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METAL ADHESIVE PROPERTIES OF POLYAMIDES HAVING 4,5-DI(1,4-PHENYLENE)- IMIDAZOLEDIYL STRUCTURE

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Key Words: Polyamides, Structural Adhesive, Tensile Strength

ABSTRACT

Polyamides were synthesized by the direct polycondensation of aromatic diamines containing 4,5-imidazolediyl structure with aliphatic dicarboxylic acids, and the metal adhesive properties of these polyamides were studied. The inherent viscosity of the obtained polyamides was in the range of 0.28 to 0.71 dl g⁻¹. The decomposition temperatures (T_d s) of the obtained polyamides were above 400°C and their glass transition temperatures (T_g s) were from 168 to 198°C. These polyamides also showed good solubilities in polar solvents, such as *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc) and formic acid. A standard tensile test was performed in order to examine the adhesive property of these polyamides for stainless steel, and the

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obtained polyamides showed excellent tensile strengths, e.g. polyamide **P1s** derived from 4,5-di(4-aminophenyl)imidazole (DAPI) and sebacic acid had values of 212 kgf cm⁻² at 20°C, 183 kgf cm⁻² at 120°C, and 133 kgf cm⁻² at 180°C. A commercially available epoxy resin was also examined, and showed great tensile strength at 20°C. However, the strength of the epoxy resin was found to decrease with increasing temperature, whereas polyamide having 4,5-imidazolediyl structure retains its strength at temperatures of up to 180°C. In addition, the polyamide was also derived from 4,4"-diamino-*o*-terphenyl(DAOT) (rather than DAPI) and sebacic acid, and the properties of the polyamides derived, respectively from DAPI and DAOT were compared.

INTRODUCTION

High-temperature-resistant polymers are required in structural adhesives that are used to bond metals in various industries, such as space development, electronics, and aircraft. Epoxy resins are widely used in such fields because of their excellent toughness, adhesion, and chemical resistance. However, these adhesives have weak thermostability, although they display great adhesion strengths at room temperature. Polybenzimidazole, polyphenylquinoxaline, and polyimide have been used as structural adhesives and show excellent adhesive properties, even at high temperatures. However, these polymers are difficult to process due to their high T_g s and low solubilities. Although the introduction of the heterocyclic unit to the polymer chain of the aromatic polyamide is effective for improving the thermostability and solubility of these polymers, it also heightened the T_g s. A high temperature is therefore required in order for a polymer having a high T_g to obtain adequate flow prior to adhesion, and this results in polymer decomposition [1]. In our previous paper, we reported on the synthesis and adhesive properties of polyamides having reduced T_g s that were derived from 2,3-bis(4-chloroformylphenyl) quinoxaline (BCFPQ) and several aliphatic diamines [2]. The polyamide prepared from BCFPQ and 1,8-octanediamine displayed high tensile strengths even at high temperature and had good solubilities and reduced T_g s. The present study reports the adhesive properties of polyamides that were prepared by direct polycondensation of aromatic diamines having 4,5-diphenylimidazolediyl structure with aliphatic dicarboxylic acids. In order to examine the effects of polarity and structure on the tensile strength of the adhesion, the polyamide was prepared from sebacic acid and DAOT, which is nonpolar, but has a zig-zagging effect and bulky structure similar to that of DAPI.

EXPERIMENTAL

Monomers

2-Methyl-4,5-diphenylimidazole (MPI) was prepared from ammonium acetate, paraldehyde, acetic acid and benzil. The reaction conditions were similar to those reported in a previous study [3]. The reaction mixture was washed with water and dried. The product was then recrystallized from ethyl acetate and yielded yellow needles. [Yield: 67%. m.p. 247.0-247.5°C [4], m.p. 246-248°C). IR (KBr, cm^{-1}): 3464 (N-H)] Nitration of 4,5-diphenyl-imidazole [5] and MPI afforded 4,5-di(4-nitrophenyl)imidazole and 2-methyl-4,5-di(4-nitrophenyl)imidazole [6], respectively. 4,5-Di(4-nitrophenyl)-2-phenylimidazole [7] and 4,4'-dinitro-*o*-terphenyl [8] were prepared by previously reported methods. All of the diamine monomers, DAPI, 4,5-di(4-aminophenyl)-2-methylimidazole (DAPMI), 4,5-di(4-aminophenyl)-2-phenylimidazole (DAPPI) and DAOT were obtained by reduction of the corresponding dinitro compounds using stannous dichloride and hydrochloric acid according to a previously reported method [9]. The present study used commercially available adipic acid and sebacic acid that were sublimed under reduced pressure prior to use. Dodecanedioic acid was also obtained commercially and was recrystallized from hot water and dried under reduced pressure before use.

