

# Various Properties of Diimide–Diacid-Modified Saturated Polyesters

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## SYNOPSIS

Polyesterdiimide prepolymers containing synthesized diimide–diacid monomer (DIDA $n$ ) were synthesized under conditions previously reported. One-component varnishes were obtained by mixing the synthesized prepolymers with phenol-blocked toluene diisocyanate (TDI) and/or hexamethylene diisocyanate (HMDI). The solubility parameter of diimide-modified polyester prepolymer was investigated using an intrinsic viscosity measurement. Thermal behavior and pyrolysis activation energy were also investigated using thermogravimetric analysis. The thermal stability increased with an increase in the content of DIDA. The diimide-modified polyester one-component varnishes coated onto an aluminum panel were found to be acceptable, according to the specification of ASTM D-3794. © 1994 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.A.). The polyester–imide was obtained through incorporating imide monomer units into a polyester main chain for modification of the heat resistance of varnishes.

The polyester–imide resins, which were blended with a cross-linker to form a one-component varnish, contain several properties that are better than those of the known alkyd resins. Polyester–imide resins also have better solubility and adhesive properties than those of the polyimide resins.<sup>1</sup>

Diimide–diacids (DIDA) were previously prepared by pyromellitic dianhydride (PMDA) and aliphatic  $\omega$ -amino acid, such as glycine, 4-aminobutanoic acid, and 6-aminohexanoic acid. The respective products with different numbers of  $-(\text{—CH}_2\text{—})_n-$  groups, where  $n$  is 1, 3, and 5, referred to as DIDA1, DIDA3, and DIDA5, respectively. The diimide–diacid partially substituting isophthalic anhydride (IPA) had then been incor-

porated with 1,6-hexanediol (HD), trimethylol propane (TMP), and phthalic anhydride (PA), followed by melt polycondensation in deriving a diimide-modified polyester prepolymer in the previous study.<sup>2</sup> The obtained prepolymers were then mixed with phenol-blocked toluene diisocyanate (TDI) and/or hexamethylene diisocyanate (HMDI) in producing a one-component varnish. Investigating the solubility parameter of the polyester prepolymer, the thermal behavior and mechanical properties of the cured polyesterdiimide varnishes, and the coating properties of resulting coil coatings were the primary objectives of this study.

## EXPERIMENTAL

### Synthesis and Cross-linking of Polyesterdiimide Prepolymers

The monomers used in synthesizing polyesters and/or polyesterdiimides prepared by a two-step procedure under laboratory conditions were treated the same as those described in a previous study.<sup>2</sup> The compositions and characteristics of polyester and polyesterdiimides are listed in Table I. The prepared prepolymers were mixed with an equivalent phenol-

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Table I Composition and Characteristics of Polyester and Polyesterdiimide

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

<sup>a</sup> Using the end-group method to evaluate.

blocked TDI and/or HMDI; the mixtures were then baked at 210°C for 30 min.

### Determination of Solubility Parameters of Polyester Prepolymers

The solubility parameters ( $d$ ) of the polyester prepolymers were measured by a single specific viscosity proposed by Ram Mohan Rao and Yaseen.<sup>3</sup> They proposed the following single-point equation for calculating intrinsic viscosity of the resin solutions:

$$[\eta] = [\eta_{sp} + \ln \eta_r]/2C$$

where  $[\eta]$  is the intrinsic viscosity;  $\eta_{sp}$ , the specific viscosity;  $\eta_r$ , the relative viscosity; and  $C$ , the concentration of the solution.

Two solutions having various concentrations for each polyester prepolymer were prepared for every solvent listed in Table II. The viscosity was measured by an Ubbelohde viscometer at  $30 \pm 0.01^\circ\text{C}$ .

### Mechanical Properties of Polyesterdiimide-Cured Films

The cured film was cut into a dumbbell shape with a length of 7 cm, a breadth within 1 cm at the neck, and a thickness less than 0.5 mm. An Instron universal tester Model 1130 with a load cell of 5 kg was employed for studying the stress-strain behavior of the sample at room temperature at a crosshead speed of 5 cm/min.

### Thermal Analysis

Thermogravimetric analysis of the cross-linked film was measured with a DuPont TGA 951 equipped with a 1090B thermal analyzer in a nitrogen atmosphere at a heating rate of  $10^\circ\text{C}/\text{min}$ . The temperature ranged from 100 to  $700^\circ\text{C}$ . The sample size used was  $15 \pm 2$  mg.

