0	59.6	43.5	10	144~210	13	2.9	34.0
THAO-20A	108.4	49.6	37.4	87.0	10	141~200	10	5.8	32.1
THAO-20B	108.4	49.6	37.4	87.0	10	141~200	12	3.5	32.3
THAO-20C	108.4	49.6	37.4	87.0	10	141~210	13	3.6	32.4
THAO-30A	87.0	47.2	15.3	130.5	10	146~200	8	5.4	29.2
THAO-30B	87.0	47.2	15.3	130.5	10	146~200	12	3.6	30.0
THAO-30C	87.0	47.2	15.3	130.5	10	146~210	13	3.5	29.8

[a]AA : adipic acid. [b]BD : 1,4-butanediol. [c]TMP : trimethylolpropane. [d]THA-adduct-4 : THA/TMP intermediate.

cyanate IL. The two-component polyurethane coating was prepared by blending 356.3 g of the alkyd modified polyester component and 237.5 g of the polyisocyanate component. The two-component polyurethane coatings prepared from THAO-10B/IL, THAO-20B/IL, and THAO-30B/IL were named THPU-10B, THPU-20B, and THPU-30B, respectively. And also, in case of modified polyester(B-2),[6] B-2/IL was named PU-2.

Instrumental Analysis. FT-IR spectra were obtained with Digilab FTS-40 Spectrometer, ^{1}H-NMR spectra were obtained with Bruker AMX-400 Spectrometer. The molecular weight and distribution were measured with Waters GPC R-410. Thermal analysis using TGA and DTA were carried out with Setaram Thermal TG-DTA 92 under nitrogen purge.

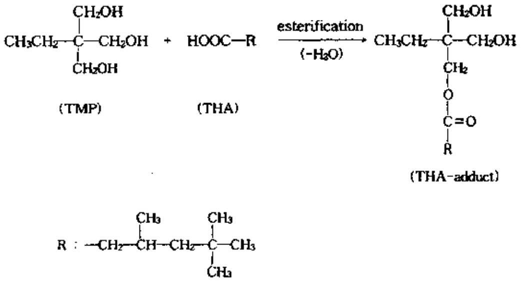
Kinematic Viscosity. The kinematic viscosity was measured according to the KS M 5000-2121 method, the test for viscosity of transparent liquids (Gardner tube method).

Physical Properties of the Coatings. Three kinds of film coating specimens were prepared to measure the physical properties. The specimens for testing coatings on cold rolled carbon steel sheets were prepared according to KS M 5000-1111,[11] those for testing coatings on tin sheets were prepared according to KS M 5000-1112,[11] and those for testing coatings on glass sheets were prepared by the same procedure as above using the glass of 200 × 150 × 5 mm size. The viscosity was measured with Krebs-Stormer Viscometer 80328 (Pacific Scientific Co.), the fineness of grind measured with the grind gauge (Precisions Gauge and Tools Co.), the drying time measured by set-to-touch and dry-hard methods, and the pot-life determined from the curing time required to reach maximum viscosity value of 140 KU(Krebs-Stormer Viscometer Unit). Hardness was measured by the pencil hardness and Sward hardness method, flexibility by KS M 5000-3331, the test method for flexibility of coatings on tin sheets, impact resistance by JIS K 5400, the test method for determining the impact strength of coatings on cold rolled carbon steel sheets (KS D 3512), 60° specular gloss by KS M 5000-3312, crosshatch adhesion by the adhesion test method for coatings on tin sheet (KS D 3516), abrasion resistance by FS 141-6152 the test method for coatings on cold rolled carbon steels, and accelerated weathering resistance by Xenon Weather-Ometer (Atlas Electric Devices Co.). Yellowness index, lightness index difference, and color difference were measured by using Spectro Color Meter ACS-5 (Data Color Ind. Co.) according to KS M 5000-3211, KS M 5000-3231, and KS A 0063, respectively. Salt spray exposure and immersion resistance tests were carried out according to KS D 9502 and KS M 5000-3411, respectively.

