Preparation and adhesion properties of polyisoimide as a high-temperature adhesive

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(Received 5 January 1994; revised 21 February 1994)

New high-temperature adhesives based on polyisoimide (PII) have been developed. PIIs were prepared by the ring-opening polyaddition of 4,4'-hexafluoroisopropylidenebis(phthalic anhydride) and 4,4'-[hexafluoroisopropylidenebis(*p*-phenyleneoxy)]dianiline or 4,4'-[isopropylidenebis(*p*-phenyleneoxy)]dianiline, followed by treatment with trifluoroacetic anhydride–triethylamine in *N*-methyl-2-pyrrolidone. Compared to those of polyimides (PIs), the glass transition temperatures (T_g) of PIIs were lower and the elasticities were greatly reduced above their T_g. Furthermore, PIIs showed stronger adhesion to copper foils. The interfacial surface morphologies of PII films after adhesion testing were investigated by scanning electron microscopy and energy-dispersive X-ray analysis. The results suggested that the good adhesion bond strength was produced by favourable anchoring between PII and copper foil due to a good flow of PII.

(Keywords: polyisoimide; adhesive properties; surface morphology)

INTRODUCTION

In recent years, high-temperature adhesives have been in high demand for their potential uses in aerospace, electronics and related industries. Various kinds of polymers have been exploited as high-temperature adhesives, including epoxides, phenolics and polyimides. Among those thermally stable polymers a class of adhesives that shows great promise is the polyimides (PIs) because of their excellent properties, such as thermal and chemical stabilities, and low dielectric constants[1].

In terms of their chemistry, PI adhesives are divided into two types. The first type of adhesives is thermoplastic PIs[2–4] such as Lark-TPI, which is prepared by the condensation reaction of aromatic tetracarboxylic dianhydrides and aromatic diamines. These PIs are linear thermoplastic polymers that generally have a high melt viscosity and must be processed at relatively high temperatures (>300°C). The second type is crosslinked PIs[5–7], which are derived from the introduction of a crosslinking site as an end-cap for low-molecular-weight oligomers or monomers. Acetylenic[8] and nadic[9] end-groups are currently used in commercially available PI adhesives. Although these highly crosslinked polymer films show impressive performance, such as high resistance to solvents and improved thermal stability, these films are relatively stiff and brittle compared to linear PIs. These propensities are undesirable for the applications of flexible printed circuits or flexible multilayer substrates.

In a preceding paper[10], we reported the preparation and properties of polyisoimide (PII) as a PI precursor, and found that PII has a lower glass transition temperature (T_g) than that of corresponding PI and is easily converted to PI without elimination of volatile compounds. Therefore, PII is of considerable interest as a candidate for high-temperature adhesives.

This paper describes the synthesis of polyisoimides and their adhesive properties as a high-temperature adhesive.

EXPERIMENTAL

Materials

N-Methyl-2-pyrrolidone (NMP), triethylamine (TEA) and pyridine (Py) were purified by distillation. 4,4'-[Hexafluoroisopropylidenebis(*p*-phenyleneoxy)]dianiline (BAPF) (**2a**) and 4,4'-[isopropylidenebis(*p*-phenyleneoxy)]dianiline (BAPP) (**2b**) were purified by recrystallization from cyclohexane and 2-propanol, respectively. 4,4'-Hexafluoroisopropylidenebis(phthalic anhydride) (6FDA) (**1**) was obtained from American Hoechst Co. Rolled copper foil (35 μm thickness) was used as an adherend. Other reagents and solvents were obtained commercially and used as received.

Polymer synthesis

A typical example is as follows.

*Polymer (**4a**) from (**1**) and (**2a**).* A solution of **2a** (2.22 g, 5.0 mmol) in NMP (43.2 ml) was cooled with an ice–water bath. With stirring, **1** (2.59 g, 5.0 mmol) was added to this solution. The mixture was stirred at room temperature for 4 h. The resulting viscous solution was diluted with NMP (48.2 ml), and TEA (1.4 ml, 10.0 mmol) was added dropwise with continued stirring. The reaction mixture was then cooled with an ice–water bath, and trifluoroacetic anhydride (1.54 ml, 11.0 mmol) was added dropwise with stirring. The mixture was stirred at room temperature for 4 h and then poured into 2-propanol (1000 ml) to precipitate the polymers. The precipitated polymer was filtered off and dried *in vacuo* at 40°C. The yield was 4.54 g (98%). The inherent viscosity of the polymer in

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0032-3861/94/18/4022–06

dimethylacetamide (DMAc) was 0.40 dl g^{-1} at a concentration of 0.5 g dl^{-1} at 30°C. I.r. (KBr), ν (cm^{-1}): 1810, (C=O), 920 (C–O). Analysis – calculated for $C_{46}H_{22}N_2O_6F_{12}\cdot H_2O$: C 58.48, H 2.56, N 2.96; found: C 58.56, H 2.78, N 2.90.

