

Synthesis and Curing Behavior of Diimide–Diacid-Modified Saturated Polyester

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SYNOPSIS

The polyester and diimide–diacid-modified polyester prepolymer have been synthesized with different molecular weights through melt polycondensation of 1,6-hexanediol (HD), trimethylol propane (TMP), isophthalic acid (IPA), diimide diacid, and phthalic anhydride (PA) at various molar ratios. The prepolymers were then mixed with an equivalent phenol-blocked TDI and/or HMDI in *m*-cresol in deriving the polyester urethane varnishes. The degree of crosslinkage and thermal behavior have been investigated here. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Polyester–imide varnishes were developed during the early 1960s by the Beck Corp. (Germany) and the Schenectady Chemical Co. (U.S.). The polyester–imide was obtained through incorporating imide monomer units into a polyester main chain for modification of the heat resistance of varnishes.

Many references exist on the synthesis and application of imide-containing compounds.^{1–10} The imide-containing compounds were reacted with diamine in many cases for preparing imide-modified polymers. These compounds have seldom directly reacted with diols and diacids in producing imide-modified polyester. The polyesterimides developed by Loncrini¹ had, for example, prepared imide-containing compounds from (1) the reaction of trimellitic anhydride (TMA) with aromatic diacetoxy compounds and (2) the reaction of trimellitic anhydride monoacid chloride with phenols. These compounds were reacted with aromatic diamines in polar solvents in deriving high molecular weight polyamic acid solutions. These soluble precursors were then converted into insoluble aromatic polyesterimide through heat. Imide-containing polyesters were previously prepared by Maros and de

Abajo⁵ through the use of melt polycondensation of propylene glycol with saturated and/or unsaturated diacids and imide diacids. New epoxy polyesterimides were also synthesized by Martinez et al.⁷ through the reaction of diimide–diacid trimellitic derivatives in *N*-methyl pyrrolidone with their corresponding diglycidylester.

The diimide–diacids (DIDA) prepared from pyromellitic dianhydride (PMDA) and aliphatic ω -amino acids^{6,11} were first synthesized here. The DIDA product was then incorporated with 1,6-hexanediol (HD), TMP, isophthalic acid (IPA), and phthalic anhydride (PA), followed by melt polycondensation in yielding a prepolymer. The obtained prepolymers were then mixed with phenol-blocked toluene diisocyanate (TDI) and/or hexamethylenediisocyanate (HMDI) in producing a one component varnish. Investigating the synthesis and curing behavior of the polyester and DIDA-modified polyester is the aim of this study.

EXPERIMENTAL

Materials

Pyromellitic dianhydride (PMDA) was purchased from Merck Co. and used before prior recrystallization in acetic anhydride. Glycine, 4-aminobutanoic acid, and 6-aminohexanoic acid were purchased from Sigma Co. and used without further purification.

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Dried *N,N*-dimethylacetamide (DMAc) and toluene were used as solvents for synthesizing diimide-diacids. Trimethylol propane (TMP, Hayashi Pure Chemicals), 1,6-hexanediol (HD), isophthalic acid (IPA), and phthalic anhydride (PA) and catalyst, *di-n*-butyl tin oxide (Tokyo Kasei Co. Ltd.), were used in synthesizing polyester prepolymer. TMP, reagent pure; toluene diisocyanate (TDI, San Ten Chemicals); hexamethylene diisocyanate (HMDI, Fluka Co.); and phenol (Wako Pure Chemicals) were used to synthesize blocked diisocyanate TDI and HMDI. The catalyst used in the crosslinking reaction were dibutyl tin dilaurate (DBTDL) and dibutyl tin diacetate (DBTDAc, Tokyo Kasei Co. Ltd.).

m-Cresol was used as a solvent of the crosslinking system (reagent grade, Wako Pure Chemicals). 1,4-Dioxane was used as a solvent for determining acid value of the prepolymers, (reagent grade, Wako Pure Chemicals).

Preparation of DIDA

DIDA were synthesized through condensation of PDMA with ω -amino acids containing different numbers of methylene groups. The preparation of one of them is described here as an example, which corresponds to $-(CH_2)_n-$ where *n* is 1, 3, and 5 referred to as DIDA 1, DIDA 3, and DIDA 5, respectively.

Recrystallized PDMA, 10.5 g (0.048 mol), and 7.26 g (0.096 mol) of glycine were dissolved in 50 mL of dried DMAc. The stirred reaction mixture was heated at 60°C for 1 h in dissolving the solids. Dried toluene (50 mL) was then added, and the mixture was heated with reflux for approximately 3 h until approximately 3–4 mL of water was distilled off azeotropically. Cooling to 80°C occurred and 30 mL of distilled water was added. It was filtered while hot. The filtrate was then cooled in a refrigerator overnight to precipitate 13.12 g of white crystalline product recrystallized in DMF (with an adequate amount of water). Purified DIDA 1, 13.05 g, was obtained, melting point 354–356°C. IR characteristic absorption bands: —OH hydroxyl at 3300 cm^{-1} , C=O carboxylic at 1720 cm^{-1} , C=O imide at 1780, and 1120 cm^{-1} , and imide ring at 740 cm^{-1} .