Results and Discussion

It is known[12] that polyester having the molecular weight, 400-6000, OH value, 210-220, and acid value 1-5 can be used in the preparation of polyurethane coatings to obtain appropriate coating properties. Therefore, in order to ensure above conditions, the modified polyester with OH group was synthesized from BD as diol, TMP as triol, and AA as dibasic acid. The result of polyurethane coatings prepared from the modified polyester was reported in the previous paper.[6]

Characterization of Alkyd Modified Polyesters. The molecular weight and viscosity can be easily controlled by reducing the average degree of functionality in the alkyd and oil-free polyester for heat-curing by adding monobasic acid, such as tall oil acid or benzoic acid. It is well known[13] that this results in the improvement on the physical properties of coatings, such as hardness, adhesion, color, gloss, drying time, and chemical resistance of the film. But, two-component polyurethane coatings prepared with both alkyd and polyester polyols, have not been reported yet. It is known[14] that THA, a polyol component, does not cause the yellowing of the coatings film at high temperature and has outstanding mechanical properties, high elasticity, and especially improved surface hardness. It is expected that the physical properties of the coatings film will be improved by introducing fatty acid, THA to modified polyester component. Therefore, modified polyester was prepared by polycondensation of BD, TMP, AA, and controlled amount of monobasic acid, THA. The amount of modified polyester was 10, 20, or 30 wt%. To investigate the existence of unreacted free acid, molecular structure and physical properties of the polymer, two step synthetic methods were attempted in this research. At first, THA-adduct was prepared by the esterification of THA with TMP, and then it was polycondensed with BD, TMP, and AA to obtain the desired physical properties of the coatings. In the preparation of THA-adduct, THA/TMP intermediate, the reaction conditions and yield were summerized in Table I, and the reaction scheme was shown in Scheme I. In Table I, toluene was used to control the viscosity of the reaction medium and to promote the dehydration, and the catalyst was used to accelerate the esterification. THA-adduct-1 to -4 were prepared with the molar ratio of the reactants [THA]/ [TMP] as 1.0, and THA-adduct-1 and -2 are the products esterified without catalyst, THA-adduct-3, THA-adduct-4 with *p*-toluenesulfonic acid and phosphoric acid as catalyst, respectively. Although the reaction was carried out for a long time at high temperature, the acid values of THA-adduct-1 and -2 remained above 5. These results indicate that the reaction was not complete. And also comparing the reaction conditions during the preparation of THA-adduct-3 and -4, the acid value of the product prepared using phophoric acid was much lowered than that prepared using *p*-tolunesulfonic acid as catalyst. Therefore, it can be concluded that preparation condition of THA-adduct-4 was the most appropriate method among the four reaction conditions studied.



Scheme I. Synthesis of THA-adduct.

FT-IR spectrum[15] of THA-adduct-4 is shown in Figure 1(a). Alkyl group was confirmed by observing CH$_3$ stretching vibration at 2960 cm^{-1}, -CH$_2$- deformation vibration at 1470 cm^{-1}, and OH group at 3440 cm^{-1}. And also, primary alcohol stretching vibration at 1250 and 1060 cm^{-1}, C=O stretching vibration at 1730 cm^{-1} and C-O-stretching vibration at 1160 cm^{-1} of ester group were observed. ^{1}H-NMR spectrum[16] of THA-adduct-4 is shown in Figure 2(a). Methyl proton at δ0.9 ppm(multiplet, 15H, CH$_3$), methylene proton at δ1.3 ppm(multiplet, 4H, C-CH$_2$-C), C-H proton at δ2.1 ppm(singlet, 1H, C-CH=), methyl ketone proton at δ2.6 ppm(singlet, 2H, C-CH$_2$-CO-), methylol proton at δ3.6 ppm(multiplet, 4H, C-CH$_2$-O-), and methylene proton due to ester at δ4.1 ppm(doublet, 2H, C-CH$_2$-OCO-) were observed. The preparation and analysis for THA-adduct-4 intermediate and alkyd modified polyester, THAO from BD, AA and TMP are as follows. THAO-10, -20, and -30 were prepared with