Polymer (5a) from (1) and (2a). Polymer **5a** was prepared from **1** and **2a** as described above using Py and acetic anhydride in place of TEA and trifluoroacetic anhydride, respectively. The yield was 4.59 g (99%). The inherent viscosity of the polymer in DMAc was 0.45 dl g^{-1} at a concentration of 0.5 g dl^{-1} at 30°C. I.r. (KBr), ν (cm^{-1}): 1780, 1720 (C=O). Analysis – calculated for $C_{46}H_{22}N_2O_6F_{12}\cdot H_2O$: C 58.48, H 2.56, N 2.96; found: C 58.34, H 2.82, N 2.97.

Evaluation of adhesion strength

A typical procedure is as follows.

Film casting. A solution of polymer **4a** was made by dissolving the polymer in chloroform to afford a 15 wt% solution. Films cast on glass plates were prebaked at 80°C for 60 min and dried *in vacuo* at 150°C for 12 h. The thickness of polymer film was 25 μm.

Hot press. Test press No. 1541 (Gonno Hydraulic Press Manufacturing Co.) was used for the adhesion between a polymer film and a copper foil. The polymer film was placed between 50 mm × 50 mm pieces of copper foils. The copper foil was washed with acetone prior to use. The assembly was placed in the hot press and melt processed at 200–260°C under 14.7 MPa. After holding for 15 min, the platens were cooled under pressure to room temperature. At least five samples were tested and the average values are reported. The peel strength was measured by a Tensilon UTM-III-500 (Toyo Baldwin) at a peel rate of 50 mm min^{-1} at room temperature (θ^0-peel method)[11].

Measurements

The infra-red spectra were recorded on a Hitachi I-5020 FT-IR spectrophotometer. Viscosity measurements were carried out by using an Ostwald viscometer at 30°C. Thermal analyses were performed on a Seiko SSS 5000-TG/DTA 200 instrument at a heating rate of 10°C min^{-1} for t.g. and on a Seiko SSS 5000-DSC220 at a heating rate of 10°C min^{-1} for differential scanning calorimetry (d.s.c.) under nitrogen.

Molecular weights were determined by gel permeation chromatography (g.p.c.) with polystyrene calibration using a Jasco HPLC system equipped with Shodex KD-80M column at 40°C in dimethylformamide (DMF).

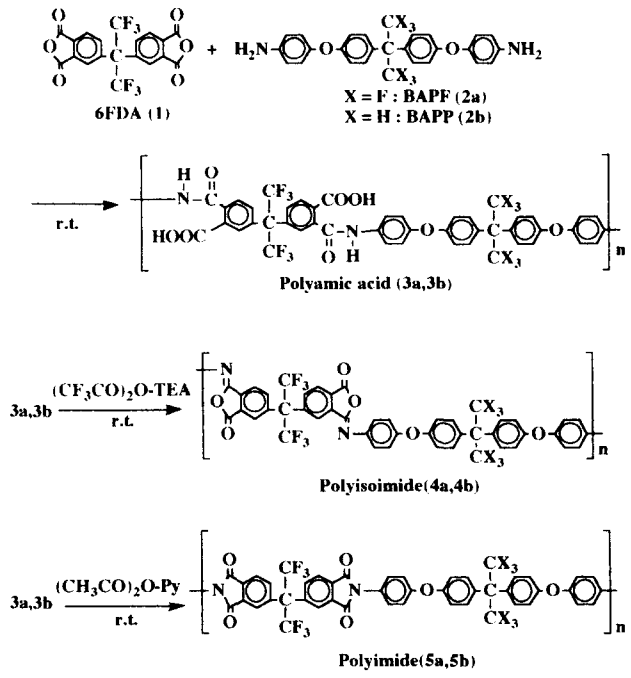
The film thickness was measured by a Dektak 3030 system (Veeco Instruments Inc.).

