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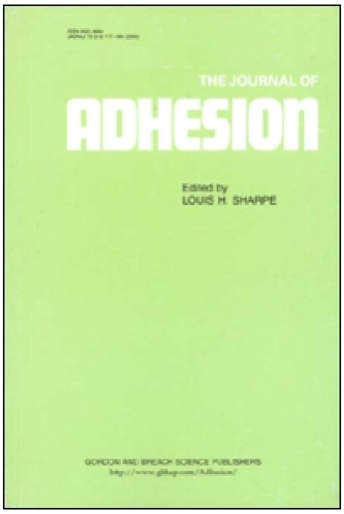

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Preparation of Aramid/Poly (Ethersulphone) Blends and Their Properties for Hot-Melt Type Adhesives*

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A wholly aromatic polyamide (aramid), prepared by the polycondensation of (3-aminophenyl) (4-aminophenyl)ether with isophthaloyl dichloride, was blended with commercially available poly(ethersulphone)s (PES and Cardo-PES) in a N-methyl-2-pyrrolidone solution. The thermal and mechanical properties of the blend films cast from NMP solution were investigated. When 80/20(w/w) aramid/Cardo-PES blend was used as an adhesive, the value of the tensile shear strength of single-lap joints had a maximum. Scanning electron microscopy (SEM) of the fracture area suggested that blending Cardo-PES enhanced some interface strength between polymer and aluminium.

KEY WORDS: aramid; PES; Cardopolymer; blend; phase structure; single-lap joint; tensile shear strength

INTRODUCTION

Much attention has been paid to a new family of high performance blends such as polyimide/polyimide and polyimide/polybenzimidazole.[1–8] During investigations of such high performance blends, an aramid/PES blend was reported.[9–12] A single-phase blend composed of an aramid **44I**, poly (imino-1, 4-phenyleneoxy-1, 4-phenyleneimino isophthaloyl), and a **PES**, poly (oxy-1,4-phenylenesulphonyl-1,4-phenylene), was amorphous and had a glass transition temperature (T_g) around 250 °C. It was easily crystallized by heating and the crystallized blend kept its high modulus even at 400 °C. If this crystallization would behave like crosslinking in an adhesive, a new type of curing system would be developed. But the rate of crystallization was so accelerated that our preliminary trial to apply the system failed.

Aramid **44I**, its isomers, and copolymers were synthesized and characterized in our studies.[13, 14] **44I** seemed to have too high a viscosity at 300 °C to adhere. Using the isomer **34I**, poly (imino-1, 3-phenyleneoxy-1, 4-phenyleneiminoisophthaloyl), or a copoly amide composed of bis(4-aminophenyl) ether (4,4-ODA), (3-aminophenyl) (4-aminophenyl) ether (3,4′-ODA), and isophthaloyl dichloride (IPC), the value of joint

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Part of this study was presented at the 24th Annual Meeting of the Union of Chemistry-Related Societies in Chuba Area, Japan, in 1993.

strength at 20 °C was much higher than that of **44I**. As the T_g of **34I** is lower than that of **44I**, the working temperature was limited to 200 °C.

The T_g of the most typical poly(ethersulphone) **PES**, poly(oxy-1,4-phenylenesulphonyl-1,4-phenylene), is as high as that of **34I**. To enhance the working temperature, it is necessary to use a PES having a higher T_g. Introducing the cardo structure is one of the ways to obtain a higher T_g. A poly(ethersulphone) from fluorene derivatives is a **Cardo–PES**, poly(oxy-1,4-phenylenesulphonyl-1,4-phenyleneoxy-1,4-phenylene-9,9-fluorene-1,4-phenylene), which has such a high T_g, 280 °C.

In this article, blends composed of an aramid **34I** and a **PES** or a **Cardo–PES** were prepared and their thermal and mechanical properties were investigated to be applied as hot-melt type adhesives.

EXPERIMENTAL

Reagents

3,4′-ODA was donated by Mitsui Petrochemical Industries, Ltd. and vacuum distilled. IPC was purchased from Tokyo Chemical Industry Co., Ltd. and vacuum distilled just before use. N-Methyl-2-pyrrolidone (NMP) was vacuum distilled over calcium hydride.

Polymers

Two kinds of poly (ethersulphone)s (**PES** and **Cardo–PES**) were kindly provided by Sumitomo Chemicals Co., Ltd. and Nippon Steel Co., respectively. The inherent viscosity of **PES** and **Cardo–PES** were 0.43 and 0.68 dL·g^{-1}, respectively, measured at a concentration of 0.5 g·dL^{-1} in NMP at 30 °C. Aramid **34I** was synthesized as follows:

2.00 g (10.0 mmol) of 3,4′-ODA was dissolved in 20 mL of NMP and cooled with a dry ice-methanol bath to solidify the solution. 2.03 g (10.0 mmol) of IPC 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 3.2 g (97%). The inherent viscosity of **34I** was 1.41 dL·g^{-1}, measured at a concentration of 0.5 g·dL^{-1} in NMP at 30 °C.