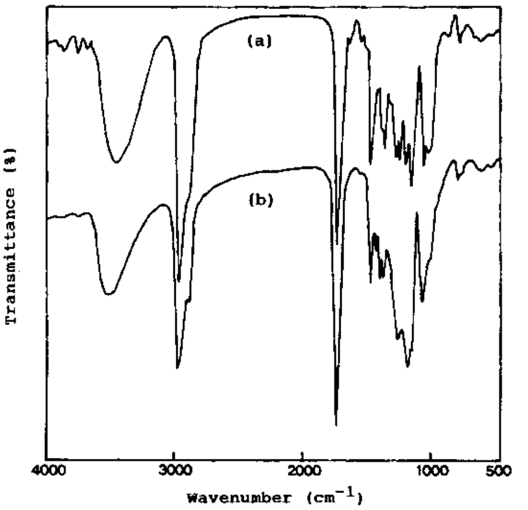


Figure 1. FT-IR spectra of (a) THA-adduct-4 and (b) THAO-10B.

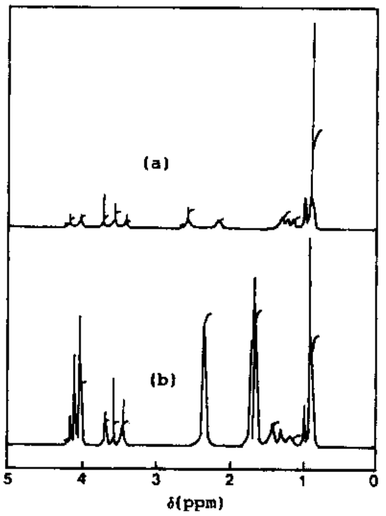
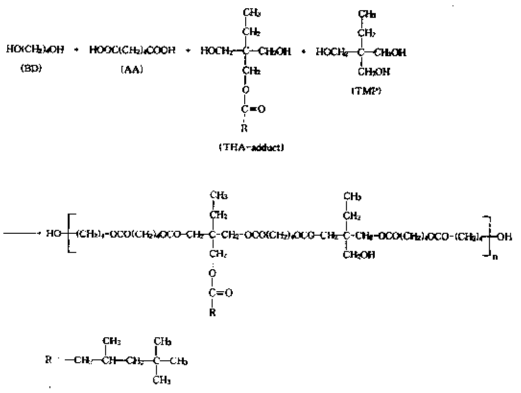


Figure 2. ^{1}H-NMR spectra of (a) THA-adduct-4 and (b) THAO-10B.



Scheme II. Synthesis of THAO.

THA content of 10, 20, and 30 wt% respectively. Reaction conditions and yield are summerized in Table II, and reaction scheme are shown in Scheme II. As shown in Table II, the reaction condition in the preparation of THAO-10A, compared with -10B, was inadequate due to the high acid value. The acid value of THAO-10C was not dropped further by the reaction for longer time and higher temperature than that of THAO-10B. It was found that the adequate reaction condition assessed from the above results was that for THAO-10B. The similar results for THAO-20B and -30B are obtained. Therefore, THAO-10B, -20B, and -30B are used as the synthetic materials of alkyd modified polyester.

