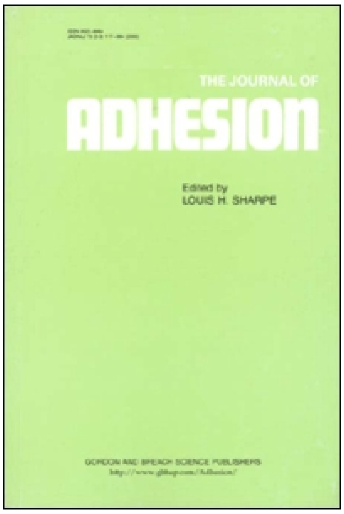

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article Takehara, Akiko , Kajiyama, Mikio and Mizumachi, Hiroshi(1996) 'Preparation and Properties of Aramid Copolymers Derived from 3,4'-ODA, 4,4'-ODA, IPC and TPC', The Journal of Adhesion, 59: 1, 101 — 109

To link to this Article: DOI: 10.1080/00218469608011080

URL: http://dx.doi.org/10.1080/00218469608011080

J. Adhesion, 1996, Vol. 59, pp. 101–109
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Preparation and Properties of Aramid Copolymers Derived from 3,4′-ODA, 4,4′-ODA, IPC and TPC*

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(In final form Janunary 19, 1996)

Two series of wholly aromatic copolyamides (aramid copolymers) derived from (3-aminophenyl) (4-aminophenyl) ether (3,4′-ODA), bis(4-aminophenyl)ether(4,4′-ODA), isophthaloyl chloride (IPC), and terephthaloyl chloride (TPC), having inherent viscosity of 0.63–1.41 $dL \cdot g^{-1}$ were synthesized. The thermal and mechanical properties of the cast films were investigated for application as hot-melt adhesives. When the aramid **34I** composed of 3,4′-ODA and IPC was used, the value of adhesive joint strength at 20°C was 8.4 MPa and this value was maintained even at 230°C. And when 20 mol % of 3,4′-ODA were replaced by 4,4′-ODA, the value of adhesive joint strength at 20°C was a maximum, 16 MPa.

KEY WORDS: Aromatic copolyamides; synthesis; thermal and mechanical properties; adhesive properties; cast films; hot-melt adhesives; thermally-stable polymers; adhesion testing; solution polycondensation; polymer crystallinity.

INTRODUCTION

There are many kinds of thermally stable polymers. Among them, polyimides have been applied as hot-melt type adhesives. Polyimide composed of 3,3′-diaminobenzophenone and 3,3′,4,4′-benzophenone tetracarboxylic dianhydride was developed as LaRC™-TPI for aeronautical use[1,2]. Another LaRC, LaRC™-IA, synthesized from 3,4′-ODA and 4,4′-oxydiphthalic anhydride, which had lower viscosity above the glass transition temperature, was also developed for aeronautical use[3]. To attain desirable properties, an asymmetric structure of (3-aminophenyl) (4-aminophenyl) ether (3,4′-ODA) was introduced in the LaRC™-IA.

On the other hand, the wholly aromatic polyamides (aramids) are also as thermally stable as polyimides, but the crystalline nature of aramids limits their use for hot-melt adhesives. Copolymerization with more than two monomers and introduction of asymmetric structure into the polymer backbone are the usual ways to decrease the degree of crystallinity.

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*Presented at the International Adhesion Symposium, *IAS'94 Japan*, at the 30th Anniversary Meeting of the Adhesion Society of Japan, Yokohama, Japan, November 6–10, 1994.