Polymerization of Polyester Prepolymer

The polyesterification reactions were carried out through a two-step procedure under laboratory conditions as follows:

Step 1—Prepolymer, where the dicarboxylic acids reacted with the total amount of the HD and TMP under nitrogen atmosphere at a temperature not higher than 210°C, up to an acid number of 10 at the highest.

Step 2—Polyesterification, where the prepolymer was reacted with PA to the desired acid number (50–60). The acid value (AV) and hydroxyl value (OHV) were measured by end group analysis, according to ASTM D 1639 and ASTM E 222 method B, respectively. The number-average molecular weight (\bar{M}_n) were calculated by the following equation

$$\bar{M}_n = (2 \times 56.1 \times 1000) / (AV + OHV).$$

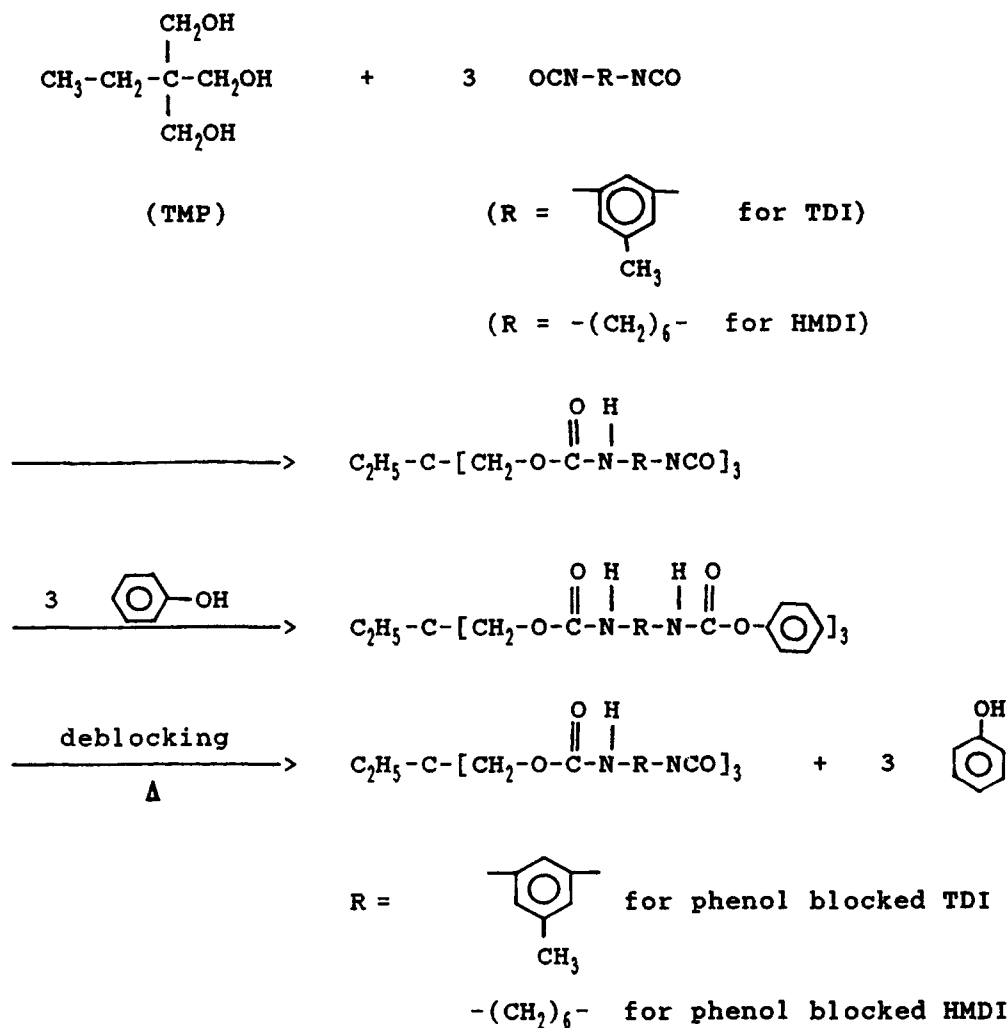
Synthesis of Blocked Diisocyanates

A three-necked flask equipped with an electric stirrer, a reflux condenser, a dropping funnel, and an inert gas blanket were charged with a calculated quantity of TDI. The mixture of TMP and phenol in the beaker was heated to 50°C for dissolution and cooled to room temperature. The mixture was then added dropwise into the flask from a dropping funnel. The mixture was heated at room temperature for 30 min and the temperature raised to 40–50°C for 1.5 h, to 80°C for 1 h, to 110°C for 3.5 h, and to 120°C for 30 min for completion. Some *m*-cresol was added into the flask after the reaction was completed. The product, a golden viscous liquid at room temperature, has been referred to here as a phenol-blocked TDI.

Phenol-blocked HMDI was prepared with the same procedure used in a phenol-blocked TDI. The blocking and deblocking reaction for phenol-blocked diisocyanates is shown in Scheme 1.

Curing of Polyester and/or Polyesterdiimide

A processing solution of a solid content, ~ 50%, was prepared by dissolving and mixing polyester and/or polyesterdiimide prepolymer and equivalent phenol-block TDI and/or phenol-block HMDI in *m*-cresol. A small portion of such a solution was poured onto a smooth surface of aluminum foil and flowed into a thin circle 10 cm in diameter and baked at 210°C for 30 min. A crosslinked film tightly adhered to the aluminum foil was formed after curing. The cured film was put into a hydrochloric acid solution (6 N) to etch the aluminum foil. A smooth crosslinked film of thickness within 0.5 mm was obtained. The gel content of the cured film was determined through acetone extraction. A weighed sample



Scheme 1 Synthesis of crosslinking agent

was extracted for a period of 24 h in a Soxhlet extractor at 80°C.