FT-IR[15] spectrum of THAO-10B is shown in Figure 1(b). The hydroxyl group in the structure was confirmed by observing OH group stretching vibration at 3510 cm^{-1}, and also C=O stretching vibration at 1730 cm^{-1} and C-O- stretching vibration at 1170 cm^{-1} of ester, CH_3 stretching vibration at 2960 cm^{-1}, -CH_2- deformation vibration at 1470 cm^{-1} were observed. ^{1}H NMR spectrum[16] of THAO-10B is shown in Figure 2(b). The structure of THAO-10B was confirmed by observing CH_3-C proton at δ0.9 ppm, -CH_2-C proton at δ1.3 ppm, C-CH_2-C proton at δ1.7 ppm, C-CH_2-CO- proton at δ2.3 ppm, C-CH_2-O- proton at δ3.6 ppm, and C-CH_2-OCO- proton at δ4.1 ppm. GPC results for THAO-10B and -30B are shown in Figure 3. $\overline{M}_n$, 1440, $\overline{M}_w$, 4430, $\overline{M}_z$, 10030, and polydispersity, 3.0 for THAO-10B, and $\overline{M}_n$, 810, $\overline{M}_w$, 1330, $\overline{M}_z$, 2050, and polydispersity, 1.64 for THAO-30B were obtained. It is noted that the polydispersity becomes narrower as THA content increases. The presence of THA increases the content of hydroxyl group in THAO, which reduces the reactivity of THAO.[17] This is the reason that the molecular weight and the polydispersity tend to decrease with increasing alkyd content.

Kinematic Viscosity of Alkyd Modified Polyesters and THA Content. Two-component polyurethane coating used in this study consists

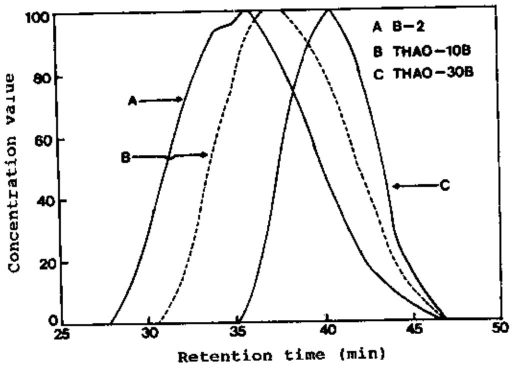


Figure 3. GPC chromatograms of B-2, THAO-10B, and THAO-30B.

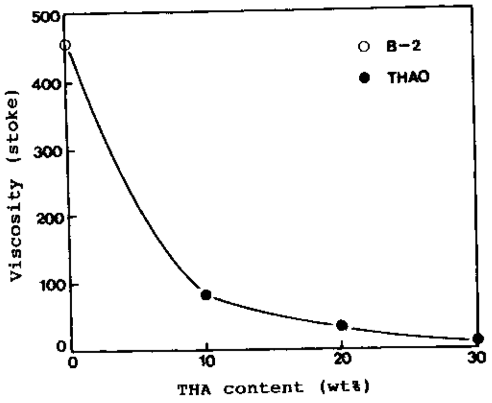


Figure 4. Effect of THA content on the viscosity of the alkyd modified polyester.

of alkyd modified polyester and polyisocyanate, and the fattening agent or thinner are generally used to control the final viscosity of the coatings. Therefore, it is important to measure the viscosity of alkyd modified polyester, since this result affects the mixing process during the final step of polyurethane coatings preparation. To control the viscosity of alkyd modified polyester, the amounts of reactants was determined while maintaining the weight ratio of TMP and BD to 1:1, and the viscosity was measured to find the fluidity according to the introduction of THA. Figure 4 shows the relationship of kinematic viscosity between the THA content in alkyd modified polyester. The kinematic viscosity of B-2 was 460 stokes, but that of THAO gradually dropped with the increase of THA content approaching 8 stokes at 30 wt% THA content. When solid content of the polyester coatings was 100%, the kinematic viscosity was maintained to 30-600 stokes.[18] It was found to come within a fitting viscosity range at 20 wt% of THAO content. Especially, high solids content is considered as a merit due to decreasing the viscosity. According to the fact that increase of hydroxyl group in alkyd resin results in the low reactivity,[17] the increasing contents of THA seem to decrease curing reaction rate and eventually lower the kinematic viscosity.

Thermal Behavior of Alkyd Modified Polyesters. For the thermal degradation mechanism of polyester, Yokouchi and Nakamura[19] reported that the end group of chain degradated first, but Pohl[20] insisted the degradation occurred with the cleavage of polyester main chain. Also, it is known[21] that carboxylic end group is increased by the thermal degradation.