### Coil Coating Test

The manufactured coil coatings were tested according to testing method ASTM D-3794.

## RESULTS AND DISCUSSION

### Effects of Diimide-Diacid on the Solubility Parameter for Polyester Prepolymer

Dissolution of a polymer in a solvent is essential so as to reduce its viscosity to the desired consistency

**Table II** Intrinsic Viscosities of Polyester Prepolymer (Charge 1) in Different Solvents

Solvent	Solubility Parameter (cal/cc) <sup>1/2</sup>	Concn (g/dL)	[ $\eta$ ]
Cyclohexane	8.18	0.1309	0.0240
		0.3308	0.0231
Isobutyl methyl ketone	8.57	0.2225	0.0421
		0.4744	0.0417
Ethyl benzene	8.80	0.1948	0.0453
		0.5140	0.0447
Toluene	8.91	0.2939	0.0528
		0.4789	0.0531
Benzene	9.14	0.2829	0.0599
		0.4956	0.0592
Tetrahydrofuran	9.52	0.2883	0.0629
		0.5365	0.0633
Acetone	9.77	0.3435	0.0552
		0.4253	0.0551
Cyclohexanone	9.88	0.3483	0.0528
		0.5263	0.0527

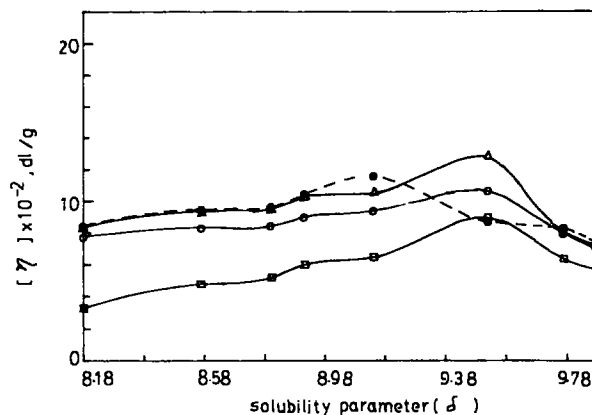
for ease of storage and application and for wetting the substrate. The selection of a solvent for a given resin or polymer can be easily made from their solubility parameters.

The solubility parameter has been previously defined by Hilderbrand and Scott<sup>4</sup> as the square root of cohesive energy density. The solubility parameter can be determined by measuring the intrinsic viscosity of a polymer in a different solvent.<sup>5</sup> A fairly good number of mathematical equations proposed by Huggins,<sup>6</sup> Schulz and Blaschke,<sup>7</sup> and Kraemer<sup>8</sup> are available for determining the intrinsic viscosity of a polymer solution. These equations have been found to hold adequately at low concentrations, and the graphical extrapolation of any one of them is expected to produce more or less the same value of intrinsic viscosity of the polymer in a solvent. Some workers such as Rudin and Wagner<sup>9</sup> proposed equations that required the viscosity of the polymer at a single concentration in a solvent for calculating intrinsic viscosity. These equations are useful in calculating intrinsic viscosity with a permissible degree of accuracy, i.e., once the concentration of the polymer in solution and the choice of solvents are within the prior validation limits.

The single specific viscosity proposed by Ram Mohan Rao and Yaseen<sup>3</sup> for calculating the intrinsic

viscosity on the oil-based polyesteramides has been studied by Praveen Kumar and Gedam.<sup>10</sup> The solubility parameters of the polyesteramide resin were observed by them to have increased with the decrease of oil length of the resin. Polyesterdiimides were prepared in this present study from BD, TMP, IPA, PA, and DIDA under previously reported conditions,<sup>2</sup> and their solubility parameters were determined from their intrinsic viscosity in a series of eight solvents having a solubility parameter range from 8.10 to 9.88 (cal/cc)<sup>0.5</sup>. Two solutions having different concentrations for each resin were prepared in each of those solvents, and the intrinsic viscosities were calculated by the Ram Mohan Rao and Yaseen single-point method. Those results are listed in Table II and Figure 1.