Infrared Spectra Measurement

The IR spectra measurements were carried out through coating the resin on a KBr window. A Jasco Model A202 IR spectrophotometer was also used.

Thermal Analysis

Thermal analysis was carried out with a DuPont TGA 951 coupled with a 1090B thermal analyzer. The 15 ± 2 mg cured film samples were heated at a heating rate of 10°C/min under a nitrogen atmosphere from an ambient temperature to 700°C. The chart recorded the change in both temperature and sample weight percentage.

RESULTS AND DISCUSSION

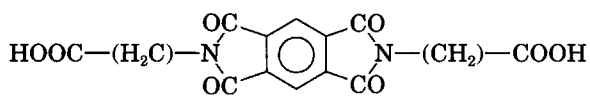
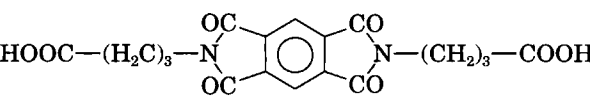
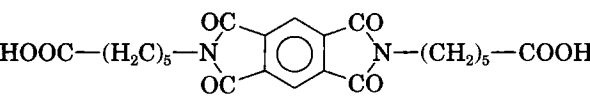
Synthesis of DIDA Monomer

The DIDA were prepared through a reaction of PMDA with ω -amino acids. The characterizations of the those compounds have been shown in Table I. The IR spectrum characteristic bands for the imide group of 1780, 1120, and 740 cm^{-1} were observed. The melting point measured by MEL-TEMP (capillary melting point apparatus) for the present compounds were about 10°C lower than the value reported in previous literature.⁴

Synthesis of Polyesterdiimide Prepolymers

The polyesterdiimide prepolymers underwent polycondensation as described in Experimental. The

Table I Structure and Characterization of DIDA *n*

Monomer	Yield (%)	Melting Point (°C)	IR (cm ⁻¹)
 (DIDA 1)	81.9	354–356 (366) ^a	COOH : CO = 1700, OH = 3300 Imide : CO = 1780, 1120, 740
 (DIDA 3)	99.0	277–278 (285) ^a	COOH : CO = 1700, OH = 3450 Imide : CO = 1780, 1120, 740
 (DIDA 5)	99.0	283 (246) ^a	COOH : CO = 1700, OH = 3400 Imide : CO = 1780, 1060, 730

n = 1, 3, 5.^a Adapted from Gonzalez et al.⁴

diimide compounds were incorporated into the resins as the dicarboxylic acid component of the polyester for partial replacing of the conventional isophthalic acid. The ideal scheme and characteristic data of the polyesterdiimide have been shown in Scheme 2 and Table II. The \bar{M}_n (Table II) increased while

increasing the DIDA content and increased while increasing the number of methylene groups (*n* value). Hence, this result has shown that the DIDA compounds participated in the polyesterification reaction. The IR spectra of some polyesterdiimides (DIDA 3) are shown in Figure 1. The intensity of

Table II Composition and Characteristics of Polyester and Polyesterdiimide

Charge	IPA (mol)	DIDA			PA (mol)	HD (mol)	TMP (mol)	Acid Value	Hydroxyl Value	Molecular Weight ^a (\bar{M}_n)
		1	3 (mol)	5						
1	0.24	—	—	—	1.00	1.25	0.15	54.52	143.38	567
2	0.24	—	—	—	1.00	1.23	0.17	58.21	102.67	697
3	0.18	0.06	—	—	1.00	1.23	0.17	58.61	99.87	708
4	0.12	0.12	—	—	1.00	1.23	0.17	59.03	95.64	725
5	0.09	0.15	—	—	1.00	1.23	0.17	59.94	93.21	733
6	0.06	0.18	—	—	1.00	1.23	0.17	54.61	97.64	737
7	0.18	—	0.06	—	1.00	1.23	0.17	59.77	96.03	720
8	0.12	—	0.12	—	1.00	1.23	0.17	59.97	92.18	737
9	0.09	—	0.15	—	1.00	1.23	0.17	59.96	90.34	747
10	0.06	—	0.18	—	1.00	1.23	0.17	57.97	91.67	750
11	0.18	—	—	0.06	1.00	1.23	0.17	50.01	102.80	734
12	0.12	—	—	0.12	1.00	1.23	0.17	59.98	91.36	741
13	0.09	—	—	0.15	1.00	1.23	0.17	59.78	89.90	750
14	0.06	—	—	0.18	1.00	1.23	0.17	58.60	89.45	758

^a Using end group method to evaluate.