Figure 5 and 6 are DTA and TGA thermograms of the prepared products. As shown in Figure 5, the endothermic peak due to the thermal degradation of B-2 is shown at 460 ℃, and of THAO-10B and -30B at the temperature range of 360-460 ℃, and of THA-adduct-4 at 320-360 ℃. While the degradation of B-2 has started at 290 ℃, and shown 97 wt% loss at about 495 ℃, THAO-10B and -30B have shown the first step weight loss at the temperature range of 225-495 ℃ and 195-495 ℃, respectively, and also the weight loss for THA-adduct-4 at 155-375 ℃ as shown in Figure 6. From the results of DTA and TGA analyses, it can be concluded that the thermal stability decreases with the following order; THA-adduct-4 > THAO-30B > THAO-10B > B-2. It is also concluded that the product with more alkyd group has the faster thermal degradation rate at the higher temperature. It is due to the increase of the side chain content in alkyd compound. It is consistent with the theory[22] that alkyd with more side chain content is more easily thermally degradated at high temperature.

Physical Properties of the Coatings. It is very important for coatings to have appropriate viscosity to ensure the best physical properties. The coatings which has the heterogeneous dispersed multiphase system has shown non-Newto-

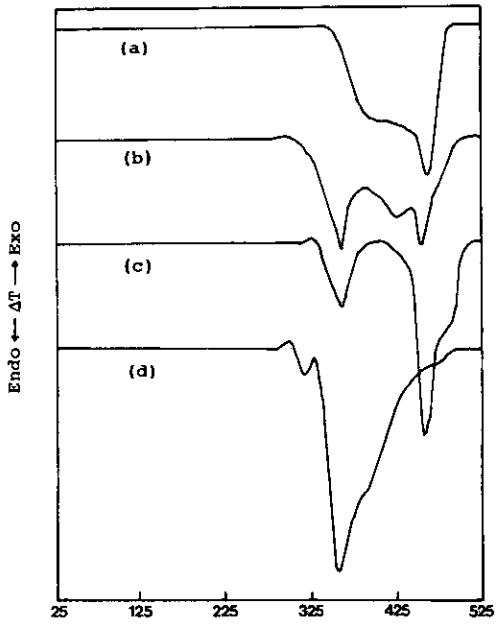


Figure 5. DTA thermograms of (a) B-2, (b) THAO-10B, (c) THAO-30B, and (d) THA-adduct-4. Scan rate, 10 °C/min.

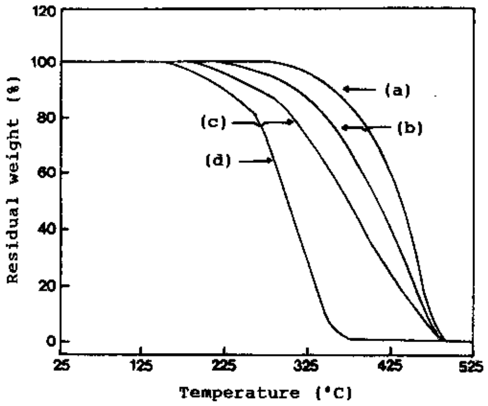


Figure 6. TGA thermograms of (a) B-2, (b) THAO-10B, (c) THAO-30B, and (d) THA-adduct-4 with heating of 25 °C/min in N_2 gas.

nian behavior, and viscosity is decreased as the shear rate increased.[23]

The viscosity variation with the pot-life of the prepared compounds is shown in Figure 7. The viscosity was slowly increased as the content of THA was increased. Physical properties of coating film for PU-2 and THPUs, two-component polyurethane coatings using alkyd modified polyester are shown in Table III. In Table III, the fineness of grind which indicates the degree of dispersion of pigment was proved to be good, because of its value showing 8^+. Drying time was so short that it was consistent with recent trend requiring the rapid drying. In the pot-life, it became longer according to increase THA content. The results obtained using alkyd polyol modified polyester was improved the physical properties of the coatings, considering the recent trend having the short drying time and long pot-life in the painting of the coatings.