The morphology of interfacial surfaces between copper and polymer was studied by scanning electron microscopy (SEM) (JEOL JSM-5300) and energy-dispersive X-ray analysis (EDX) (Kevex Delta IV). Dynamic mechanical analysis (d.m.a.) was carried out using a DVE-V4 PT Rheospectra (Rheology Co. Ltd) at 100 Hz.

RESULTS AND DISCUSSION

Polymer synthesis

We prepared the polyisoimides (PIIs) (**4**) and polyimides (PIs) (**5**) by chemical cyclization methods to investigate their properties as melt-processable adhesives. In order to obtain soluble PIIs, tetracarboxylic dianhydride and diamines having ether and hexafluoroisopropylidene linkages were used. In a previous investigation[10], we found that trifluoroacetic anhydride–triethylamine (TFAA–TEA) was a good dehydrating agent in the formation of isoimide. Thus, the ring-opening poly-additions of tetracarboxylic dianhydride and diamines were carried out in NMP for 4 h at room temperature (*Scheme 1*), yielding poly(amic acids), which were converted to PIIs and PIs by using TFAA–TEA and acetic anhydride–pyridine, respectively. *Table 1* indicates that polymers **4** and **5** were produced in excellent yields with inherent viscosities of up to 0.75 dl g^{-1}.



Scheme 1

Table 1 Synthesis of polymers

Run	Polymer	Yield (%)	η_{inh} (dl g^{-1})[a]
1	**4a**	96	0.40
2	**4b**	94	0.75
3	**5a**	99	0.45
4	**5b**	95	0.71

[a]Measured at a concentration of 0.5 g dl^{-1} in DMAc at 30°C

Polymer characterization

Polymers **4** and **5** were confirmed to be the corresponding PII and PI by means of infra-red spectroscopy and elemental analysis. The i.r. spectra of polymer **4a** exhibited a characteristic absorption at 1810 cm^{-1} due to the isoimide carbonyl. On the other hand, characteristic absorptions at 1780 and 1720 cm^{-1} due to the imide carbonyl were found in polymer **5a**. Imide contents determined by i.r. spectroscopy were less than 5% for polymers **4**. Elemental analyses also supported the formation of expected polymers **4** and **5**.

Polymers **4** were soluble in DMAc, NMP and cyclohexanone. Polymer **4a** was even soluble in dichloromethane, tetrahydrofuran, acetone and methyl ethyl ketone. Transparent yellow films were cast from the

Table 2 Molecular weights of polymers[a]

Run	Polymer	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
1	**4a**	78000	140000	2.0
2	**5a**	72000	210000	2.9

[a]Measured by g.p.c. in DMF

polymer solutions in chloroform or cyclohexanone. The molecular weights of polymer **4a** and **5a** were determined by g.p.c. (*Table 2*). Relative $\bar{M}_n$ and $\bar{M}_w$ values of polymer **4a** were 78000 and 140000, respectively.

Thermal properties of polymers 4 and 5

It is important to determine the thermal properties of polymers **4** and **5** prior to adhesion testing. Therefore, the thermal stability of the polymer was examined by thermogravimetry (t.g.), differential scanning calorimetry (d.s.c.) and dynamic mechanical analysis (d.m.a.). Typical t.g. traces for polymers **4** and **5** are shown in *Figure 1*. Both polymers **4a** and **5a** showed a 10% weight loss in nitrogen at 525°C.

D.s.c. curves for polymers **4a** and **5a** are shown in *Figure 2*. Polymer **4a** exhibited an endotherm at 215°C and a large exothermic peak at around 270°C in the first heating process. In the second heating process, these peaks were not observed and a new endothermic peak appeared at 250°C. After the large exothermic peak, the i.r. spectrum of polymer **4a** showed strong imide carbonyl absorptions at 1780 and 1720 cm^{-1}, while the characteristic absorption bands of the isoimide group at 1810 and 920 cm^{-1} had entirely disappeared, suggesting that polymer **4a** was immediately converted to PI **5a**. Furthermore, no t.g. weight loss was observed at any transition temperature of polymer **4a** (*Figure 1*). Polymer **5a** exhibited an endothermic peak at 250°C in both the first and the second heating processes.

