Metal Adhesive Properties of Polyamides Having the 2,3-Bis(1,4-phenylene)quinoxalinediyl Structure

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Received 16 November 1998; accepted 17 March 1999

ABSTRACT: Polyamides were synthesized by interfacial polycondensation of 2,3-bis(4-chloroformylphenyl)quinoxaline (BCFPQ) and several aliphatic diamines using a phase transfer catalyst, and their adhesive property for stainless steel was investigated. The inherent viscosity of the obtained polyamides ranged from 0.37 to 1.24 dL g^{-1}. The glass transition temperatures of the polyamides ranged between 154 and 201°C, and their thermal decomposition temperatures were above 450°C. The polyamides were soluble in several organic solvents, including *m*-cresol, *N*-methyl-2-pyrrolidone (NMP), and formic acid. The adhesive property for stainless steel was examined by a standard tensile test. One member of the series, polyamide **P8**, derived from BCFPQ and 1,8-octanediamine, displayed high tensile strength with values of 232 kgf cm^{-2} at 20°C, 173 kgf cm^{-2} at 120°C, and 137 kgf cm^{-2} at 180°C. Thus, the tensile strength of **P8** decreased at 180°C, but the decrease was much smaller than that of an epoxy resin in wide use as a metal adhesive. Heat distortion temperature, measured by thermal mechanical analysis, of **P8** was 191°C. This suggested that **P8** possessed high thermal resistance in metal adhesives. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 1366–1370, 1999

Key words: polyamides; structural adhesive; tensile strength

INTRODUCTION

Structural adhesives for metals in general use, such as epoxy resins, show high bond strength at room temperature, but the bond strength decreases dramatically at high temperature.[1] High-temperature organic adhesives, such as polybenzimidazoles and polyimides, possess high thermal resistance; however, the bond strength is lower than those of the epoxy resins at room temperature, and their processability is low.[1,2] Aromatic polyamides also have high thermal resistance, but their processability is low due to their poor solubility and high glass transition temperatures (T_g's).[3] We previously reported that wholly aromatic polyamides with the rigid, zigzag, bulky, and polar 2,3-bis(1,4-phenylene)quinoxaline unit showed high T_g's as well as improved solubility in several organic solvents.[4,5] The present study deals with the stainless steel adhesive property of polyamides having the 2,3-bis(1,4-phenylene)quinoxaline unit. Wholly aromatic polyamides with high T_g's above 300°C are inappropriate for use as the adhesives because their bonding process needs high temperature and pressure, resulting in thermal decomposition. Therefore, polyamides

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Journal of Applied Polymer Science, Vol. 74, 1366–1370 (1999)
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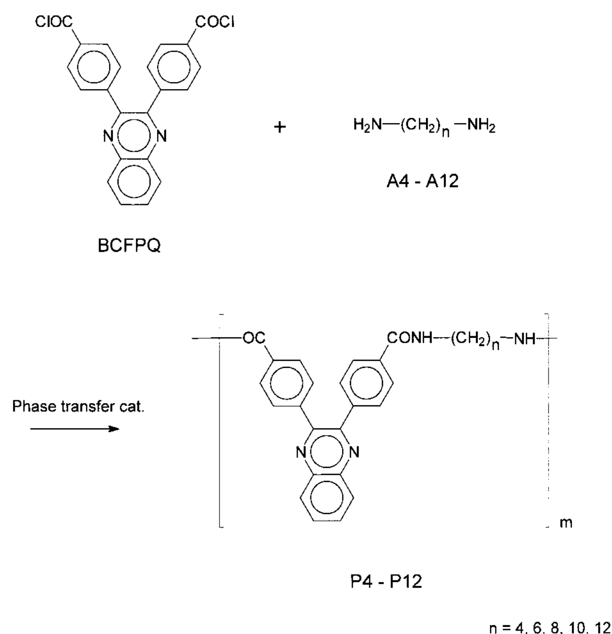

Scheme 1

were synthesized from 2,3-bis(4-chloroformylphenyl)quinoxaline (BCFPQ) and several aliphatic diamines, instead of aromatic diamines, in order to decrease T_g.