Preparation of Blend Films

An aramid and a PES were dissolved individually in NMP at a concentration of 20 wt%. These two solutions were mixed and the mixed solution was stirred at 80 °C for 2 hours. Then the solution was cast on a glass plate. The cast film was dried at 80 °C for 1 hour, then at 150 °C for 2 hours, and finally at 230 °C *in vacuo* for 24 hours for complete removal of the solvent. The thickness of the film thus obtained was about 0.1 mm. The blend compositions used in this study were 80/20, 60/40, 40/60, and 20/80 aramid/PES (w/w).

Adhesive Joints

A1050P aluminium plates (100 mm × 25 mm × 1.6 mm, Al > 99.50%) etched according to JIS K-6848 (similar to ASTM D-2674) were used as adherends. The blend film (25 mm × 10 mm × 0.1 mm) was sandwiched between the aluminium plates with an overlap of 10 mm and heated to 300 °C for 1 hour at a pressure of 3 MPa to make a single-lap joint (provided for in JIS K-6850, which is similar to ASTM D-1002). The thickness of the adhesive layer was about 0.05–0.09 mm.

Measurements

Differential scanning calorimetry (DSC) was performed with a Perkin Elmer DSC7 at a heating rate of 40 K·min^{-1} under nitrogen. Thermogravimetry (TG) was performed with a Perkin Elmer TGA7 at a heating rate of 5 K·min^{-1} under air. Dynamic mechanical analysis (DMA) was performed with an Orientec Rheovibron DDV-II at a frequency of 110 Hz in a tensile mode at a heating rate of 4 K·min^{-1} under nitrogen. The dimensions of the test specimen were about 45 mm × 3 mm × 0.1 mm. Mechanical properties of blend films and tensile shear strengths of singlelap joints were measured with an Orientec Tensilon UCT-5T at a crosshead speed of 10 mm·min^{-1}. 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 and five test specimens and the single lap joint with thermocouple were put in the oven. When the temperature of the adhesive layer reached the temperature of the atmosphere around the test specimen in the oven, the test specimen was set in the Tensilon. After confirming that the temperature in the oven was equal to that of adhesives, the joint was broken at a crosshead speed of 10 mm· min^{-1}. An average of at least five individual determinations was taken. Scanning electron microscopy (SEM) was performed with a Hitachi S-4000 scanning electron microscope.

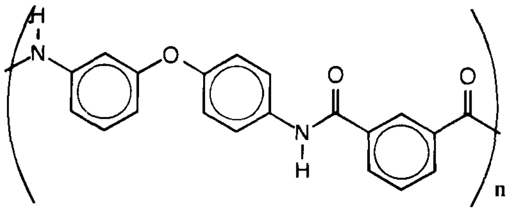
RESULTS AND DISCUSSION

Polymer Preparation

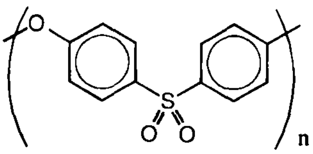
Aramid **34I** (Figure 1–a) was successfully synthesized by conventional low temperature solution polycondensation with a high yield and inherent viscosity. **34I** thus obtained was soluble in 1,1,1,3,3,3-hexafluoro-2-propanol, pyridine, and common polar aprotic solvents like NMP and N,N-dimethylacetamide. Tough and transparent films were cast on a glass plate from solutions.

PES (Figure 1–b) provided by Sumitomo Chemicals was soluble in dichloromethane, pyridine, and common polar aprotic solvents. The value of inherent viscosity was somewhat small but the molecular weight seemed high enough to form tough and transparent films cast from solutions.

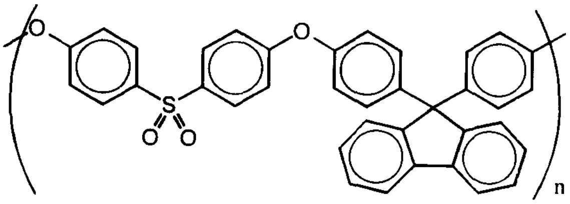
Cardo-PES (Figure 1–c) from Nippon Steel was only soluble in boiling pyridine, hot NMP, and hot 1,3-dimethylimidazolidinone. 20 wt% NMP solution at 80°C was translucent and the cast film after one hour's drying at 80°C was still translucent.



(a) : 34I



(b) : PES



(c) : Cardo-PES

FIGURE 1 Polymers used in this study; (a): **34I**, (b) : **PES**, and (c): **Cardo-PES**.

The cast film became transparent after one hour's drying at 150°C, but it was kept at that temperature for another one hour to remove most of solvent. Traces of the solvent were difficult to remove at ambient pressure, so the film was removed from the glass plate and vacuum dried at 230°C for 24 hours. A tough and transparent film was obtained.