Based on these data, the first endotherm at 215°C and a large exothermic peak at around 270°C observed in the first heating process of polymer **4a** are assigned to the T_g and the thermal isomerization temperature (T_i) of polymer **4a**, respectively. The endothermic peak at 250°C during the second heating process of polymer **4a** reflects the T_g of polymer **5a**. The thermal behaviours of the polymers are listed in *Table 3*. In this table, it is found that the T_g values of PIIs are about 35–50°C lower than those of corresponding PIs.

Films of polymer **4a** and **5a** were prepared by casting cyclohexanone solutions on glass plates, which were then heated on a hot plate at 60°C, and subsequently dried at 150°C for 12 h *in vacuo*. D.m.a. of cast films was carried out on a Rheospectra. *Figure 3* shows the dynamic storage modulus of polymers **4a** and **5a**. The storage modulus for polymer **4a** declined sharply around 200°C, which corresponded to the glass transition temperature of polymer **4a**. Polymer **5a** maintained mechanical integrity at this temperature and the storage modulus did not drop until 250°C. These results indicate that a large difference in flow behaviour between polymers **4a** and **5a** can be expected over 200°C.

Adhesion properties of polymers 4 and 5

On the basis of the above results, the adhesion properties of PII were studied. The adhesion test was evaluated by the peel strength of the copper foil at 180° from the polymer film, as shown in *Figure 4*. Specimens of the polymer film between two copper foils were prepared by heat compression as illustrated in *Figure 5*. The heat compression was conducted employing the process shown in *Figure 6*. The assembly was placed in the hot press and compressed at 200–260°C for 15 min

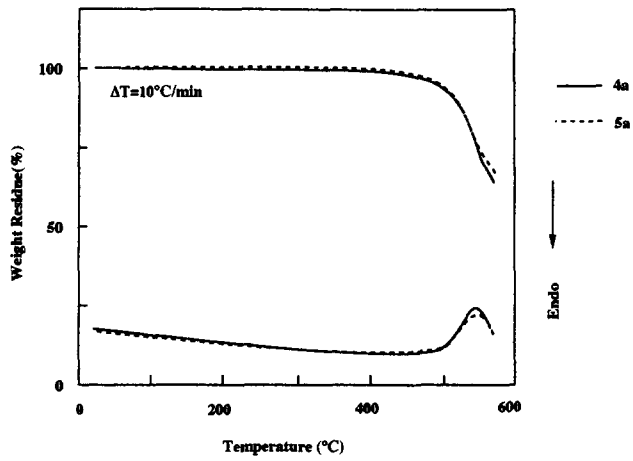


Figure 1 T.g. curves of polymers **4a** and **5a** in nitrogen

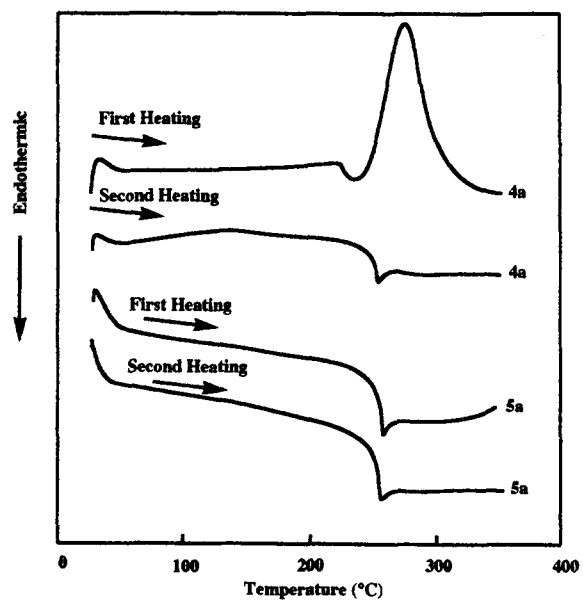


Figure 2 D.s.c. curves of polymers **4a** and **5a** in nitrogen

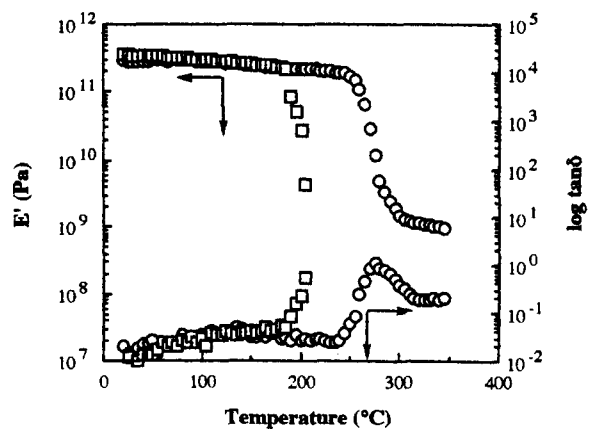


Figure 3 Dynamic mechanical analysis of polymer films: (□) polymer **4a**; (○) polymer **5a**