Polymer Synthesis

A typical polyamide synthesis is as follows [10]. In a 10-ml four-necked flask equipped with a mechanical stirrer, a nitrogen inlet, a reflux condenser and a thermometer were placed 0.15 g of calcium chloride, 0.05 g of lithium chloride, 2 ml of NMP and 1 ml of pyridine. These substances were then mixed until the salts dissolved. Into this solution, DAPI (0.250 g, 1.00 mmol), sebacic acid (0.225 g, 1.11 mmol) and triphenyl phosphite (0.53 ml, 2.03 mmol) with 0.5 ml of NMP were added under a nitrogen atmosphere, and the temperature was then raised to 115°C. The reaction was maintained under these conditions for 5 hours, and then cooled to room temperature. The mixture was poured into aqueous methanol ($\text{MeOH:H}_2\text{O}=1 : 1$ in volume) for the purpose of precipitation. The precipitates were collected on a G3 glass filter, washed with water and then dried at 60°C under reduced pressure. [87% yield. $\eta_{\text{inh}} = 0.71 \text{ dl g}^{-1}$ (0.5 g dl^{-1} in conc. sulfuric acid at 30°C). IR (Cast, cm^{-1}): 1622, 1528 (amide I, II)] Other polyamides were synthesized by similar procedures.

Measurements

T_g s were obtained by differential scanning calorimetry (DSC) on a MAC Science DSC 3100 at a heating rate of $10^\circ\text{C min}^{-1}$. T_d s were obtained by thermogravimetry (TG) on a MAC Science TG-DTA 2000 at a heating rate of $10^\circ\text{C min}^{-1}$. Thermal mechanical analyses (TMA) were performed by means of the penetrometer on a MAC Science TMA 4000 according to the method of JIS K-7196 under the following conditions: heating rate, 5°C min^{-1} ; ϕ of needle, 1 mm; load, 50 gf. All of the above measurements were carried out in a nitrogen atmosphere IR spectra were recorded on a Hitachi 270-30 spectrophotometer.