Preparation of Blend Films

The blend compositions were 80/20, 60/40, 40/60, and 20/80 (w/w) both of **34I/PES** and **34I/Cardo–PES** (Table I). An aramid and a poly (ethersulphone) were dissolved individually in NMP at a concentration of 20 wt%. These two solutions were mixed

TABLE I
Preparation of Aramid/Poly (ethersulphone) Blends

34I/PES series			34I/Cardo-PES series		
Code	Weight percentage		Code	Weight percentage	
	34I	PES		34I	Cardo-PES
PES	0	100	Cardo-PES	0	100
20/80 34I/PES	20	80	20/80 34I/Cardo-PES	20	80
40/60 34I/PES	40	60	40/60 34I/Cardo-PES	40	60
60/40 34I/PES	60	40	60/40 34I/Cardo-PES	60	40
80/20 34I/PES	80	20	80/20 34I/Cardo-PES	80	20
34I	100	0	34I	100	0

and the mixed solution was stirred at 80°C for 2 hours. The solution was clear and uniform except for **20/80 34I/Cardo–PES**. The cast film was dried at 80°C for 1 hour, then at 150°C for 2 hours, and finally at 230°C *in vacuo* for 24 hours for complete removal of the solvent. No residual solvent in the film was detected by TG, where no weight loss was observed until 400°C. All of the blend films were tough and translucent, indicating phase-separated structures. These blend films were used for measurement of thermal, mechanical, and adhesive properties.

Thermal Properties

The glass transition temperatures (T_g) of the blend films were measured by means of DSC. T_g of **34I**, **PES**, and **Cardo–PES** were 229, 227, and 273°C, respectively. As the T_g

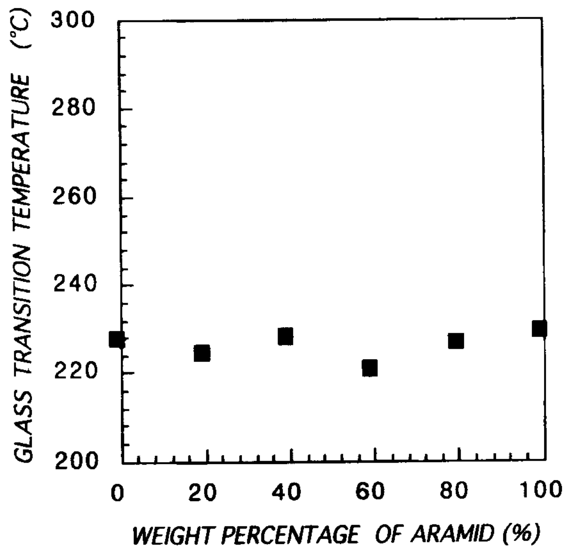


FIGURE 2 Glass transition temperature of **34I/PES** system determined by DSC at a heating rate of 40 K·min^{-1} under nitrogen.

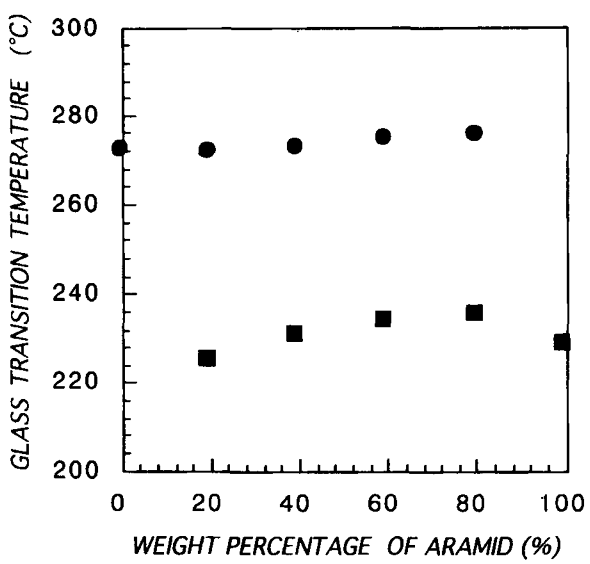


FIGURE 3 Glass transition temperatures of **341/Cardo–PES** system determined by DSC at a heating rate of 40 K·min^{-1} under nitrogen.

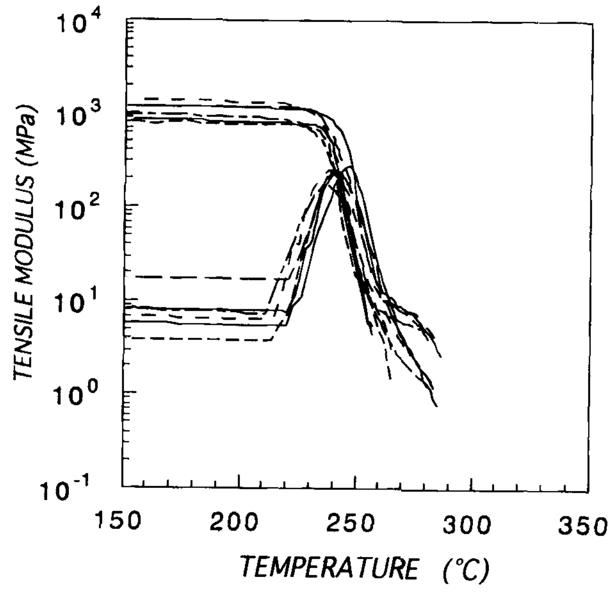


FIGURE 4 Temperature dependence of storage and loss modulus for **341** (—), **80/20 341/PES** (----), **60/40 341/PES** (———), **40/60 341/PES** (———), **20/80 341/PES** (----), **and PES** (———) measured by DMA at a heating rate of 4 K·min^{-1} under nitrogen at 110 Hz.