RESULTS AND DISCUSSION

Polyamide Synthesis

Polyamides **P4**, **P6**, **P8**, **P10**, and **P12** were synthesized by interfacial polycondensation[6] of BCFPQ[4] and the diamines, 1,4-butanediamine (**A4**), 1,6-hexanediamine (**A6**), 1,8-octanediamine (**A8**), 1,10-decanediamine (**A10**), and 1,12-dodecanediamine (**A12**), respectively, as shown in Scheme 1. Sodium lauryl sulfate was used as a phase-transfer catalyst. The results are summarized in Table I.

Reaction conditions were investigated using the polymerization of **P6** as the probe. Acetophenone, *m*-xylene, and toluene were used as the organic solvent in runs 1, 2, and 3, respectively. Toluene was the most suitable among the solvents for the polycondensation. Volumes of organic and aqueous layer were investigated in runs 3–6. When the volume of toluene was equal to that of the aqueous layer (run 4), the inherent viscosity of the obtained polyamide was highest. Large-scale polycondensations (runs 7–11) were carried out under conditions similar to those of run 4. The polyamides were obtained in 68–83%

Table II Thermal Properties of Polyamides

Polymer	T_g[a] (°C)	T_d[c] (°C)
P4	—[b]	451
P6	201	458
P8	185	459
P10	166	459
P12	154	461

[a] Glass transition temperature, observed by DSC in a nitrogen atmosphere.
[b] Not observed.
[c] Thermal decomposition temperature, observed by TGA in a nitrogen atmosphere.

Table I Results of Preparations of Polyamides[a]

Run	Polyamide	Each Monomer (mmol)	Organic Solvent	Organic Solvent/Water (mL)	Yield (%)	η_{inh}[b] (dL g^{-1})
1	**P6**	1.00	acetophenone	7.0/4.0	24	0.47
2	**P6**	1.00	*m*-xylene	7.0/4.0	75	0.37
3	**P6**	1.00	toluene	7.0/4.0	70	0.41
4	**P6**	1.00	toluene	7.0/7.0	77	0.60
5	**P6**	1.00	toluene	7.0/10.0	81	0.42
6	**P6**	1.00	toluene	8.5/7.0	75	0.37
7	**P4**	2.50	toluene	17.5/17.5	83	0.37
8	**P6**	2.50	toluene	17.5/17.5	73	0.57
9	**P8**	2.50	toluene	17.5/17.5	72	0.73
10	**P10**	2.50	toluene	17.5/17.5	68	0.81
11	**P12**	2.50	toluene	17.5/17.5	78	1.24

[a] Polycondensations were carried out at room temperature for 10 min. Sodium lauryl sulfate was used as a phase-transfer catalyst. All polyamides obtained were white.
[b] Inherent viscosity, measured in conc sulfuric acid (0.50 g dL^{-1}) at 30°C.

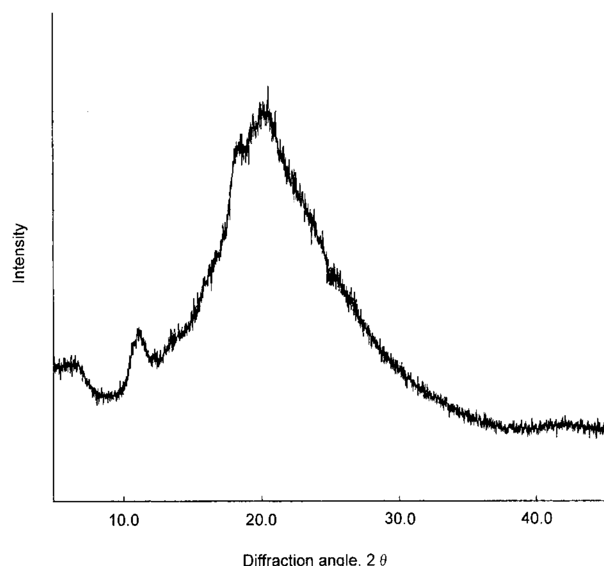

Figure 1 Wide-angle X-ray diffraction pattern of **P8.**

yield, and their inherent viscosity ranged from 0.37 to 1.24 dL g^{-1}.