Table 3 Thermal properties of polymers

Run	Polymer	T_g (°C)	T_i (°C)[a]	TG_{10} (°C)[b]
1	**4a**	215	270	525
2	**5a**	250	–[c]	525
3	**4b**	190	285	540
4	**5b**	240	–[c]	540

[a]Temperature at which exothermal peak was recorded by d.s.c. measurement
[b]Temperature at 10% weight loss recorded with t.g. at heating rate of 10°C min^{-1} in nitrogen
[c]No detection of T_i

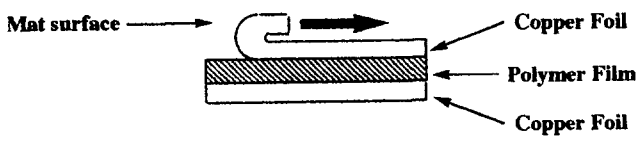


Figure 4 Measurement of peel strength

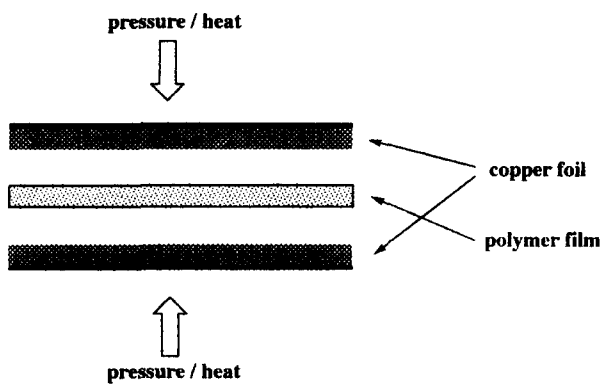


Figure 5 Assembly for hot press

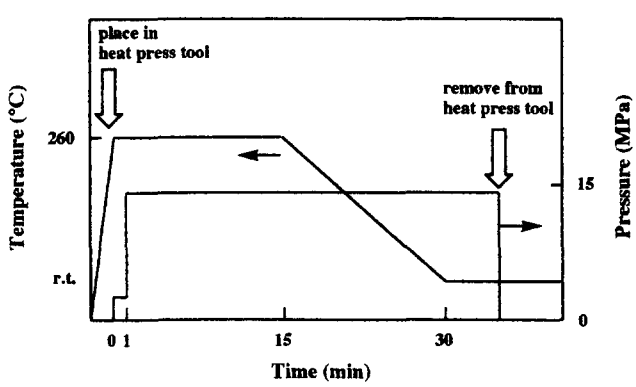


Figure 6 Typical hot press cycle

under 14.7 MPa. Subsequently, the platens were cooled to a temperature below 50°C and the assembly was removed from the heat press tool.

The results of peel strengths of films of polymers **4a** and **5a** on copper foils are shown in *Table 4*. Polymer **4a** exhibited peel strengths of 780 and 400 g cm^{-1} at press temperatures of 260 and 230°C, respectively. On the other hand, the peel strengths of polymer **5a** film on copper foils were very weak even at a press temperature of 260°C. Polymers **4b** and **5b** based on 6FDA/BAPP exhibited similar adhesion behaviours. In addition, polymer **4a** film after compression at 260°C was flexible and free of voids. The isomerization to the corresponding PI was confirmed by i.r. spectroscopy.

The greater adhesive nature of PII can be elucidated by considering the lower T_g and the drastic changes in elasticity above its T_g compared to that of the corresponding PI as shown in *Figure 3*. Furthermore, the advantage of using the PII films as a high-temperature adhesive has also been shown with the conversion to the corresponding PIs during the heat compression process without the generation of volatile compounds.

Adhesion interface

The SEM micrographs of the samples were taken at a magnification of 10000×, which provided some evidence of the peel strength difference between PIIs and PIs on copper foils (*Figure 7*).