of two of the components were so close, only one T_g was detected in the **341/PES** system. In contrast, two T_gs were observed around 230 and 270°C in the **341/Cardo–PES** system. The values of both T_g were almost constant and equal to those of homopolymers. The results are summarized in Figures 2 and 3. These results were

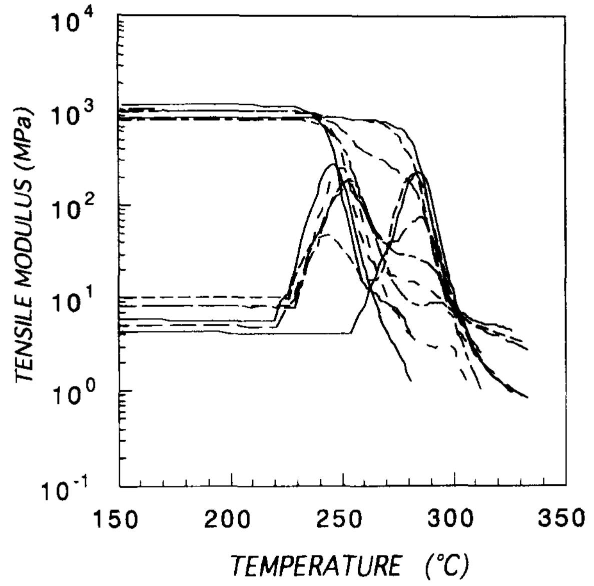


FIGURE 5 Temperature dependence of storage and loss modulus for **34I** (——), **80/20 34I/Cardo-PES** (---), **60/40 34I/Cardo-PES** (·······-----). **40/60 34I/Cardo-PES** (— —), **20/80 34I/Cardo-PES (---), and Cardo-PES** (·· ·· ··) measured by DMA at a heating rate of 4 K·min^{-1} under nitrogen at 110 Hz.

TABLE II
Tensile Properties of Films of Aramid/Poly (ethersulphone) Blends

Code	Tensile strength	Elongation at break	Tensile modulus
	MPa	%	GPa
PES	82	9.3	1.4
20/80 34I/PES	83	9.8	1.2
40/60 34I/PES	91	9.3	1.4
60/40 34I/PES	97	9.2	1.7
80/20 34I/PES	103	10.0	1.5
Cardo-PES	57	4.7	1.8
20/80 34I/Cardo-PES	36	2.8	1.4
40/60 34I/Cardo-PES	30	2.7	1.5
60/40 34I/Cardo-PES	56	4.9	1.5
80/20 34I/Caro-PES	85	8.2	1.6
34I	101	10.1	1.7

confirmed by DMA. Figures 4 and 5 show the temperature dependence of storage and loss modulus for the blend systems. In the **34I/PES** system, the storage moduli of all the films of the **34I/PES** series changed at around 240°C, where a maximum of loss modulus was observed. The behavior was the same for all blend compositions. This is because the temperature dependence of storage and loss modulus for the homopolymers themselves were almost the same. In the **34I/Cardo–PES** systems, two

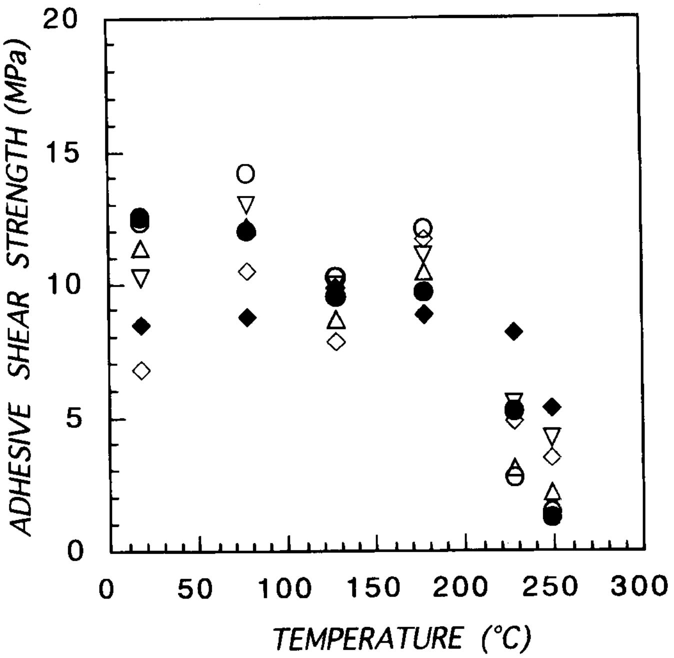


FIGURE 6 Temperature dependence of adhesive shear strength for **34I** (◆), **80/20 34I/PES** (◇), **60/40 34I/PES** (▽), **40/60 34I/PES** (△), **20/80 34I/PES** (○), **and PES** (●).