Hardness was indicated with pencil and Sward hardness. Although the hardness for THPU-10B and -20B were better than that of PU-2, that for THPU-30B was poor. As the results, the appropriate THA content showing the good hardness was found to be 20 wt%. The flexibility and impact resistance of the film for the prepared coatings was good, but THPU-30B showed poor impact resistance. 60° specular gloss for PU-2 and THPUs was and THPUs prepared with alkyd polyol modified polyester showed superior cross hatch adhesion and abrasion resistance to PU-2. And also, all of our products have shown reasonable accelerated weathering resistance, the outstanding yellowness index and lightness index difference, and good color difference.

The salt spray exposure and immersion resistance were also carrid out. All the products have shown good rust and chemical resistance in al-

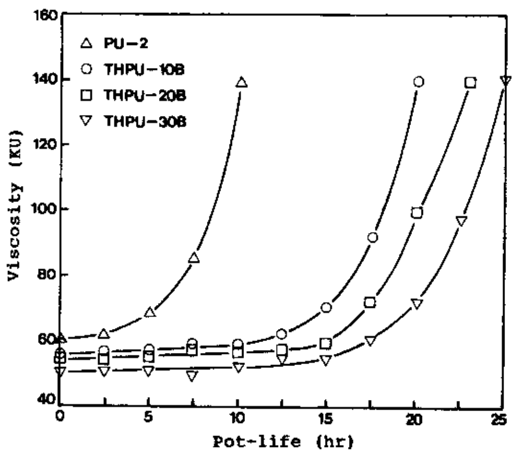


Figure 7. Relationship between viscosity and pot-life of two-component polyurethane coatings.

Table III. Physical Properties of Two-Component Polyurethane Coatings

Test types	Sample names			
	PU-2	THPU-10B	THPU-20B	THPU-30B
Fineness of grind	7^+	8^+	8^+	8^+
Drying time :				
S.T.T(min)	3	3	3	4
D.H(h)	$1\frac{2}{3}$	2	$2\frac{1}{3}$	$2\frac{1}{2}$
Pot-life(h)	10	20	23	25
Pencil hardness (7 days)	H	2H	2H	H
Sward hardness (7 days)	46	52	48	38
Flexibility (1/8")	good	good	good	good
Impact resistance (1000 g/50 cm) :				
Direct	good	good	good	good
Reverse	good	good	good	good
60° Specular gloss	97.5	96.0	95.0	95.5
Cross hatch adhesion(%)	60	100	97	100
Abrasion resistance (mg loss/100 cycles)	40	20	24	20
Accelerated weathering resistance (% gloss retension)	58	63	55	50
Yellowness index (ΔN)	0.149	0.145	0.145	0.144
Lightness index difference (ΔL)	1.74	1.91	3.53	1.32
Color difference (ΔE)	2.86	3.00	3.65	1.87

kaline and acid solution.

Conclusions

Oligo alkyd modified polyesters(THAO-10B, -20B, and -30B) were prepared by polycondensation of fatty acid(THA) with polyester, and then two-component polyurethane coatings (THPUs) with three dimensional network structure was prepared by crosslinking THAOs with polyisocyanate in order to develope THUP coexisting alkyd and polyester polyols. The following results were obtained through the various measurements of the physical properties.

1. Appropriate reaction conditions were obtained for the preparation of THAO-10B, -20B, and -30B, and the products with $\overline{M}_n$, 810-1440, $\overline{M}_w$, 1330-4330, $\overline{M}_z$, 2050-10030, and polydispersity, 1.64-3.01 were obtained. The yield was 88-91%.
2. Polyurethane coatings having high slid content was developed by the introduction of alkyd polyol which resulted in the decrease of kinematic viscosity of THAO.
3. The advantage of alkyd group according to increasing THA content were proved to be rapid drying coatings with long pot-life.
4. Crosshatch adhesion and abrasion resistance of THPUs coatings were better than those of PU-2. The advantages of the introduction of alkyd group in THPU coatings were identified.

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