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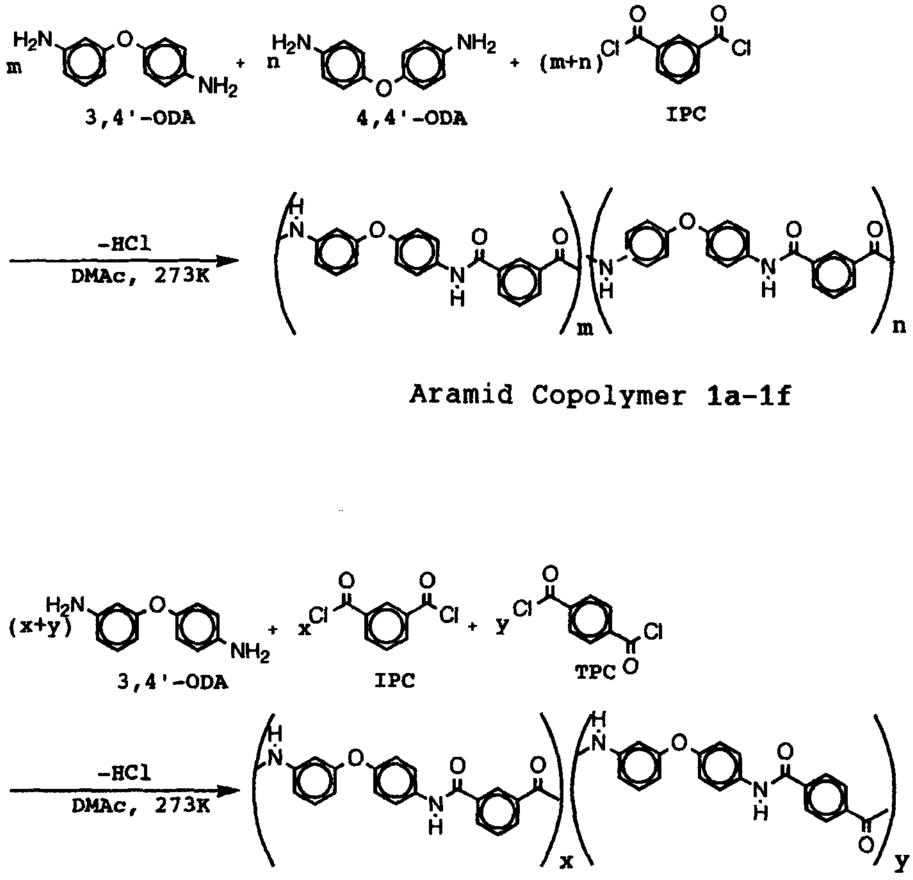
We have already reported the properties of some polyamides, copolyamides and polyamide blends using asymmetric 3,4′-ODA as a comonomer[4–10]. In this article, two series of aramid copolymers, **1a–1f** and **2a–2f**, were synthesized from 3,4′-ODA, 4,4′-ODA, IPC and TPC, and their various properties were characterized for application as hot-melt adhesives.



SCHEME 1

EXPERIMENTAL

Materials

All the reagents used in this study were commercially available and purified by distillation. Aluminum based on JIS H4000, Al050P (Al > 99.50%), was used for adherends.

Polymerization

Aramid 2f 2.00 g (10.0 mmol) of 3,4′-ODA was dissolved in 20 mL of N,N-dimethylacetamide (DMAc) and cooled in a dry ice-methanol bath to solidify the solution. 2.03 g (10.0 mmol) of TPC was added at once into the reaction flask, then the dry ice-methanol bath was replaced with an ice bath and the polycondensation reaction was continued with gentle stirring for 3 hours under nitrogen at 0°C. After that, the reaction mixture was poured into methanol and the precipitated polymer was filtered and dried *in vacuo*. The yield was 3.20 g (97 %). The inherent viscosity in DMAc was 1.41 $dL{\cdot}g^{-1}$, measured at a concentration of 0.5 $g{\cdot}dL^{-1}$ at 30°C. All other aramids and aramid copolymers were synthesized in a similar manner. The yields and the inherent viscosities are summarized in Table I.