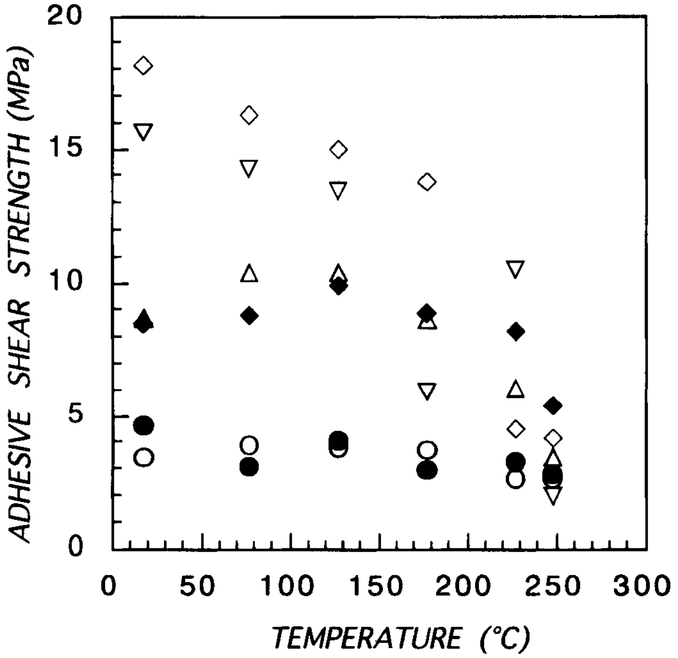


FIGURE 7 Temperature dependence of adhesive shear strength for **34I** (◆), **80/20 34I/Cardo-PES** (◇), **60/40 34I/Cardo-PES** (▽), **40/60 34I/Cardo-PES** (△), **20/80 34I/Cardo-PES** (○), and **Cardo-PES** (●).