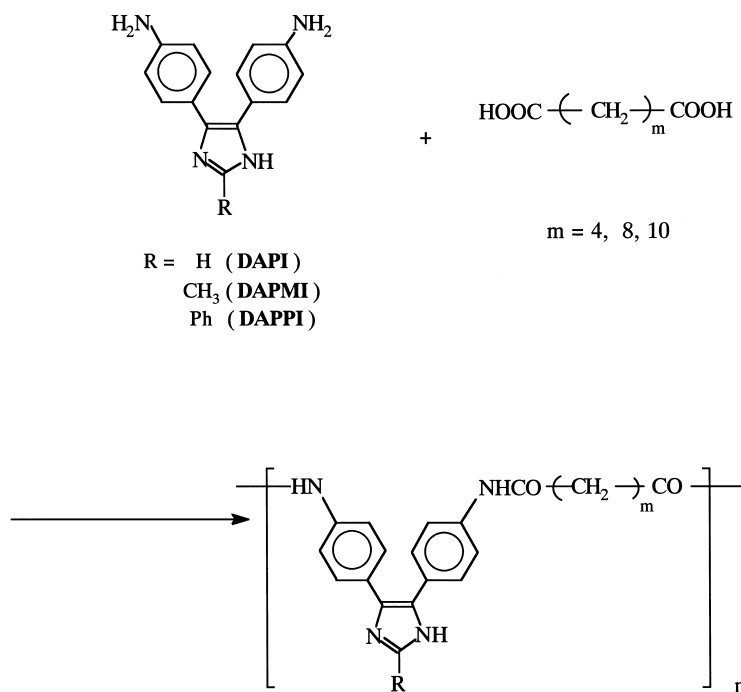
Tensile Tests

Tensile tests were accomplished in the following manner. Stainless steel test pieces (ϕ , 1 cm^2) were polished using alumina, cleaned by immersion in an ultrasonic bath of water and then acetone, and dried before adhesive application. 15% (w/v) NMP solutions of polyamide were applied on surfaces of polished test pieces, degassed under reduced pressure at room temperature for 2 hours, and then heated at 60°C for 4 hours and at 90°C for 2 hours in order to remove the solvent. Next, two polyamide applied test pieces were bound together, pressed under 7 kgf cm^{-2} at a fixed temperature for 1 hour and cooled to room temperature. The test pieces were maintained at 20, 120, and 180°C , respectively for 15 minutes in a thermostat. Tensile strengths were measured at each temperature using a universal-testing machine (Shimadzu Autograph DSS-2000) at a crosshead speed of 1 mm min^{-1} . The epoxy resin, examined for the purpose of comparison, was Hi-Bon 3593, Hitachi Kasei Polymer, Co., Ltd.

RESULTS AND DISCUSSION

Polymer Synthesis

The polyamides were synthesized by direct polycondensation of aromatic diamines having 4,5-di(1,4-phenylene)imidazolediyl structure with aliphatic dicarboxylic acids using lithium chloride, calcium chloride, triphenyl phosphite and pyridine as condensing agent, as shown in Scheme 1. The results of the polycondensations are listed in Table 1. The polycondensations of DAPI and sebasic acid were carried out in DMAc and NMP, and reaction in NMP afforded polyamide **P1s** having higher yield and value of inherent viscosity (runs 1 and 2). In addition, the monomer concentration of the reaction of **P1s** was examined



	R	m
P1a	H	4
P1s	H	8
P1d	H	10
P2s	CH ₃	8
P3s	Ph	8

Scheme 1.

in 0.2, 0.4, and 0.5 mol l⁻¹ NMP, respectively. Reaction in 0.4 mol l⁻¹ NMP solution afforded the polymer having the highest inherent viscosity (runs 2 - 4). Therefore, a series of polycondensations was carried out in 0.4 mol l⁻¹ NMP solution. All of the reactions proceeded in a homogeneous system, and the polyamides obtained had inherent viscosities in the range of 0.28 - 0.71 dl g⁻¹.

Thermal Properties

Table 2 shows the thermal properties of the obtained polyamides. T_g s were determined on a DSC using the second scan after quenching from the tem-

TABLE 1. Results of Polycondensations

Run	Polymer	Solvent	Concentration (mol/l)	Yield (%)	η_{inh}^1 (dl g ⁻¹)	Color
1	P1s	DMAC	0.4	76	0.39	White
2	P1s	NMP	0.4	87	0.71	White
3	P1s	NMP	0.2	96	0.32	White
4	P1s	NMP	0.5	97	0.28	White
5	P1a	NMP	0.4	- ²⁾	- ²⁾	- ²⁾
6	P1d	NMP	0.4	94	0.46	White
7	P2s	NMP	0.4	84	0.38	Yellow
8	P3s	NMP	0.4	85	0.45	Brown
9	P4s	NMP	0.4	90	0.54	White

Conditions:

1) Measured at a concentration of 0.5 g dl⁻¹ in conc. sulfuric acid at 30°C.

2) Polymer was not obtained.

peratures that were approximately 30°C higher than the T_g s obtained by the first scan. The T_g s of the obtained polyamides ranged from 158 to 203°C. This temperature range is adequate for general-use adhesives. It was reported earlier that the T_g s of wholly aromatic polyamides containing 4,5-imidazolediyl structures were approximately 300°C [9] and that those containing *o*-terphenyl structures were approximately 290°C [11]. Apparently, the T_g s of polyamides were reduced by almost 100°C, due to the introduction of methylene units. The T_g of P1d was somewhat lower than that of P1s because the proportion of the methylene unit in the polymer is increased. Despite the reduction of the T_g s, the T_d s of the obtained polyamides measured by TG under a nitrogen atmosphere were as high as 400°C or greater. There was little difference in the T_d s of the polyamides, presumably because these T_d s depend on the decomposition related to the amide groups [12] and are not affected by the length of the methylene unit. Thus, the obtained polyamides exhibited high thermostabilities and a wide gap between T_g s and T_d s.