Although the rolled copper foil used in this study had micropores on the mat surface, these surfaces retained their original configuration and morphology after the peel testing. However, considerable penetration of polymer into the pores of the mat surface was observed on the surface of polymer **4a**.

As shown by the obvious surface deformation of polymer **4a**, the interfacial surface morphologies between polymer **4a** and polymer **5a** are significantly different. Furthermore, in *Figure 7c*, a small particle was observed on the surface of the polymer **4a**.

In order to understand the phenomenon involved, the interfacial surface of polymer **4a** was analysed by energy-dispersive X-ray analysis (EDX). The result is shown in *Figure 8*. The existence of copper in the small particles in *Figure 7c* was confirmed, and no copper was observed in the polymer film in *Figure 7c*. Therefore, it can be suggested that enhanced adhesive bond performance is attributed to favourable interfacial anchoring induced by the good flow characteristics of PIIs.

CONCLUSION

In summary, polyisoimides were successfully prepared from corresponding poly(amic acids) using trifluoroacetic anhydride–triethylamine system as a dehydrating agent. The films cast from these PIIs were strong and flexible. Furthermore, PII exhibited better flow properties than those of PI and also performed as a suitable high-temperature adhesive for bonding copper foil.

Table 4 Peel strength of polymer films on copper foil[a]

Run	Polymer	Press temp. (°C)	Peel strength (g cm^{-1})
1	**4a**	260	780
2	**4a**	230	415
3	**4a**	200	–[b]
4	**5a**	260	77
5	**5a**	230	–[b]
6	**5a**	200	–[b]
7	**4b**	250	590
8	**4b**	200	180
9	**5b**	250	110
10	**5b**	200	–[b]