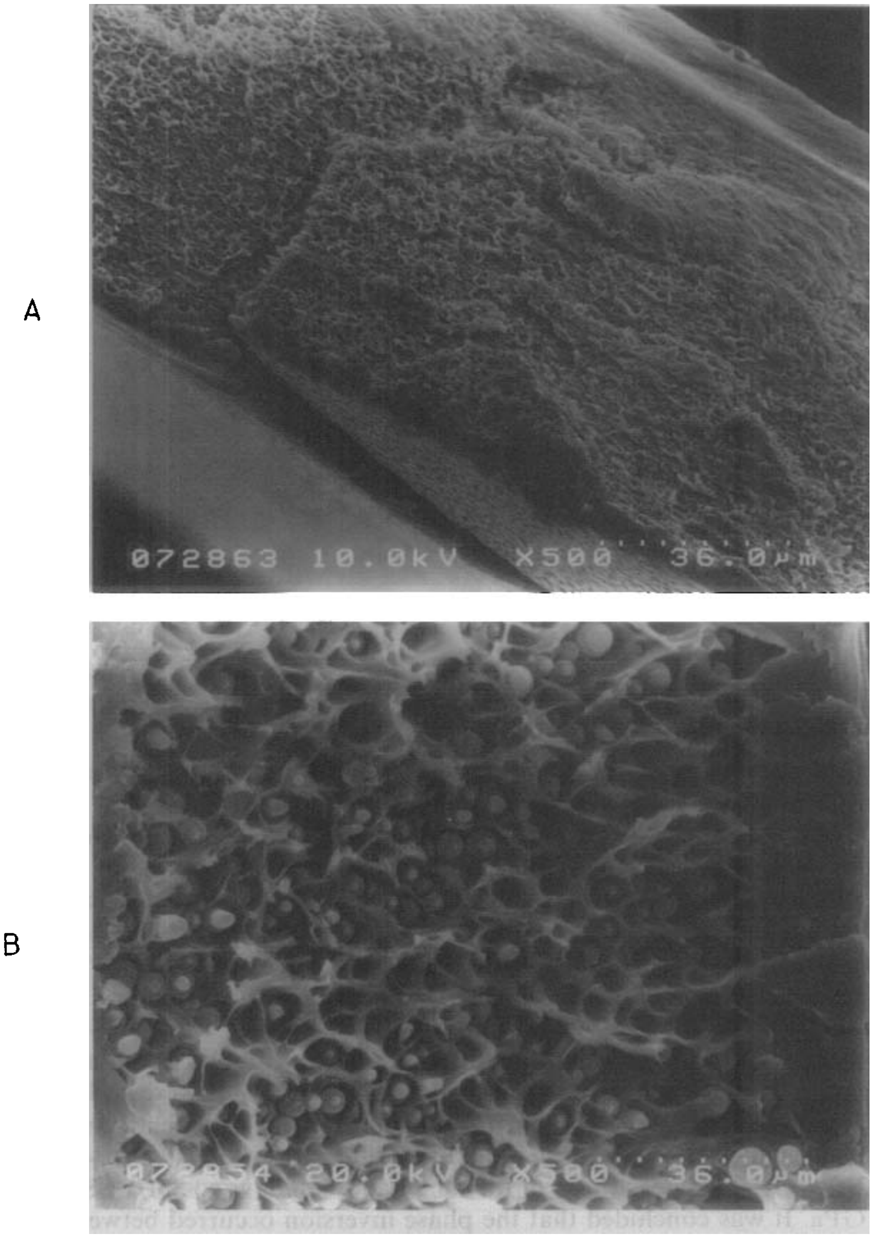


FIGURE 8 Scanning electron micrograph of **20/80 34I/Cardo-PES** film section (A), **60/40 34I/PES** film section (B), and **60/40 34I/Cardo-PES** film section (C).

peaks of loss modulus were observed and the heights of the two peaks changed as the composition was varied. The storage modulus above 250°C decreased as the proportion of aramid component in the blend increased. The fact that the values of both T_g were almost constant and equal to those of the homopolymers suggested that the aramid and poly(ethersulphone)s are practically immiscible.

C

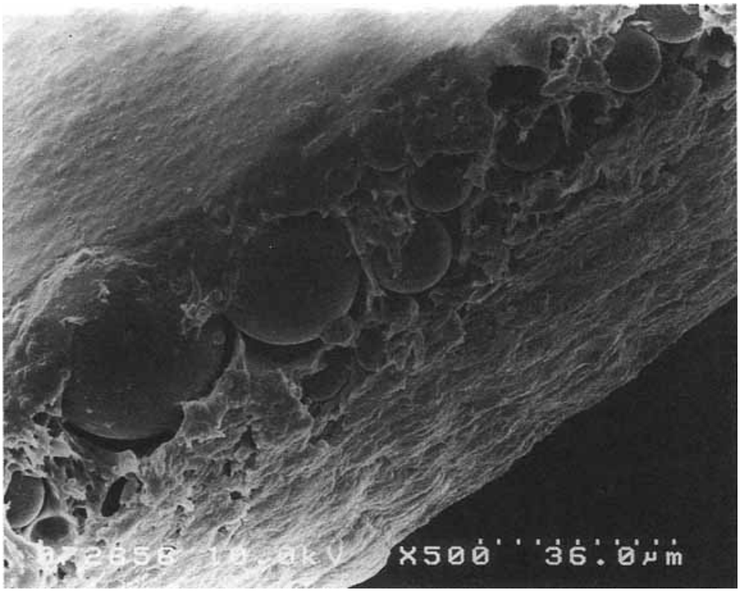


FIGURE 8 *(Continued)*.

Mechanical Properties

Mechanical properties of the films (tensile strength (T), elongation at break (E), and tensile modulus (M)) were evaluated by tensile testing of film specimens at 20 °C. 75 mm × 10 mm × 0.1 mm strips were cut from cast films and tested at least five times with a gauge length of 25 mm at an elongation rate of 40%·min^{-1}. The results are summarized in Table II. The tensile properties of the films were dependent on the **34I** content in the blends. As shown in Table II, aramid **34I** had T/E/M of 101 MPa/10.1%/1.7 GPa, **PES** had T/E/M of 82MPa/9.3%/1.4 GPa, and **Cardo–PES** had T/E/M of 57 MPa/4.7%/1.8 GPa. In the case of the **34I/Cardo–PES** blend series, **20/80** and **40/60** (w/w) **34I/Cardo–PES** blends were slightly brittle. **Cardo–PES** was thought to be the continuous phase and its values of elongation at break and strength were small. Those of **34I** were so large that the values became larger as the content of **34I** increased in the blend systems. In the **34I/PES** series, the values of tensile modulus of **20/80** and **40/60** (w/w) **34I/PES** blend were 1.2–1.4 GPa, whereas those of the **80/20** and **60/40** (w/w) **34I/PES** blends were 1.5–1.7 GPa. It was concluded that the phase inversion occurred between 40/60 and 60/40 in both series.