Solubilities

The solubilities of the polyamides measured at a concentration of 2.0% (w/v) are listed in Table 3. Almost all of these polyamides showed good solubility in polar solvents, such as DMAc, NMP, dimethyl sulfoxide and formic acid, even at room temperature. Furthermore, DMAc or NMP solutions containing greater than 15% (w/v) of P1s were easily prepared without any addition of salts. It is reported that the substituents at 2-position affected on the solubilities of polyamides in the case of wholly aromatic polyamides having 4,5-imidazolediyl

TABLE 2. Thermal Properties of Polyamides

Polymer	T_g (°C) ¹⁾	T_d (°C) ²⁾
P1s	199	418
P2s	198	408
P3s	203	421
P1d	168	416
P4s	158	418

1) Glass transition temperature, measured by DSC.

2) Initial decomposition temperature, observed by TG.

All measurements were performed in a nitrogen atmosphere.

TABLE 3. Solubilities of Polyamides

Polyamide	Py	<i>m</i> -Cr	DMAc	NMP	HMPA	DMF	HCOOH	DMSO	H ₂ SO ₄
P1s	-	(+)	+	+	(+)	+	+	+	+
P2s	-	+	+	+	(+)	(±)	+	+	+
P3s	-	(+)	+	+	(+)	+	+	+	+
P1d	(±)	+	+	+	(+)	+	+	+	+
P4s	-	+	+	+	+	+	-	(+)	+

Measured at 2.0% (w/v). Data in parentheses were obtained during heating at 90°C.

The symbols and abbreviations in the table have the following meanings: +, soluble; -, insoluble;

±, partially soluble; Py, Pyridine; *m*-Cr, *m*-cresol; DMAc, *N,N*-dimethylacetamide; NMP, *N*-methyl-2-pyrrolidone;

HMPA, hexamethylphosphoric triamide; DMF, *N,N*-dimethylformamide; DMSO, dimethyl sulfoxide.

structure [9], there was no significant difference between the solubilities of **P1s**, **P2s** which is methyl derivative of **P1s**, and **P3s** which is phenyl derivative of **P1s**. The methylene units in the polymer appear to be so flexible that the solubilities are not influenced by the bulkiness of the substituents or resonance between imidazole unit and the substituent. Thus, based on their reduced T_g s, which are adequate for general-use adhesives, excellent thermostabilities, and good solubilities, these polyamides are expected to be applicable as thermal resistant adhesives.

Adhesive Properties

For the tensile testing of the adherences of the polyamides to the stainless steel test pieces, 15% (w/v) NMP solutions of polyamides were prepared and were applied to the polished and cleaned surfaces of test pieces. After the solvent was dried, two test pieces were bound together and pressed under 7 kgf cm^{-2} at 300°C for 1 hour, except for **P1d**. The temperatures at which 5% weight loss was observed for **P1d** was confirmed to be 239°C by TG, and the bonding temperature of **P1d** was fixed under that temperature. The samples were then cooled down to room temperature, and the tensile tests were carried out at 20,

TABLE 4. Adhesive Properties of Polyamides

Polymer	Bonding Temperature ¹⁾ (°C)	Solvent	Tensile Strength (kgf cm^{-2})		
			20°C	120°C	180°C
P1s	300	NMP	212	183	133
	300	Formic Acid	-	-	146
P2s	300	NMP	131	108	98
P3s	300	NMP	168	137	131
P1d	230	NMP	122	50	4
P4s	300	NMP	132	108	18
Epoxy resin ²⁾	100	-	308	170	33

- 1) The temperature at which stainless steel test pieces were bonded under a pressure of 7 kgf cm^{-2} for 1 hour. (Epoxy resin was bonded under a pressure of 7 kgf cm^{-2} for 5 hours). 2) Hi-Bon 3593 (Hitachi Kasei Polymer Co., Ltd.).