Preparation of Films

Polymers were dissolved in N-methyl-2-pyrrolidone (NMP) and cast on glass plates individually. Films were prepared with the following heat cycle: 27°C for 12 hours, 127°C for 12 hours, and finally 227°C for 24 hours *in vacuo*. The thickness of the films thus obtained was about 0.1 mm.

Adhesion Test Specimens

Aluminum plates (100 mm x 25 mm x 1.6 mm) were prepared according to JIS K-6848 (similar to ASTM D-2674). Single lap joints (provided for in JIS K-6850, which is similar to ASTM D-1002) were made of the aluminum plates and the film (25 mm x 10 mm x 0.1 mm) of aramid copolymer. The film was sandwiched between aluminum plates with an overlap of 10 mm and heated for 1 hour under a pressure of 3 MPa at a temperature of 300°C to complete the joint. The thickness of the resulting adhesive layer was 0.04–0.09 mm.

Measurement

Differential scanning calorimetry (DSC) was performed using a Perkin Elmer DSC7 at a heating rate of 40 $K{\cdot}min^{-1}$ under nitrogen. Dynamic mechanical analysis

TABLE I
Preparation of Aramid Copolymer

copolymer series 1				copolymer series 2			
		yield	η_{inh} a)			yield	η_{inh} a)
code	m:n	%	$dl.g^{-1}$	code	m:n	%	$dl.g^{-1}$
1a	5:0	96	0.79	2a	5:0	100	0.79
1b	4:1	95	0.63	2b	4:1	100	0.81
1c	3:2	100	0.79	2c	3:2	99	1.03
1d	2:3	98	0.71	2d	2:3	98	1.26
1e	1:4	100	0.76	2e	1:4	98	1.35
1f	0:5	100	0.85	2f	0:5	97	1.41

a) Measured at a concentration of 0.5 g·dL-1 in DMAc at 30°C.

(DMA) was done on an Orientec Rheovibron DDV-II at a frequency of 110 Hz in a tensile mode at a heating rate of about 4 $K \cdot min^{-1}$ under nitrogen. The dimensions of the test specimen were about 45 mm × 3 mm × 0.1 mm. Static mechanical tests were performed on an Orientec Tensilon UTM-III and UCT-5T at various temperatures. To monitor the temperature of the adhesives, a single lap joint with a thermocouple in the adhesive layer was made. The oven attached to the Tensilon was heated to the desired temperature, then five test specimens and the single lap joint with thermocouple was put in the oven. When the temperature of the adhesive layer reached the temperature of the atmosphere in the oven, the test specimen was attached to the Tensilon. After the temperature in the oven was equal to that of adhesive, the joint was tested at a crosshead speed of 10 $mm \cdot min^{-1}$. The joint strength was determined by the average value of five specimens thus measured.

RESULTS AND DISCUSSION

Preparation of Aramid Copolymers

As shown in Table I, aramid copolymers **1a**–**1f** and **2a**–**2f** having inherent viscosities of 0.63–1.41 $dL \cdot g^{-1}$ were obtained by conventional low temperature solution polycondensation with high yield. The high yield suggested to us that the ratios of 3,4′-ODA/4,4′-ODA and IPC/TPC in the copolymers were the same as those in the feed. The solubilities of the copolymers are shown in Table II. Aramid **34I**, composed of 3,4′-ODA and IPC, which was named **1a** and also **2a**, was soluble in various polar aprotic solvents and pyridine. Aramid **1f** and **2f** were soluble only in NMP and DMAc, because the increasing 1,4-phenylene linkage produced stronger intermolecular forces by hydrogen bonding. When the ratio of 3,4′-ODA/4,4′-ODA or IPC/TPC was over 1/1, the solubilities of copolymers were the same as that of **34I**. And when the ratio was under 1/1, it was soluble in NMP, DMAc, and N,N-dimethylformamide (DMF). It was concluded that copolymerization improved the solubility a little. The films prepared from the NMP solutions by the casting method were tough and ductile.