Single-lap Joint Strength

The test specimen for lap joint strength was made by hot-pressing the blend film between aluminium plates. The press conditions were determined by our preliminary tests and equipmental restriction. At least five individual singlelap joints thus made

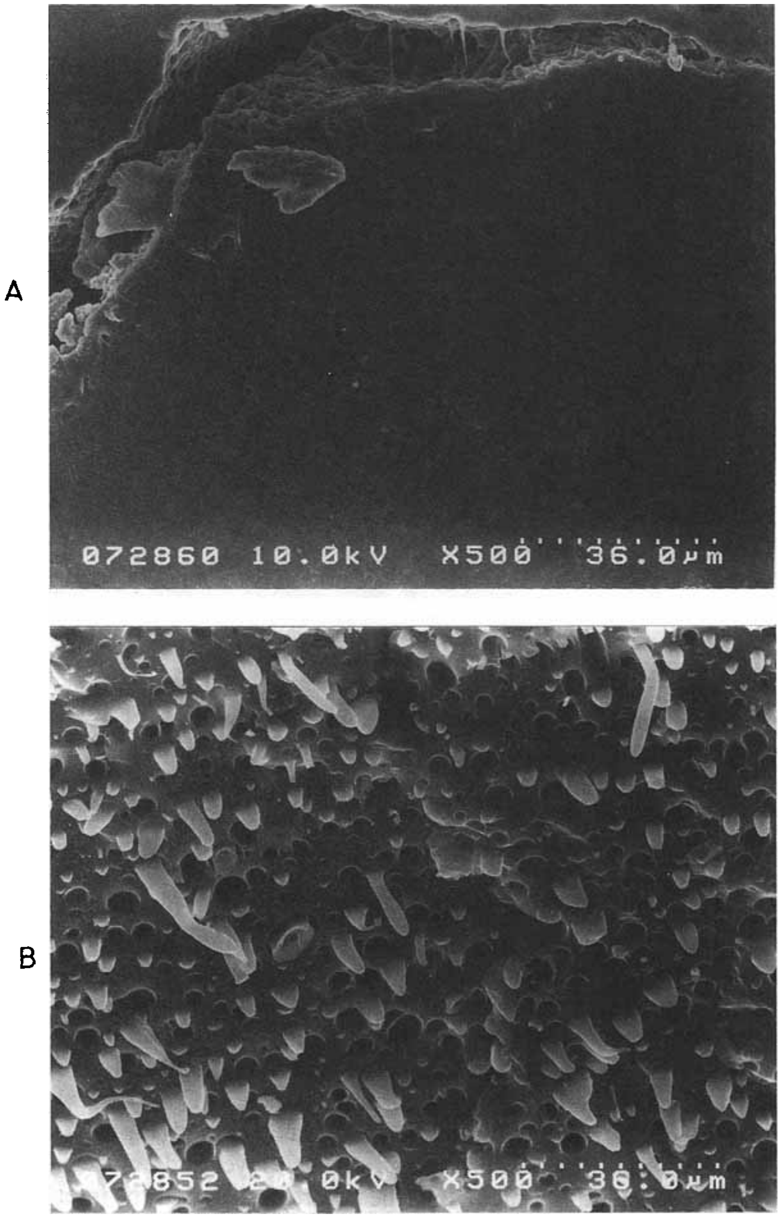


FIGURE 9 Scanning electron micrograph of **20/80 34I/Cardo-PES** broken surface (A), **60/40 34I/PES** broken surface (B), and **60/40 34I/Cardo-PES** broken surface (C).

were tested at various temperatures. The results are shown in Figures 6 and 7. All compositions of the **34I/PES** series in this study had almost the same tendencies, *i.e.*, the tensile shear strengths at 20°C were about 10 MPa, a value up to 190°C, and failure occurred at the interface for all specimens.

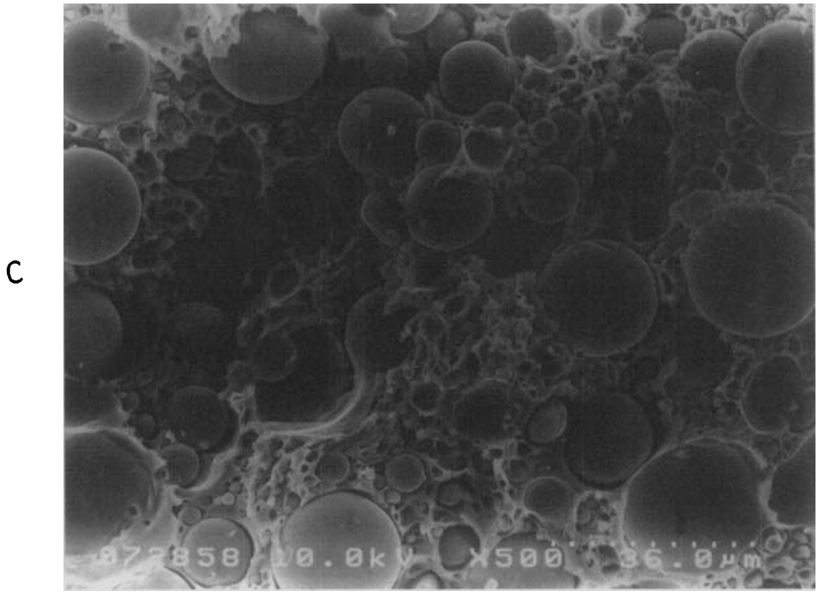


FIGURE 9 *(Contined)*

In contrast, it is interesting that when **80/20** and **60/40** (w/w) **34I/Cardo–PES** blends were used as adhesives, the tensile shear strength of singlelap joints at 20°C increased to 16–20 MPa and both adhesive and cohesive failures occurred, whereas the tensile shear strengths of **Cardo–PES** and **20/80** (w/w) **34I/Cardo–PES** were 3–4 MPa and only adhesion failures took place. The interfacial strength between polymer and aluminium might have increased, because cohesive failure occurred in spite of good mechanical properties of the **80/20** and **60/40 34I/Cardo–PES** blends.