The intrinsic viscosity illustrated in Figure 1 for each prepolymer increases with the increase of the solubility parameter of the solvents up to a certain point and then decreases with the further increase of the solubility parameter of the solvents, precisely as that cited in previous literature.<sup>10</sup> This can be adequately explained by considering solvent-polymer and polymer-polymer interactions. The polymer-polymer interactions are more probable than are the solvent-polymer interactions if the solvent interacts poorly with the polymer. The polymer chain would therefore curl up, demonstrating less hydrodynamic resistance. On the other hand, if the solvent interacts well with the polymer, the solvent that contacts with the polymer molecules would then be more probable than are polymer-polymer contacts and the polymer chain would uncurl, offering more hydrodynamic resistance. The intrinsic vis-



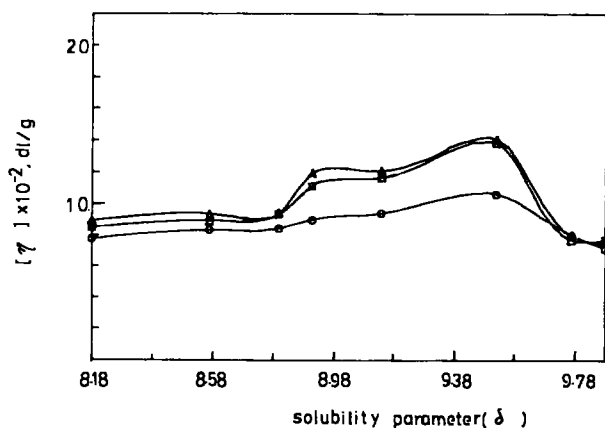
**Figure 1** Relationship between intrinsic viscosity and solubility parameter for DIDAn-modified polyester prepolymer in different solvents: (□) no DIDA; (○) 0.06 mol DIDA1; (Δ) 0.06 mol DIDA3; (●) 0.06 mol DIDA5.

cosity of a polymer solution in a poor solvent is consequently lower than in a good one.

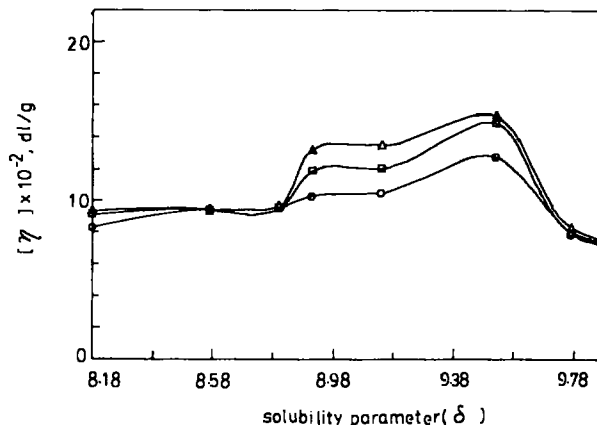
The solubility parameter of a solvent in which the polymer exhibits the maximum value for intrinsic viscosity is taken as the solubility parameter of the polymer. The resin containing no DIDA (charge 1) can therefore be seen from Figure 1 and Table II to possess the highest intrinsic viscosity in the THF solvent. The solubility parameter of that resin consequently becomes equal to the solubility parameter of the THF, i.e., 9.52 (cal/cc)<sup>0.5</sup>. Similarly, the solubility parameter of the prepolymer containing DIDA1 and DIDA3 is apparently 9.52, but the prepolymer containing DIDA5 has shifted to 9.14.

The intrinsic viscosities are observed from Figures 2-4 to increase with the increase of molecular weight (see Table I), and the polyesterdiimides containing DIDA1 and DIDA3 possessed the same solubility parameter of 9.52. Meanwhile, the polyesterdiimides containing DIDA5 have a lower solubility parameter of 9.14. Although their intrinsic viscosities increased with increasing of the molecular weight, the polyesterdiimides containing DIDA3 is nearly equal to those containing DIDA1 and higher than those containing DIDA5.

This occurrence could be attributed to the discrepancy in the length of the —CH<sub>2</sub>— group within DIDA<sub>n</sub>. The polarity of the polyesterdiimides decreases with the increase of the length of the —CH<sub>2</sub>— group. The polyesterdiimides containing DIDA5, which has the lowest polarity, would, consequently, exhibit the lowest cohesive energy due to a low degree of intermolecular association. Hence, this polyesterdiimide requires weaker solvents, such as benzene, for good solubility.