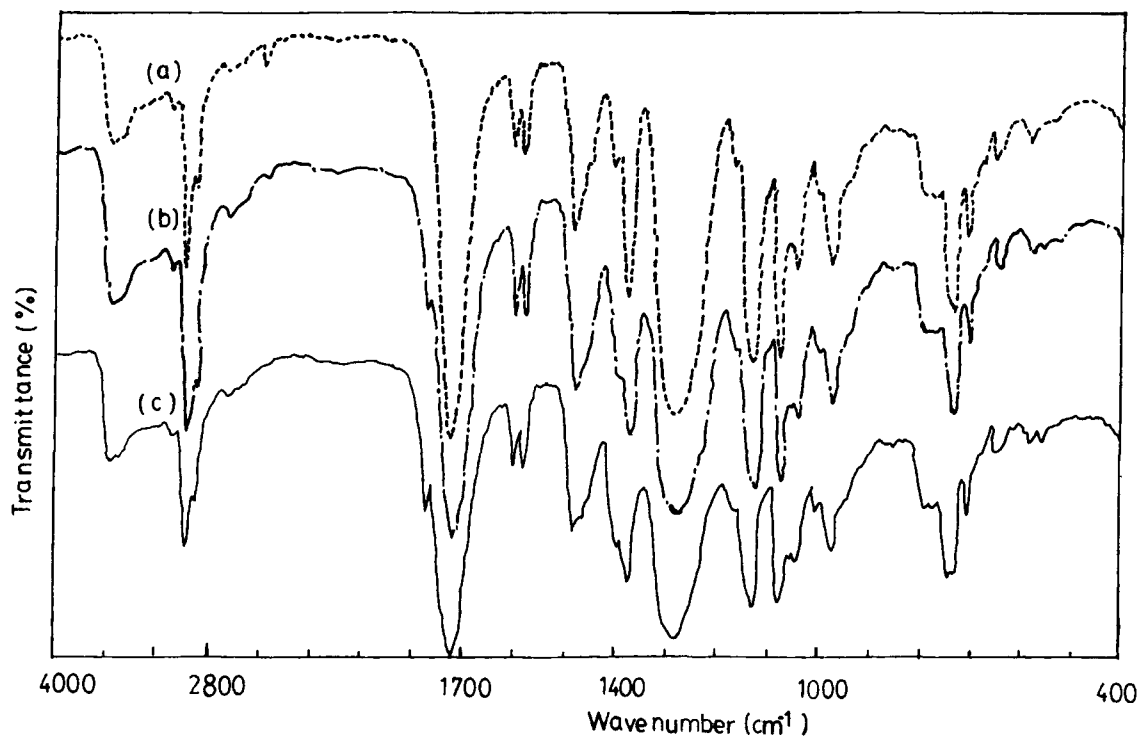


Figure 1 IR spectra of polyesterdiimide based on 1,6-hexanediol, isophthalic acid, phthalic anhydride, and different DIDA 3 containing: (a) (---) no DIDA 3; (b) (-·-·-) 0.06 mol DIDA 3; (c) (—) 0.18 mol DIDA 3.

the absorption band at 1780 cm^{-1} that is a characteristic band of carbonyl absorption in cyclic imides increased while increasing the DIDA 3 contents.

Effect of Curing Agent Content on Crosslinking Degree

Polyester-urethane coatings are thermosettings. The coating properties greatly depend on the crosslinkage of the coating film. This crosslinkage depends on curing temperature, curing time, and the quantity of the catalyst and the curing agent being used in the coating.

Figure 2 indicates the effects of the quantity of the curing agent on the crosslinking degree for 0.15 mol TMP content polyester-phenol-blocked TDI system at 210°C . Three different quantities of curing agents were respectively considered, that is, equivalent hydroxyl group of the prepolymer, equivalent hydroxyl and carboxylic group, and excessive (10% larger) hydroxyl and carboxylic group. The regenerated isocyanate groups of excess system have been revealed by a comparison of curves in Figure 2 to be larger at 15 min. The greater the probability of

collision occurring between isocyanate and the hydroxyl group exists because the more regenerated isocyanate groups have been present. At 30 min the crosslinkage of the cured film prepared from the equivalent ($-\text{OH}$) curing agent used reached a maximum; the degree of the crosslinkage was greater than 90%. Only the prepolymer has therefore been mixed here with an equivalent (OH) curing agent hereafter and baked for 30 min.

Curing Behavior of Polyester with Blocked Isocyanates

The solutions of polyester prepolymer and equivalent of phenol-blocked isocyanates were formulated and baked at 210°C for 30 min. The cured film was then obtained. The IR spectra before and after curing are shown in Figure 3 that clearly exhibits that the hydroxyl group was completely reacted by the isocyanate group retrieved from the deblocking reaction. The characteristic absorption peak for the urethane group occurring after curing was recorded at 3350 cm^{-1} for $\text{N}-\text{H}$ stretching and $1700\text{--}1740\text{ cm}^{-1}$ for $\text{C}=\text{O}$ stretching of urethane and ester