[a]Bonded at 14.7 MPa
[b]No adhesion

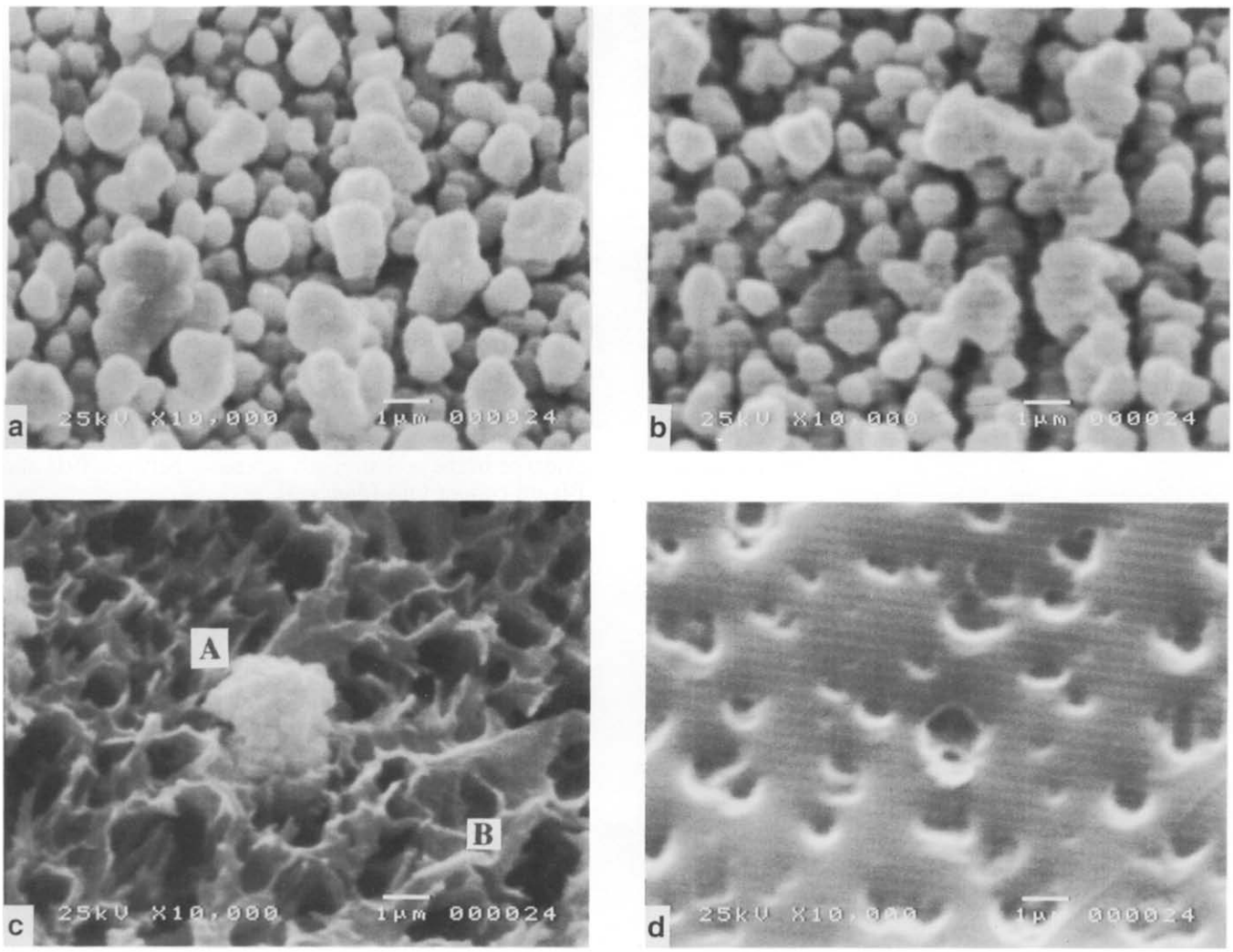


Figure 7 Morphology of the interfacial surface of copper foil and polymer: (a) copper surface for polymer **4a**; (b) copper surface for polymer **5a**; (c) surface of polymer **4a**; (d) surface of polymer **5a**

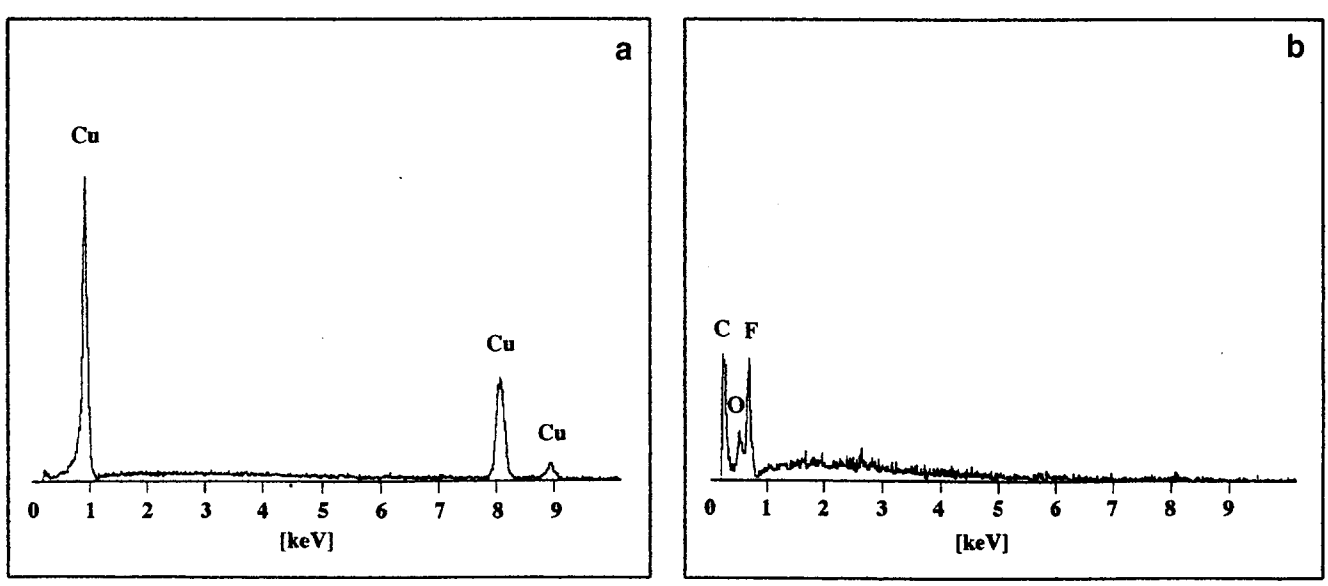


Figure 8 EDX analysis of peeled polymer film **4a**: (a) part A and (b) part B in *Figure 7c*

ACKNOWLEDGEMENTS

The authors are indebted to Hitoshi Nagasawa and Sadao Kato for their technical assistance and Takeyoshi Takahashi for performing the elemental analyses. We also wish to acknowledge financial support from the Ministry of Education, Science and Culture of Japan (No. 05453140).

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