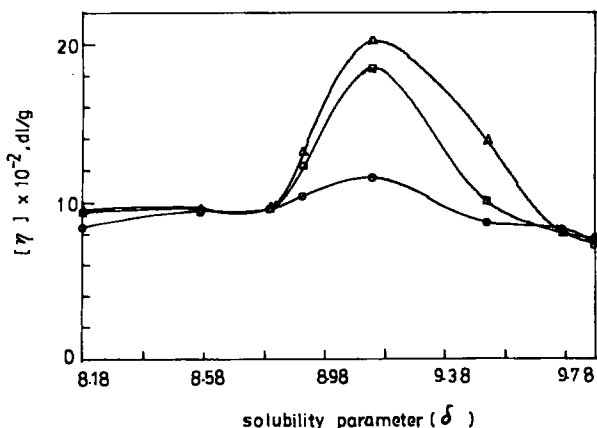
**Figure 2** Relationship between intrinsic viscosity and solubility parameter for DIDA1-modified polyester prepolymer in different solvents: (○) 0.06 mol; (□) 0.12 mol; (△) 0.15 mol.



**Figure 3** Relationship between intrinsic viscosity and solubility parameter for DIDA3-modified polyester prepolymer in different solvents: (○) 0.06 mol; (□) 0.12 mol; (△) 0.15 mol.

#### Thermal Behavior of Polyesterdiimide Varnish-Cured Films

The diimide-modified polyester prepolymers were mixed with an equivalent phenol-blocked TDI and/or phenol-blocked HMDI and then baked at 210°C for 30 min to form cured films. The temperature characteristics of cured films,  $T_0$  (initial decomposition temperature),  $T_{10}$  (temperature for 10% weight loss),  $T_{50}$ , and  $T_{max}$  (temperature for maximum rate of decomposition) were determined with TGA thermograms.  $T_0$ ,  $T_{10}$ , and  $T_{max}$  are feature criteria, and it is therefore possible to correlate the thermal stability with the integral procedural decomposition temperature (IPDT) measurement so



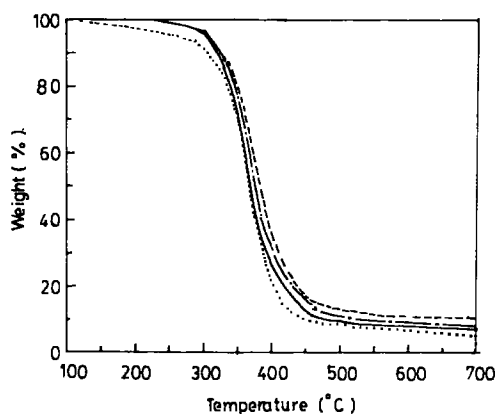
**Figure 4** Relationship between intrinsic viscosity and solubility parameter for DIDA5-modified polyester prepolymer in different solvents: (○) 0.06 mol; (□) 0.12 mol; (△) 0.15 mol.

as to obtain a quantitative indication of the relative stability of cured films. The IPDT, proposed by Doyle,<sup>11</sup> is an index of thermal stability in terms of decomposition temperature. The typical thermogram and temperature characteristic data are shown in Figure 5 and Table III.

The IPDT values listed in Table III are in agreement with the characteristic temperature ( $T_0$ ,  $T_{10}$ , and  $T_{50}$ ). The tendency of the thermal stability increases with increasing the content of the heat-resistant monomer (DIDA) added. The order is as follows: 0.18 mol DIDA  $>$  0.12 mol DIDA  $>$  0.06 mol DIDA  $>$  no DIDA. The tendency of thermal stability for the same amount DIDA (such as 0.18 mol) added is in the order of DIDA3  $>$  DIDA1  $>$  DIDA5 for the initial decomposition temperature, 10% weight loss, and 50% weight loss. The above-mentioned results have the same results as those of the IPDT values. Hence, the quantitative criteria of thermal stability (IPDT) exhibit a better heat resistance of the phenol-blocked HMDI-cured films than that of phenol-blocked TDI-cured films (comparing series a with series b). This is due to the films cured by phenol-blocked HMDI possessing higher gel contents.<sup>2</sup>

#### Investigation of the Activation Energy for the Cured Polyesterdiimide Varnish Films

The activation energy ( $E$ ) for the decomposition of the cured polyesterdiimide varnish films has been calculated according to the method previously devised by Coats and Redfern.<sup>12</sup> Those results are listed in Table III and Figure 6. The activation energy shown in Table III increases with an increase in the



**Figure 5** Typical thermogravimetric thermograms for DIDA3-modified polyester prepolymer cured with phenol-blocked-HMDI: (· · ·) none; (—) 0.06 mol; (---) 0.12 mol; (- · -) 0.18 mol.