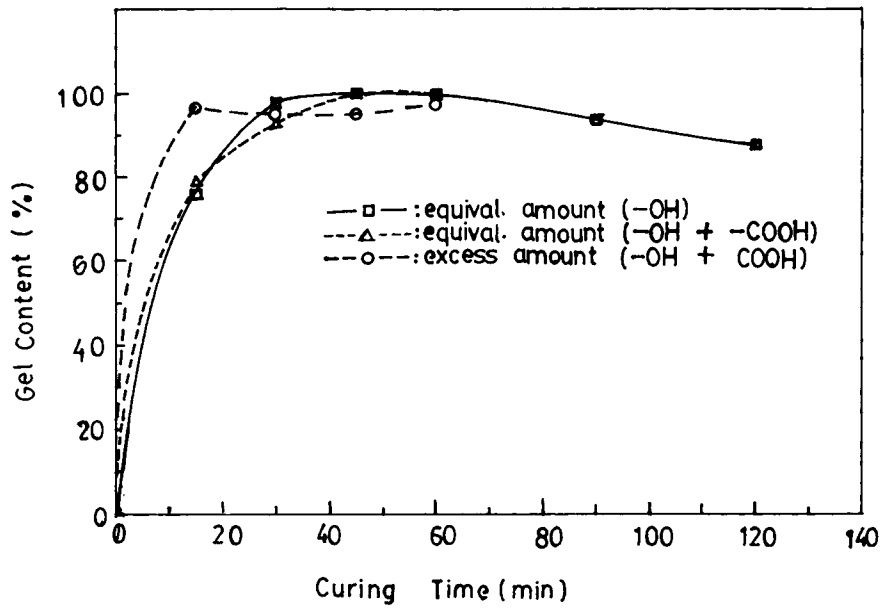


Figure 2 Effect of the quantity of crosslinking agent on the crosslinkage for 0.15 mol TMP content polyester at 210°C, using phenol-blocked TDI as curing agent.

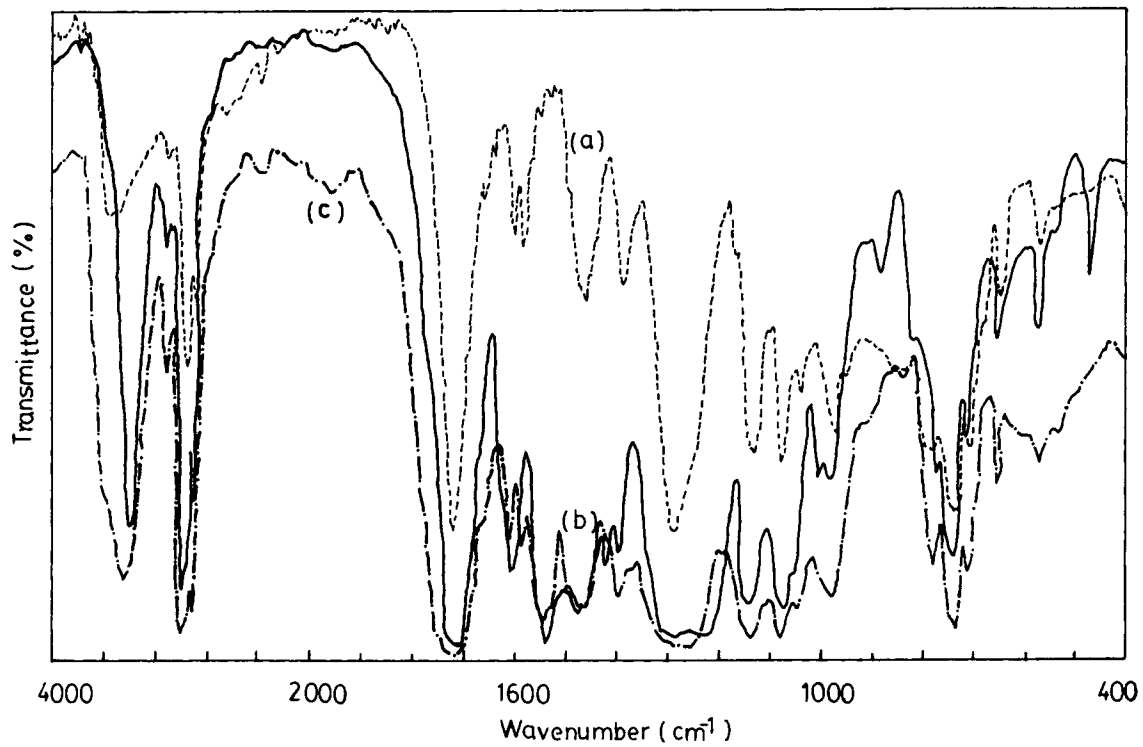


Figure 3 IR spectra of the variation of 0.15 mol TMP content polyester before and after curing with equivalent phenol-blocked TDI and HMDI at 210°C for 30 min: (a) (---) before curing; (b) (—) after curing blocked TDI; and (c) (- - -) blocked HMDI.