Thermal Properties and Solubility of Polyamides

The thermal properties of the polyamides are shown in Table II. T_g's of polyamides **P6–P12** ranged from 154 to 201°C as determined by differential scanning calorimetry (DSC). The DSC thermogram of **P4** showed no clear endotherm corresponding to glass transition. T_g's of the polyamides depended upon the aliphatic chain length of the diamine unit, but not upon the inherent viscosity. It was previously reported that the wholly aromatic polyamides derived from BCFPQ showed T_g's above 300°C.[4,5] T_g's of the polyamides derived from BCFPQ and aliphatic diamines were about 100°C lower than those of the wholly aromatic polyamides. T_g's of the polyamides were thus suitable for the adhesive. Thermal decomposition temperatures (T_d's) of all polyamides were above 450°C, as determined by thermogravimetric analysis (TGA) in a nitrogen atmosphere. Thus, the polyamides exhibited high thermal stability.

The crystallinity of **P8** was examined by powder X-ray diffractometry (XRD) analysis. The XRD pattern, shown in Figure 1, suggested that **P8** is not amorphous nature but the crystallinity is low. The DSC thermogram of **P8** showed no clear endotherm corresponding to melting behavior. It is known that many polyamides have the crystalline nature. The characteristic low crystallinity of **P8** is attributable to the influence of the introduction of the rigid and zigzag 2,3-di(1,4-phenylene)quinoxaline.

Solubility in several organic solvents at 2.0% (*w/v*) was examined at room temperature and at 90°C. The results are listed in Table III. The polyamides possessed good solubility in several organic solvents such as formic acid, *N*-methyl-2-pyrrolidone (NMP), and *m*-cresol. In particular, each polyamide except **P4** showed excellent solubility in NMP exceeding 15% (*w/v*). **P4** was not dissolved in NMP at 15%, but it was soluble in *m*-cresol at 15%.

Stainless Steel Adhesive Property

Samples for tensile testing were prepared as follows. Solutions of polyamides were prepared in *m*-cresol at 15% (*w/v*) (**P4**), or in NMP at 15–20% (all other polyamides) and applied to polished surfaces of test pieces made of stainless steel. After drying, two test pieces were put together with polyamide-coated surfaces apposed and pressed under 7 kgf cm^{-2} at 300 or 350°C for 1 h in order to be bonded. Tensile testing of the bonded test pieces was carried out at 20, 120, and 180°C,

Table III Solubilities[a] of Polyamides

Polyamide	*m*-Cre[b]	DMAc	NMP	DMF	HCOOH	DMSO	H_2SO_4
P4	+	−	+	−	+	(±)	+
P6	+	−	+	−	+	(±)	+
P8	+	(±)	+	−	+	(±)	+
P10	+	(+)	+	−	+	(±)	+
P12	+	−	(+)	−	+	−	+

[a] Measured at 2.0% (*w/v*). Data in parentheses were obtained during heating at 90°C. The symbols have the following meanings: +, soluble; ±, partially soluble; −, insoluble.

[b] *m*-Cre is *m*-cresol; DMAc, *N,N*-dimethylacetamide; NMP, *N*-methyl-2-pyrrolidone; DMF, *N,N*-dimethylformamide; HCOOH, formic acid; DMSO, dimethyl sulfoxide.

Table IV Adhesive Properties of Polyamides

Polyamide	Bonding Temperature[b] (°C)	Tensile Strength[d] (kgf cm^{-2})		
		20°C	120°C	180°C
P4	350	—[c]	—[c]	—[c]
P6	300	28	12	—[c]
P6	350	97	50	50
P8	300	232	173	137
P10	300	248	202	24
P12	300	177	136	—[c]
Ep[a]	—	308	170	33

[a] Epoxy resin (Hi-Bon 3593; Hitachi Kasei Polymer Co., Ltd.).
[b] The temperature at which the test pieces were bonded under pressure of 7 kgf cm^{-2} for 1 h.
[c] The bonded test pieces came off before the tensile test.
[d] Measured at a crosshead speed of 1 mm min^{-1}.

respectively. The results are summarized in Table IV.