**Table III** Results of Thermogravimetric Analysis of Cured Films Prepared from Polyesterdiimide Resins

Charge	Weight Loss (%) at Temp. (°C)			Weight Residue at 500°C	IPDT (°C)	$E$ (kcal/mol)
	$T_0$	$T_{10}$	$T_{50}$			
1a	252	288	362	11.0	276.3	20.25
2a	283	303	374	15.2	307.7	36.15
3a	293	309	378	16.8	313.7	36.90
5a	298	315	384	20.3	318.0	38.07
6a	289	305	375	14.0	310.9	39.20
7a	298	311	380	15.8	317.2	39.83
9a	303	318	385	18.2	325.5	40.71
10a	276	300	374	13.9	303.8	30.59
11a	283	305	377	16.0	307.6	30.88
13a	288	310	382	18.0	313.7	31.46
1b	270	305	360	8.1	293.6	22.26
2b	298	318	367	10.5	310.6	39.33
3b	300	321	382	11.9	322.2	39.54
5b	309	329	380	13.2	333.8	40.50
6b	303	319	370	9.3	324.3	41.84
7b	307	323	376	11.2	333.2	42.26
9b	316	332	385	13.1	340.5	43.10
10b	290	316	369	9.0	305.3	32.26
11b	292	318	374	10.2	313.2	32.47
13b	297	319	376	12.1	323.8	33.18
9c	308	324	385	15.5	333.0	41.59

$T_0$ : initial decomposition temperature; IPDT: integral procedural decomposition temperature;  $E$ : activation energy for the decomposition reaction, using Coats's method to evaluate.

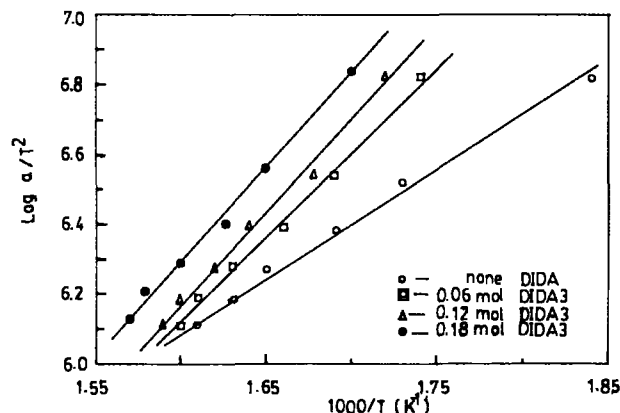
<sup>a</sup> Cured with phenol-blocked TDI.

<sup>b</sup> Cured with phenol-blocked HMDI.

<sup>c</sup> Cured with phenol-blocked TDI/phenol-blocked HMDI = 1/1.

content of the heat-resistant monomer (DIDA) added. The order is as follows: 0.18 mol DIDA3  $>$  0.12 mol DIDA3  $>$  0.06 mol DIDA3. Table III has also shown the following tendency: 0.18 mol DIDA3  $>$  0.18 mol DIDA1  $>$  0.18 mol DIDA5 for different DIDA. The  $E$  values shown in Table III for the DIDA3-modified polyester diimide-cured films using different curing agent compositions have demonstrated the order of phenol-blocked HMDI  $>$  phenol-blocked HMDI/TDI = 1/1  $>$  phenol-blocked TDI, i.e., 9b  $>$  9c  $>$  9a.

The addition of a heat-resistant monomer notably increases the pyrolysis activation energy substantially, e.g., 20.3 kcal/mol for 1a, 36.15 kcal/mol for 2a, and 39.33 kcal/mol for 2b. While adding various amounts of the same monomer, the activation energy increases with an increase in the adding amount, e.g., 36.15 kcal/mol for 2a, 36.90 kcal/mol for 3a, and 38.07 kcal/mol for 5a. These results are similar to their IPDT values.



**Figure 6** Application of the Coats and Redfern's method to experimental data in a nitrogen atmosphere for DIDA3-modified polyester prepolymer cured with phenol-blocked HMDI.

#### Effect of DIDA $n$ Contents on the Tensile Strength for the Cured Polyesterdiimide Films

The cured polyesterdiimides with varied DIDA $n$  amount exhibited better tensile strength (shown in Fig. 7) than those cured films without DIDA $n$  ( $n = 1, 3, \text{ and } 5$ ). Also, the tensile strength increases with the increase of the content of DIDA $n$ . Additionally, the cured films containing DIDA5 were found to possess the highest tensile strength, since they also possessed the highest molecular weight. Figure 7 also indicated that the strain had just the opposite tendency than that of the tensile strength.