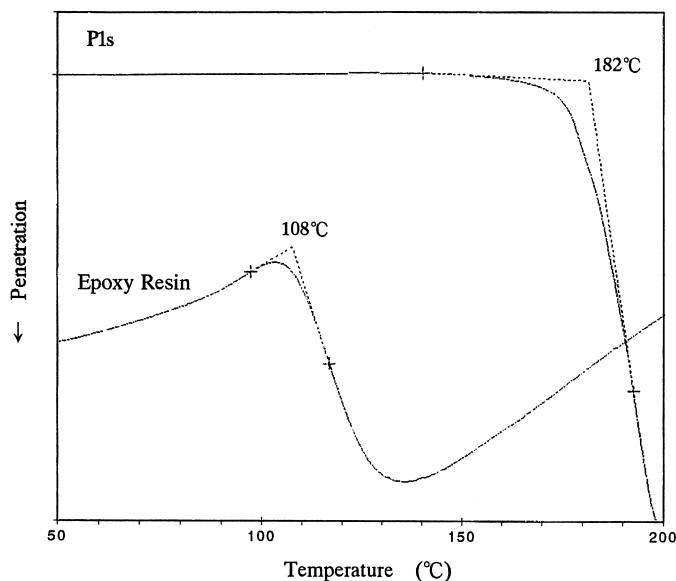
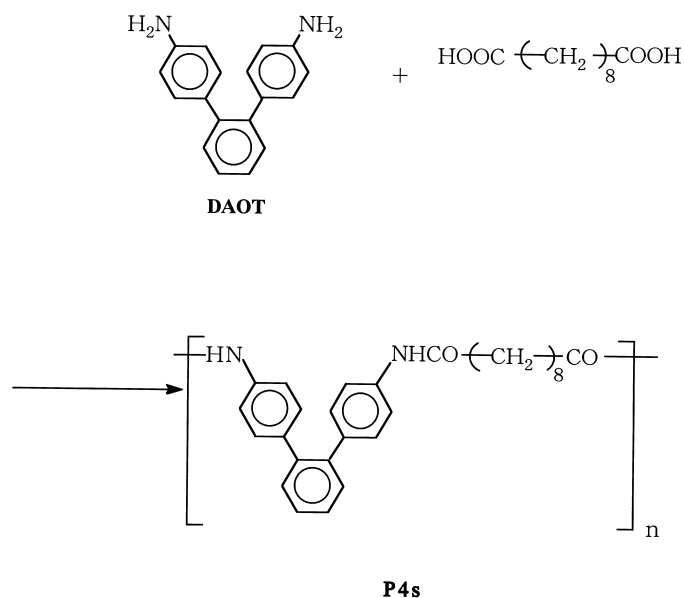


Figure 1. TMA Curves of P1s and Epoxy Resin.

120, and 180°C, respectively. For comparison, a commercially available epoxy resin (Hi-Bon 3593, Hitachi Kasei Polymer Co., Ltd.) was cured at 100°C for 5 hours and tested. The results of this test are summarized in Table 4. At 20°C, the epoxy resin showed the greatest tensile strength (308 kgf cm⁻²) among the polymer examined. However, the tensile strength decreased dramatically at higher temperatures: 170 kgf cm⁻² at 120°C and 33 kgf cm⁻² at 180°C. In contrast, although the tensile strength of **P1s** was exceeded by that of epoxy resin at 20°C, **P1s** retained its tensile strength even at high temperatures: 212 kgf cm⁻² at 20°C, 183 kgf cm⁻² at 120°C and 133 kgf cm⁻² at 180°C. The respective heat distortion temperatures (HDTs) of **P1s** and epoxy resin were measured on a TMA by means of a penetrometer and the TMA curves are shown in Figure 1. The HDT of **P1s** (182°C) was considerably higher than that of epoxy resin (108°C). Although the tensile strengths of **P2s** and **P3s** were not as high as that of **P1s**, the decrease in tensile strength with the increase in temperature for **P2s** and **P3s** were very small, as was the case with **P1s**. Fractured surfaces of **P1s**, **P2s**, and **P3s** were caused by cohesive failure. The results suggest that the polyamide having a 4,5-imidazolediyl unit in the polymer chain provides enhanced thermal resistance compared to other polymers without a reduction in processability. The tensile strengths of **P4s** and **P1d** were extremely low at high temperature because

**Scheme 2.**

the T_g s of these polymers are particularly low. Compared with **P4s** having *o*-terphenyl units instead of 4,5-diphenylimidazole units, **P1s** had better tensile strengths. Both of these units have similar characteristic zig-zagging and bulky structures. However, great tensile strength at high temperature was not due to the structure of these units, but rather to the introduction of a polar heterocyclic moiety. Thus, polyamides derived from aromatic diamine having a 4,5-di(1,4-phenylene)imidazolidiyl unit and sebacic acid showed excellent thermal properties. The introduction of the polar imidazole unit to the polyamide structure in the main chain was found to improve the tensile strength of the adhesion of the polyamide to stainless steel.

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