P8 indicated the highest tensile strength at 180°C in the polyamides examined, and the values of the tensile strength were 232 kgf cm^{-2} at 20°C, 173 kgf cm^{-2} at 120°C, and 137 kgf cm^{-2} at 180°C. The destruction of the adhesion of **P8** was mainly the cohesive failure of the adhesive at all temperatures tested. Table IV also shows the tensile strength of an epoxy resin (**Ep**) based on a diglycidyl ether of bisphenol A and cured with aromatic diamine, examined by the tensile testing under similar conditions, in order to compare bond strengths. The tensile strength of **P8** was lower than that of the epoxy resin at 20°C. However, at 180°C, the tensile strength of **P8** was much higher than that of the epoxy resin. Thus, the tensile strength of **P8** decreased by 40% at 180°C, while the tensile strength of the epoxy resin at 180°C decreased to about one-tenth of the tensile strength observed at room temperature. Heat distortion temperatures (HDTs) of **P8** and **Ep** were measured by thermal mechanical analysis (TMA) using a penetrometer. TMA thermograms are depicted in Figure 2. The HDT of **P8** was 191°C whereas that of **Ep** was 108°C. This suggests that **P8** possesses high thermal resistance in metal adhesives.

Although **P10** showed high tensile strength at both 20 and 120°C, the tensile strength decreased remarkably at 180°C. The destruction of the adhesion of **P10** at each temperature was due mainly to the interfacial peeling. The destruction of the adhesion at 180°C was due to the low T_g of **P10**. The tensile strength of **P12** was low, even at 20 and 120°C. At 180°C, the bonded test pieces came off before the tensile test. The destruction of the adhesion of **P12** was also due mainly to the interfacial peeling at each temperature. The low tensile strengths of **P12** appear to be attributable to the decrease in the amide linkage ratio incumbent upon the longer aliphatic chain in **P12** than in those of the other polyamides. Test pieces bonded by **P4** came apart before the tensile test at all temperatures was carried out. The tensile strength of **P6** was also extremely low. Therefore, the tensile test of **P6** was carried out by bonding test pieces at 350°C since T_g of **P6** was the highest in the polyamides examined. However, the tensile strength was improved moderately over that obtained by bonding at 300°C. The reason for the low tensile strength of **P6** is not clear.

In conclusion, polyamide **P8** shows excellent adhesive property to stainless steel at room temperature, and the tensile strength at 180°C is much higher than that of an epoxy resin in general use as a metal adhesive, although the tensile strength at 180°C is lower than that at room temperature.

EXPERIMENTAL

Polyamide Synthesis

BCFPQ, as a diacyl dichloride monomer, was prepared as reported previously.[4] A typical proce-

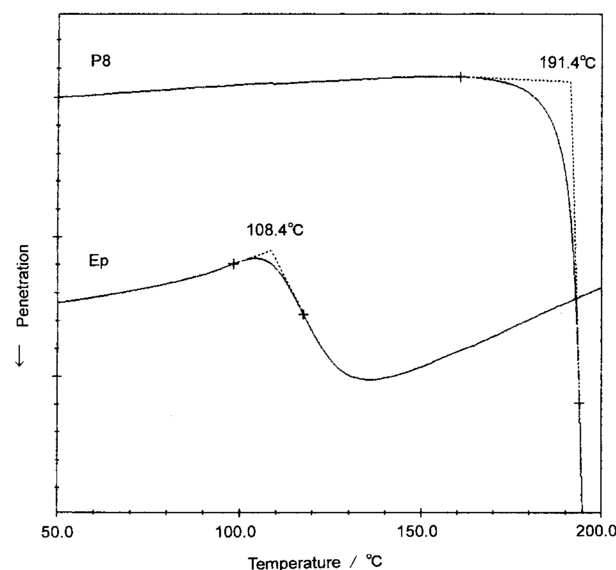

Figure 2 TMA curves of **P8** and **Ep**.