Thermal and Mechanical Properties

Glass transition temperatures (T_g's) of the aramid copolymers were evaluated by DSC and DMA. The results of the DSC measurements are shown in Figure 1. The

TABLE II
Solubility of Aramid Copolymers

	Polymer					
solvent	1a-1c	1d,e	1f	2a-c	2d,e	2f
N-methyl-2-pyrrolidone	+	+	+	+	+	+
N,N-dimethylacetamide	+	+	+	+	+	+
N,N-dimethylformamide	+	+	−	+	+	−
pyridine	+	−	−	+	−	−
acetone	−	−	−	−	−	−
methanol	−	−	−	−	−	−

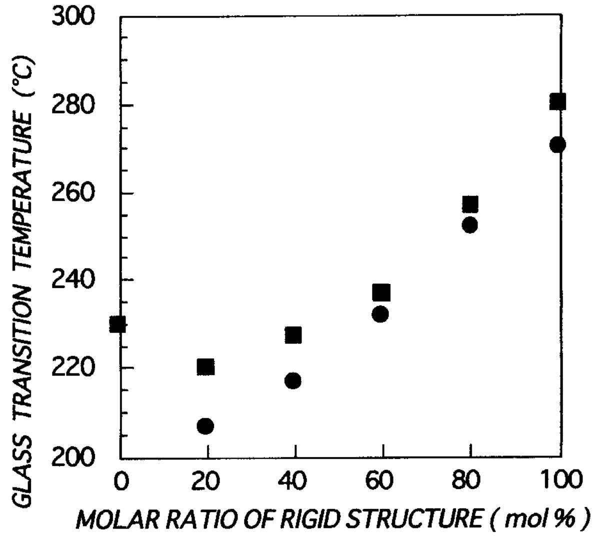


FIGURE 1 Glass transition temperature for aramid copolymers (■ ; 1a–1f, ● ; 2a–2f).

value of T_g increased as the frequency of 1,4-phenylene linkages increased in the copolymers. This result was confirmed by measuring the temperature dependence of the complex modulus, the results of which are shown in Figures 2 and 3. The maximum was the loss modulus was shifted to higher temperature as the frequency 1,4-phenylene linkages increased. Conversely, the maximum was shifted to lower temperature as the 1,4-phenylene linkages decreased, *i.e.*, the T_g decreased with decreasing frequency of 1,4-phenylene linkages. As shown in Figures 2 and 3, because of semicrystalline nature of the aramids the storage modulus of both **1f** and **2f** were maintained around 1 GPa. The high storage modulus above T_g indicated the presence of crystals. The crystallinity of the copolymers decreased with decreasing frequency of the 1,4-phenylene linkage. It was concluded that the introduction of the 1,3-phenylene linkage into the polymer backbone decreased the degree of crystallinity and enhanced the fluidity of the polymers. Static modulus (tensile modulus), together with tensile strength and elongation at break, was also evaluated by a tensile test of the film specimen at 20°C. 75 mm × 10 mm × 0.1 mm strips were cut from the cast film and tested (at least five individual specimens) with a gauge length of 25 mm at an elongation rate of $40\% \cdot \text{min}^{-1}$. The results are summarized in Table III. While the values of tensile strength remained constant at about 100 MPa, the values of tensile modulus increased and those of elongation decreased, as the frequency of 1,4-phenylene linkages increased. This result was also due to the crystallinity of the copolymers, because highly crystalline **1f** and **2f** had higher moduli but tended to break at relatively smaller elongation. The increase of tensile modulus and the decrease of elongation at break meant an increase in the degree of the crystallinity in this case.