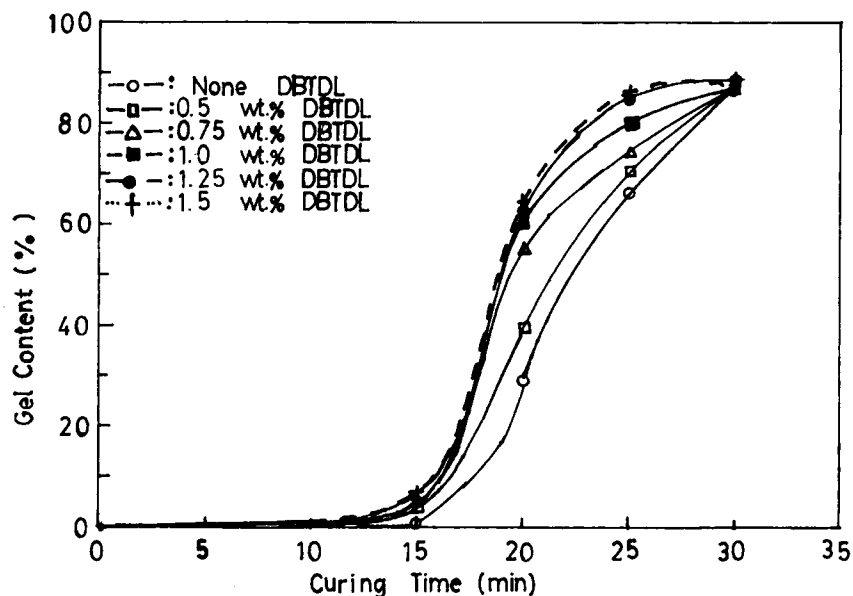


Figure 4 Effect of DBTDL content on the degree of crosslinkage for 0.17 mol TMP content polyester systems at 210°C, using phenol-blocked TDI as curing agent.

structure. The general widening in the bands all over the spectra of polymers is also attributed to the accumulation of identical groups within the polymer chain.

Effect of Catalyst on Crosslinking Degree

The rate of curing was previously studied by Squiller and Rosthanser¹² by investigating various catalysts

on different isocyanates with a polyester triol. Tin catalysts, DBTDL and DBTDAc, are the best two catalysts for an isocyanate-hydroxyl reaction. These two catalysts of 0.05, 0.75, 1.0, 1.25, and 1.5 wt % (based on curing agent used) were therefore incorporated, then cured at a given baking condition.

The respective influence of the quantity of DBTDL and DBTDAc on the crosslinkage of the

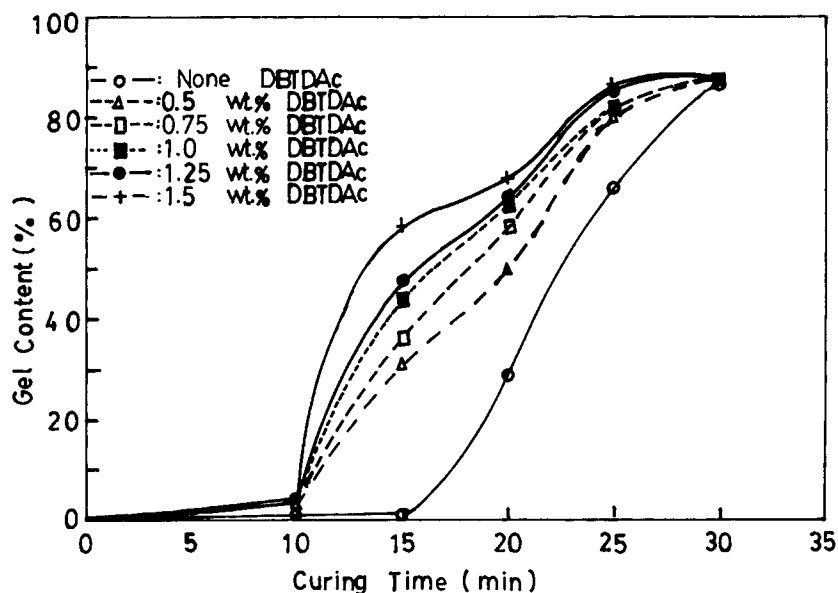


Figure 5 Effect of DBTDAc content on the degree of crosslinkage for 0.17 mol TMP content polyester system at 210°C, using phenol-blocked TDI as curing agent.

Table III Comparison of Rate of Curing (210°C, 15 min)

Catalyst	Quantity of Catalyst (wt %)					
	None	0.5	0.75	1.0	1.25	1.5
	Rate ^b (%/min)					
DBTDL	0.048	0.253	0.318	0.344	0.428	0.467
DBTDAc	0.048	2.054	2.435	2.924	3.885	3.885

^a Based on the amount of the crosslinking agent used.

^b Rate = degree of crosslinkage/curing time (15 min).

Table IV Comparison of Rate of Curing (210°C, 20 min)

Catalyst	Quantity of Catalyst ^a (wt %)					
	None	0.5	0.75	1.0	1.25	1.5
	Rate ^b (%/min)					
DBTDL	1.444	1.962	2.750	3.023	3.139	3.217
DBTDAc	1.444	2.468	2.911	3.139	3.218	3.399

^a Based on the amount of the crosslinking agent used.

^b Rate = degree of crosslinkage/curing time (20 min).

coatings is shown in Figures 4 and 5. The comparison of the curing rate with DBTDL and DBTDAc as catalyst for 15 and 20 min cured, respectively, is shown in Tables III and IV. The curing rate of DBTDAc system is revealed by these data to be higher than the DBTDL system, especially at 15 min. They are almost eight times larger, and the curing rate with a catalyst is much more than without a catalyst. The desired crosslinkage is also obtainable (Figs. 4, 5) when adding 1.25 and 1.5 wt % DBTDL or DBTDAc for curing 25 min, 5 min shorter than without a catalyst.