dure of the polymerization (run 4) is as follows. In a homogenizer equipped with a mechanical stirrer, 1,6-hexanediamine (0.14 g, 1.2 mmol), 1*M* aqueous sodium hydroxide solution (2.2 mL), sodium lauryl sulfate (10 mg), and water (4.8 mL) were added. A solution of 0.407 g (1.00 mmol) of BCFPQ in 7.0 mL toluene were added all at once with vigorous stirring. The reaction mixture was stirred for 10 min at room temperature and poured into aqueous methanol (1 : 1 by volume) to precipitate. The products were collected, washed with hot water and hot methanol, and dried under reduced pressure at 60°C [yield 77%; η_{inh} = 0.60 dL g^{-1} (0.50 g dL^{-1} in concd sulfuric acid at 30°C); IR (KBr) 1626, 1530 cm^{-1} (amide I, II)]. Other polyamides were synthesized by a similar procedure.

Measurements

T_d's were obtained by TGA (MAC Science TG-DTA 2000). T_g's were determined by DSC (MAC Science DSC 3100). These thermoanalytical measurements were carried out with a heating rate of 10 K min^{-1} and in a nitrogen atmosphere. T_g's were determined by second scannings. IR spectra were recorded on a Hitachi 270-30 spectrophotometer. Powder XRD analysis of **P8** was performed on a MAC Science MXP-18 XRD apparatus with Cu–K_α radiation (40 kV, 200 mA) using a virgin sample. TMA analysis by means of a penetrometer (MAC Science TMA 4000) was carried out according to the procedure of JIS K-7196 under the following conditions: heating rate, 5 K min^{-1}; ϕ of needle, 1 mm; load, 50 gf; nitrogen atmosphere.

Tensile Testing

Samples for tensile testing were prepared as follows. Surfaces of test pieces made of stainless steel (ϕ, 1 cm^2) were polished with alumina and cleaned ultrasonically in water and in acetone. An NMP solution of the polyamide (15–20 wt %) was applied to the polished surfaces of the test pieces, and the test pieces were dried at 60°C for 4 h, 90°C for 2 h under ordinary pressure and 100°C for 12 h under reduced pressure in order to remove NMP. These two test pieces were put together with polyamide-coated surfaces apposed and pressed under pressure of 7 kgf cm^{-2} at 300°C for 1 h for adhesion. In the cases of **P4** and **P6**, after application of the polyamide solution, the test pieces were dried at 60°C for 4 h, and 90°C for 2 h under ordinary pressure, and the test pieces were bonded at 350°C. The bonded test pieces were cooled to room temperature, and the tensile test was carried out at 20, 120, and 180°C, respectively. Tensile strength was measured with a universal testing machine (Shimadzu Autograph DSS-2000) at a crosshead speed of 1 mm min^{-1}. The epoxy resin, used for comparison, was Hi-Bon 3593, Hitachi Kasei Polymer, Co., Ltd.

The authors thank Mr. Tatsuya Mizoguchi, and Ms. Satoko Shitagaki, Graduate School of Science and Technology, Chiba University.

REFERENCES

1. Shaw, S. J. Handbook of Adhesion; Packham, D. E., Ed.; Longman Scientific & Technical, UK, Essex, 1992.
2. Hergenrother, P. M. Handbook of Adhesives, 3rd ed.; Skeist, I., Ed.; Van Nostrand Reinhold, New York, 1990; Chap. 29.
3. Cassidy, P. E. Thermally Stable Polymers; Dekker: New York, 1980.
4. Akutsu, F.; Hirata, H.; Hayashi, H.; Miura, M.; Nagakubo, K. Makromol Chem, Rapid Commun 1985, 6, 215.
5. Akutsu, F.; Matsuo, K.; Naruchi, K.; Miura, M. Polym Commun 1989, 30, 182.
6. Morgan, P. W. Condensation Polymers by Interfacial and Solution Methods; Interscience: New York, 1965.