Adhesive Properties

The results of adhesive shear test are shown in Figures 4 and 5. The aramid **34I** gave a value of adhesive joint strength at 20°C of 8.4 MPa and maintained this value at

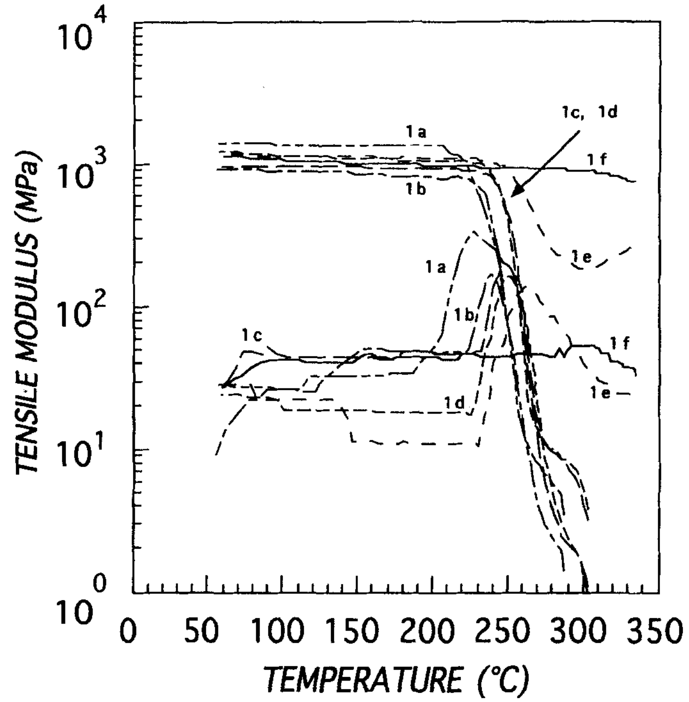


FIGURE 2 Temperature dependence of dynamic moduli for copolymer 1a(–··–), 1b(–·–), 1c(– –), 1d(– –),1e(- - -), and 1f (–).

TABLE III
Tensile Properties of the Films of the Aramid Copolymers

	tensile strength	elongation at break	tensile modulus
code	MPa	%	GPa
1a	101	10.1	1.71
1b	96	12.4	1.39
1c	91	15.1	1.41
1d	108	12.8	1.50
1e	104	12.5	1.49
1f	109	10.2	2.02
2a	101	10.1	1.71
2b	94	10.6	2.08
2c	104	14.7	1.94
2d	92	6.4	2.47
2e	93	8.3	2.52
2f	98	9.6	1.95

230°C. The values of joint strength of **1e**, **1f** and **2f** were small, because those adhesives were not flowable enough at 300°C to adhere, as shown in the DMA data. The values of joint strength at 20°C became larger as the degree of crystallinity decreased. When 20 mol % of 3,4′-ODA were replaced with 4,4′-ODA, the values of

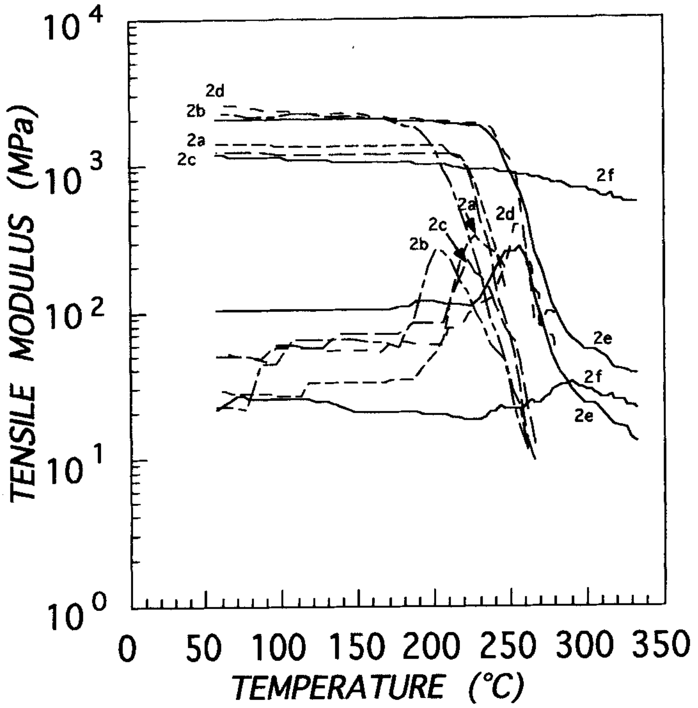


FIGURE 3 Temperature dependence of dynamic moduli for copolymer 2a(——), 2b(—·—), 2c(– –), 2d(- - -), 2e(–), and 2f (–).