#### Effect of the Composition of the Curing Agent on the Mechanical Properties

The tensile strength-tensile strain properties for the cured films prepared from 0.18 mol DIDA3 content

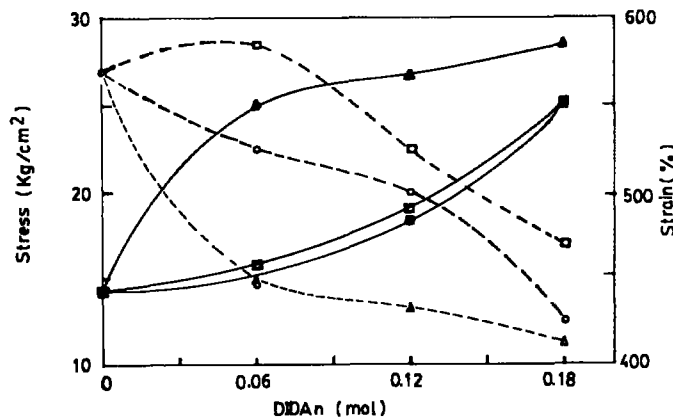
polyesterdiimide prepolymer using different compositions are plotted in Figure 8. The tensile strength is indicated from the results shown in Figure 8 to have increased with an increase of the molar ratio of phenol-blocked TDI/(phenol-blocked TDI + blocked HMDI). The strain decreased with an increase in the blocked-TDI ratio. This result showed that the properties of the cured films exhibit the following trend: soft and tough, hard and tough, hard and strong, and hard and brittle.

#### Test Results of the Synthesized Varnishes for Coil Coating

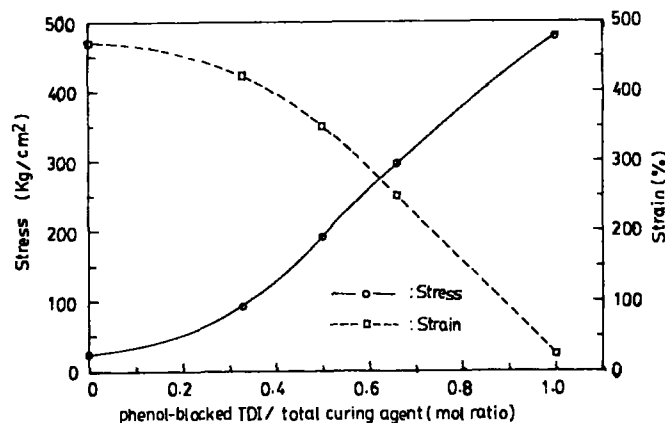
The phenol-blocked HMDI-cured films are observed from the test results of coil coating to be soft and elastic and the phenol-blocked TDI-cured films were hard and brittle. Hence, the polyesterdiimide-cured films with controlled phenol-blocked TDI/HMDI compositions showed excellent properties, such as chemical resistance, adhesiveness, flexibility, and solvent resistance.

#### CONCLUSION

The polyesterdiimide containing DIDA5 was indicated from the observed results to possess a lower solubility parameter of 9.14 (cal/cc)<sup>0.5</sup> than that of DIDA1, DIDA3, and no-DIDA-containing polyesterdiimide, which were 9.52, since the lowest polarity of DIDA5 contained polyesterdiimides. The tensile strength reached a maximum at 0.18 mol DIDA $n$  and the cured films containing DIDA5 possess the highest tensile strength. The integral procedural decomposition temperature (IPDT) and pyrolysis activation energy of the cured varnish were mea-



**Figure 7** Effect of DIDA $n$  contents on the tensile strength and tensile strain for the DIDA $n$ -modified polyester prepolymer cured with blocked HMDI systems: (---) strain; (—) stress; (O)  $n = 1$ ; (□)  $n = 3$ ; (Δ)  $n = 5$ .



**Figure 8** Effect of the curing agent content on the tensile strength and tensile strain for the 0.18 mol DIDA3-modified polyester prepolymer cured with phenol-blocked (HMDI + TDI).

sured. The order of the thermal stability for diimide-modified polyesters was indicated from those results to be as follows: 0.18 mol DIDA3 > 0.18 mol DIDA1 > 0.18 mol DIDA5 > no DIDA. Additionally, the stability increased with an increase in the content of DIDA. The properties of these resins became acceptable by the ASTM D-3794 once those polyestertediimides had been coated onto pretreated panel so as to form coil coating.

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