In order to get further information on the fracture mechanisms, SEM was performed. Figure 8 shows a typical section of films broken in liquid nitrogen. A smooth surface and a phase-separated structure were observed in all of the specimens, in which there was a spherical discrete phase in the continuous phase.

Figure 9 shows the fracture area of a singlelap joint tested at 20°C. In the case of **20/80 34I/Cardo–PES**, which had a tensile shear strength of 3 MPa, there was a smooth surface and small cracks in which a discrete phase was observed (Fig. 9–A). Though the film of **20/80 34I/Cardo–PES** was brittle, the adhesive layer had only few cracks. Since the weak adhesive film did not break and the failure occurred at the interface, it could be said that the interfacial strength between polymer and aluminium was very small.

In the case of **60/40 34I/PES**, which had a tensile shear strength of 10 MPa, a smooth surface and cracks were observed. In Figure 9–B, an SEM of the crack area is shown, where the dispersed phase was stretched and torn off. The size of the crack was larger than that of **20/80 34I/Cardo–PES**, while the adhesive film of **60/40 34I/PES** was thought to be stronger than that of **20/80 34I/Cardo–PES**. It must be concluded that the interfacial strength between polymer and aluminium became larger compared with that of **20/80 34I/Cardo–PES**.

In the case of **60/40 34I/Cardo–PES**, which had a tensile shear strength of 16 MPa, almost half of the joint exhibited adhesion failure and the rest had cohesive failure, in which region a spherical phase was clearly observed (Fig. 9–C). As cohesive failure took place despite good mechanical properties of the adhesive film, it should be considered that the interfacial strength between polymer and aluminium increased, so that failures occurred both at the interface and in the adhesive. It was assumed that mixing a small portion of **Cardo–PES** into **34I** enhanced interfacial strength and provided maximum adhesive bond strength.

CONCLUSIONS

Tough and flexible blend films were obtained by a solution blending and a casting method. All the blend films had a phase-separated structure. The aramid and poly (ethersulphone)s are practically immiscible. But mixing a small portion of **Cardo–PES** into **34I** enhanced the interfacial strength between polymer and aluminium. Strong lap joints were obtained from **80/20** and **60/40** (w/w) **aramid/Cardo–PES** systems.

References

1. R. Yokota, R. Horiuchi, M. Kochi, H. Soma and I. Mita, *J. Polym. Sci., Part C: Polym. Lett.* **26**, 215 (1988).
2. L. Leung, D. J. Williams, F. E. Karasz and W. J. MacKnight, *Polym. Bull.* **16**, 457 (1986).
3. G. Guerra, D. J. Williams, F. E. Karasz and W. J. MacKnight, *J. Polym. Sci., Part. B: Polym. Phys.* **26**, 301 (1988).
4. S. Stankovic, G. Guerra, D. J. Williams, F. E. Karasz and W. J. MacKnight, *Poly. Commun.* **29**, 14 (1988).
5. G. Guerra, S. Choe, D. J. Williams, F. E. Karasz and W. J. MacKnight, *Macromolecules* **21**, 231 (1988).
6. P. Musto, F. E. Karasz and W. J. MacKnight, *Polymer* **30**, 1012 (1989).
7. J. Grobelny, D. M. Rice, F. E. Karasz and W. J. MacKnight, *Macromolecules* **23**, 2139 (1990).
8. D. S. Lee and G. Quin, *Polym. J.* **21**, 751 (1989).
9. S. Nakata, M. Kakimoto, Y. Imai and T. Inoue, *Polym. J.* **22**, 80 (1990).
10. M. Matsuura, H. Saito, S. Nakata, Y. Imai and T. Inoue, *Polymer* **33**, 3210 (1992).
11. S. Nakata, M. Kakimoto and Y. Imai, *Polymer* **33**, 3873 (1992).
12. H. Tomura, M. Matsuura, H. Saito, and T. Inoue, *Kobunshi Ronbunshu* **49**, 7 (1992).
13. Y. Imai, M. Kajiyama, S. Ogata and M. Kakimoto, *J. Polym. Sci., Polym. Chem. Ed.* **22**, 3183 (1984).
14. A. Takehara, M. Kajiyama and H. Mizumachi, to appear in the "Proceedings of IAS 94 JAPAN", a conference held in Yokohama, Japan, in 1994.