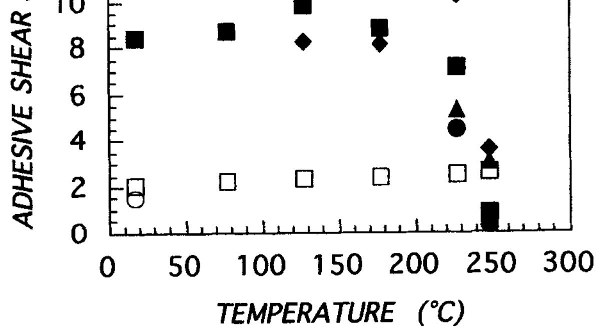


FIGURE 4 Temperature dependence of adhesive shear strength for 1a(■), 1b(●), 1c(▲), 1d(◆), 1e(□), and 1f(○).

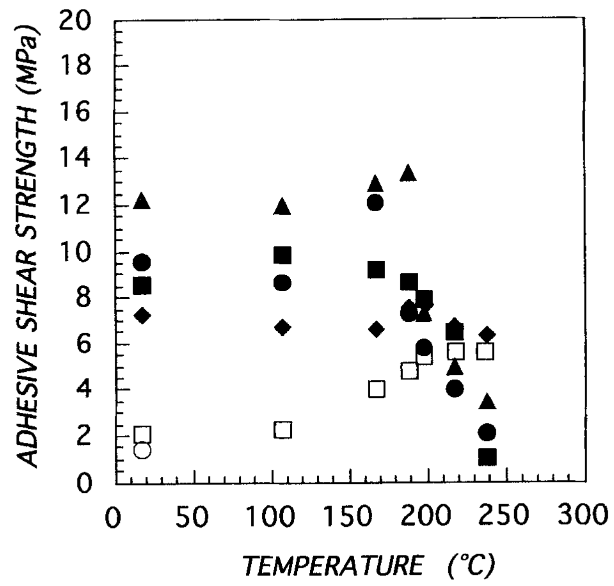


FIGURE 5 Temperature dependence of adhesive shear strength for 2a(■), 2b(●), 2c(▲), 2d(◆), 2e(□), and 2f(○).

adhesive joint strength at 20°C reached a maximum of 16 MPa. The temperature at which the value of joint strength began to decrease moved upward as the T_g of the aramid copolymer increased. The value of joint strength at higher temperature became the largest when almost one-fourth of the 1,3-phenylene linkages were replaced with 1,4-phenylene linkages. This was because copolymerization decreased the crystallinity and enhanced the fluidity of the polymers to wet the substrates.

SUMMARY

Aramid copolymers were successfully synthesized by conventional low temperature solution polycondensation. Films of the aramid copolymers prepared from NMP solutions by the casting method were tough and ductile. Introduction of the 1,3-phenylene linkage into the aramid backbone was effective in decreasing the degree of crystallinity. The values of joint strength at 20°C became larger as the degree of the crystallinity decreased, and when 20 mol % of 3,4′-ODA was replaced with 4,4′-ODA, the values of adhesive joint strength at 20°C had a maximum of 16 MPa. The value of joint strength at higher temperature became largest when almost one-fourth of 1,3-phenylene linkages were replaced with 1,4-phenylene linkages. This was because copolymerization lowered the crystallinity and enhanced the fluidity of the polymers to wet the substrates.

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