Effect of DIDA Content on Degree of Crosslinkage for Diimide-Modified Polyesters

The effect of DIDA n ($n = 1, 3, \text{ and } 5$) contents on the degree of crosslinkage for diimide-modified polyester prepolymers cured with phenol-blocked TDI and HMDI systems at 210°C for 30 min is respectively shown in Figures 6 and 7. The degree of crosslinkage for diimide-modified polymers containing DIDA 1 or DIDA 3 is shown in Figure 6 to be lower than that of a nonmodified polyester with the blocked TDI curing systems. It is, however, in-

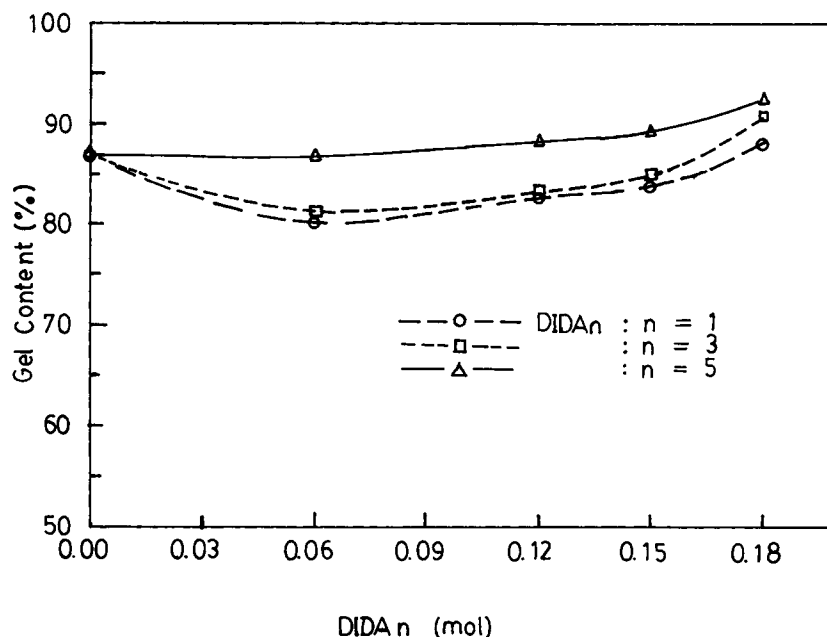


Figure 6 Effect of DIDA n content on the degree of crosslinkage for polyesterdiimide resin system at 210°C for 30 min, using phenol-blocked TDI as curing agent.

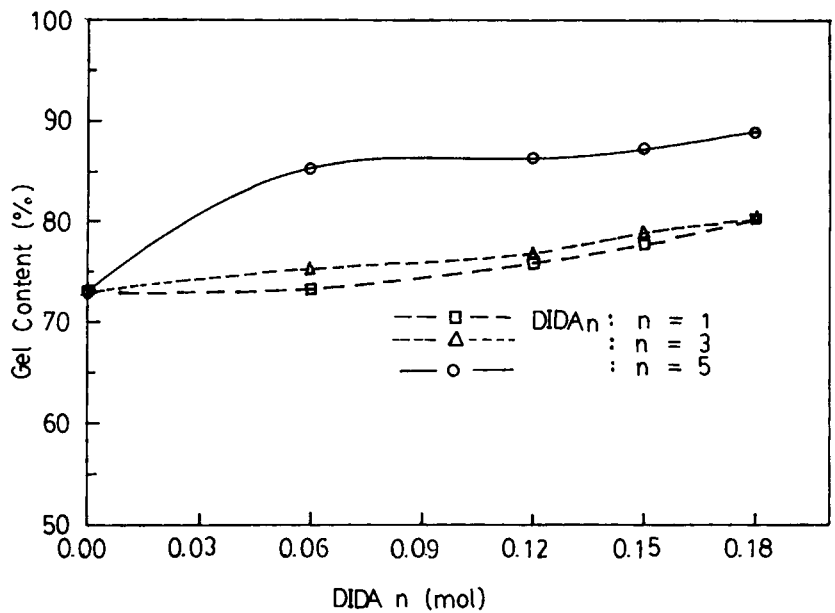


Figure 7 Effect of DIDA *n* content on the degree of crosslinkage for polyesterdiimide resin system at 210°C for 30 min, using phenol-blocked HMDI as curing agent.

creased while increasing the DIDA contents. The degree of crosslinkage for diimide-modified polymers is shown in Figure 7 to increase while increasing the DIDA contents of blocked HMDI curing systems. Two curing systems are compared. The blocked TDI systems have a higher gel content than blocked

HMDI systems for these diimide-modified polyesters. On the other hand, the modified polyesterdiimides containing DIDA 5 record the highest degree of crosslinkage (Figs. 6, 7). This is because the DIDA 5 having the longest chain length and the steric hindrance of the reaction between isocyanate

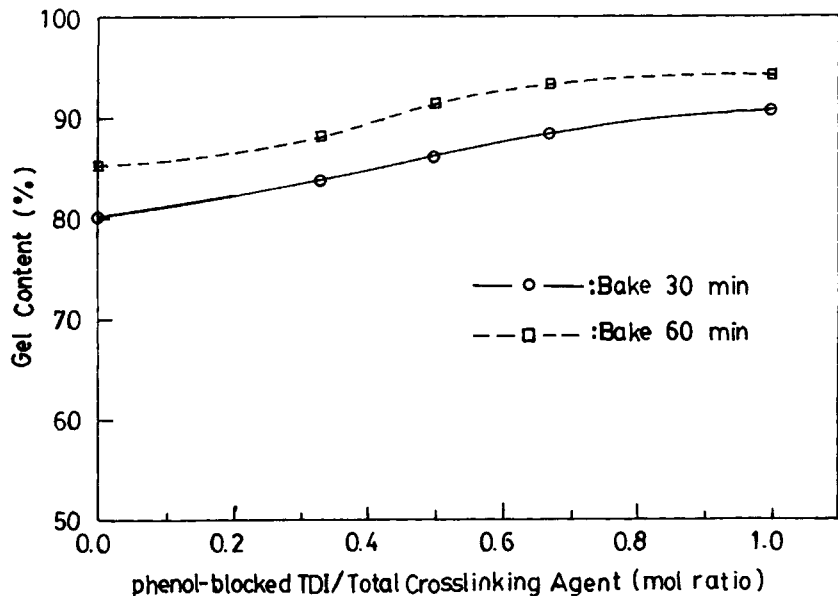


Figure 8 Effect of different curing agent composition on the degree of crosslinkage for 0.18 mol DIDA 3 content polyesterdiimide resin at 210°C for 30 min.

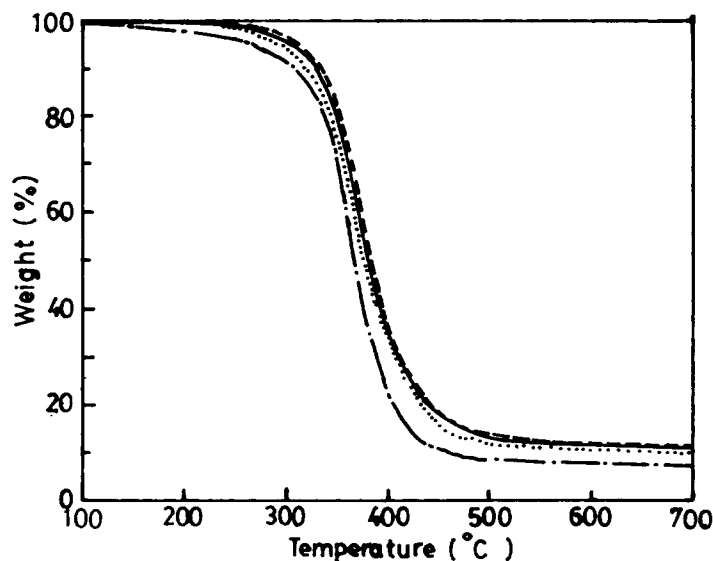


Figure 9 TGA thermogram of 0.18 mol DIDA n content polyesterdiimide resins with $n = 1$ (—); $n = 3$ (---); $n = 5$ (-.-); and no DIDA (· · ·) cured by phenol blocked HMDI.

and hydroxyl group is reduced. This results in a higher crosslinkage. The degree of crosslinkage can also be noted to follow such a tendency: DIDA 5 > DIDA 3 > DIDA 1. This tendency is the same as that followed by their chain length.

Effect of Different Mixing Compositions of Crosslinking Agent on Degree of Crosslinkage for Modified Polyesterdiimide

The effect of the different mixing compositions of curing agent, blocked TDI and HMDI, and curing temperature on the degree of crosslinkage for 0.18 mol DIDA 3-modified polyester prepolymer cured at 210°C for 30 and 60 min is shown in Figure 8. The degree of crosslinkage is shown by the results to gradually increase while increasing the molar ratio of phenol blocked TDI/(phenol blocked TDI + HMDI) = 0 – 1.0/1.0. This is because the reaction activity of the isocyanate group on TDI is higher than the isocyanate group on HMDI (the reaction temperature of TDI with the OH group is lower than the temperature of HMDI). The effect of curing time for these systems on the gel content is very significant.

Thermal Analysis

The diimide-modified polyester prepolymer can be mixed with an equivalent phenol-blocked HMDI and/or TDI, and then baked at 210°C for 30 min

in forming cured films. The thermal behavior of the cured films has been examined with thermogravimetric traces at a heating rate of 20°C/min. The results shown in Figure 9 are blocked HMDI cured samples. The temperature of 50% weight loss is shown by the TGA curves to be in the order of DIDA 3 (385°C) > DIDA 1 (382°C) > DIDA 5 (376°C) > no DIDA (360°C). The modified polyesters are indicated by this result to have a higher thermal stability than that of a nonmodified polyester. Additionally, the dicarboxylic diimide component consisting of fewer methylene groups should theoretically have a higher thermal resistance for an identical molecular weight.⁴ The molecular weight of DIDA 3 containing prepolymer is, however, larger than DIDA 1 containing prepolymer (see Table II). This tendency, DIDA 3 > DIDA 1 > DIDA 5, is therefore reasonable.

CONCLUSIONS

The DIDA-modified polyester prepolymers have been successfully synthesized through melt polycondensation. The prepolymers were mixed with phenol blocked isocyanates (TDI or HMDI) in *m*-cresol in deriving the polyester urethane varnishes. The quantity of crosslinking agent that is only the hydroxy value of prepolymer has been shown to contain a degree of crosslinkage greater than 90%. The catalyst effect of DBTDAc was much greater

than DBTDL on the rate of curing. The tendency of the degree of crosslinkage for diimide modified polyesters was as follows: DIDA 5 > DIDA 3 > DIDA 1. This tendency is followed by their chain length. The order of the thermal stability for these modified systems was: DIDA 3 > DIDA 1 > DIDA 5.

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