
Preparation and Properties of Thermoplastic Polyamide-imide and Polyurea-amide-imide/Copper Foil Composites

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Received: 5 November 2004 Accepted: 17 March 2005

SUMMARY

Polyamide-imide (PAI) and polyurea-amide-imide (PUAI) resins were polymerized from five reactants: 4,4'-oxydianiline, 4-nitrobenzoyl chloride, 4,4'-diphenylmethane diisocyanate, 1,2,4,5-benzenetetracarboxylic dianhydride, and 3,3'-4,4'-benzophenone tetracarboxylic dianhydride. Their chemical structures were characterized using elemental analysis, FTIR and ^1H NMR spectroscopy.

Their thermal properties, adhesive properties, electrical properties, heat resistance, and chemical resistance were studied. The experimental results show that the glass transition temperatures of PAI and PUAI films occurred respectively at 360 °C and 229 °C, and the 10% weight loss occurred respectively at approximately 481 °C and 420 °C. The optimal hot-press conditions for PAI/copper foil (CU) composite were 380°C and 4.90 MPa, whereas those for PUAI/copper foil (CU) composites were 250 °C and 4.90 MPa.

Values of the peel strength, dielectric constant, and dissipation factor were obtained and the peel strength was re-measured after a thermal stability test. The chemical resistance tests showed that the peel strength retention values of the PAI/CU and PUAI/CU composites were respectively more than 95% and more than 94% after immersing in 10% H_2SO_4 solution at 70 °C for 1 h.

1. INTRODUCTION

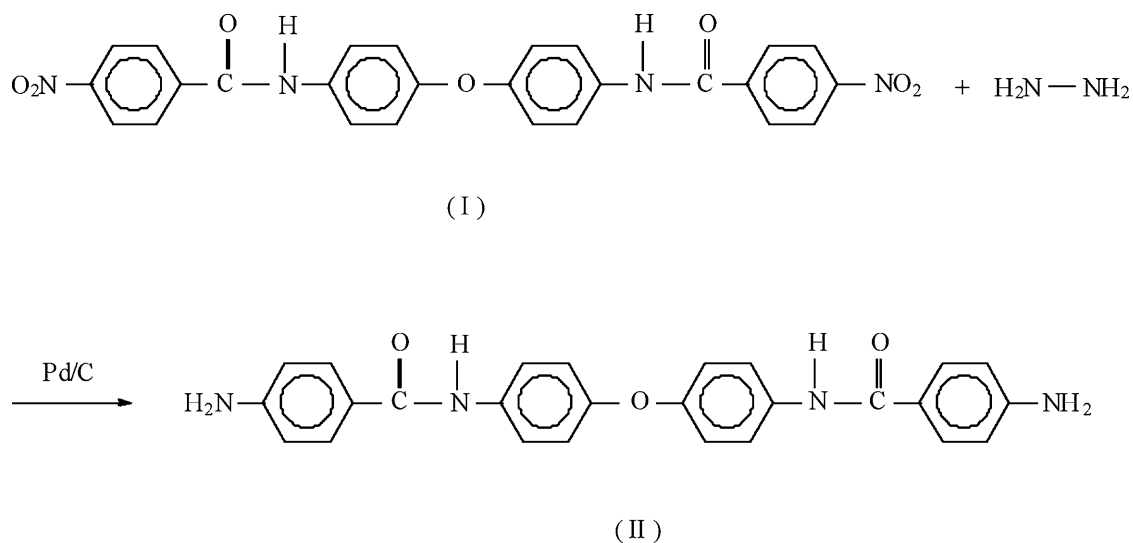
Polyimides are used extensively in printed circuit boards (PCB) owing to their excellent thermal stabilities, low dielectric constant, and chemical resistance. However, their applications have been limited due to their high softening or melting temperatures and their insoluble nature in most organic solvents because of their rigid backbones and strong interchain interactions. Many attempts have been made to curtail these drawbacks, for example, by introducing flexible linkages, non-symmetric structures, or bulky substitutes into the molecular chain¹⁻⁵. Various resins have been developed and reported. Among them are polyamide-imide (PAI) and polyurea-imide (PUI) resins, which include amide and urea groups respectively in their main chains to improve the solubility and adhesion. Moreover, both PAI and PUI still exhibit good heat resistance as well as other useful physical and chemical properties⁶⁻¹⁵.

In the manufacture of flexible PCBs, copper is coated with polyamic acid precursors and then

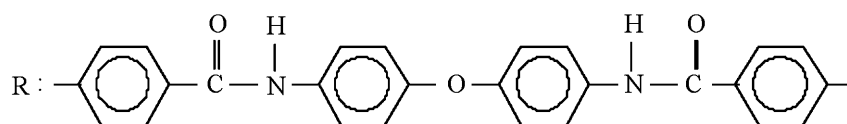
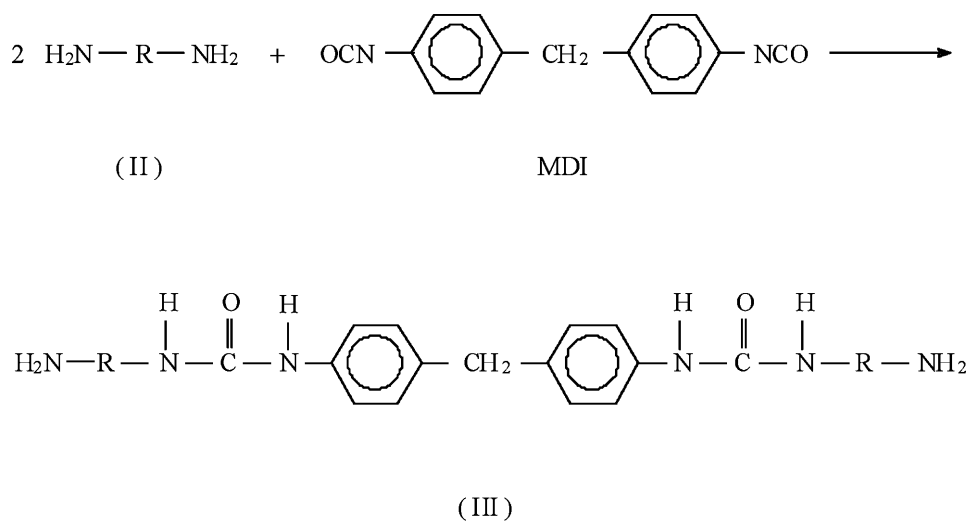
the precursors are cured to form polyimides. Alternatively, copper is coated onto polyimide by vacuum evaporation or sputtering. Conventional coating methods may result in limited adhesion between the copper and the polyimide¹⁶. Extensive research has been carried out to improve the adhesion between copper and various polymers such as aromatic thermosetting copolyester (ATSP), epoxy, and phenoxy¹⁷⁻¹⁹.

In this study, we synthesized PAI and polyurea-amide-imide (PUAI) resins from 4,4'-oxydianiline (4,4'-ODA), 4-nitrobenzoyl chloride (NBC), 4,4'-diphenylmethane diisocyanate (MDI), 1,2,4,5-benzenetetracarboxylic dianhydride (PMDA), and 3,3'-4,4'-benzophenone tetracarboxylic dianhydride (BTDA). Then the PAI/CU and PUAI/CU composites were prepared, without any pre-treatment or adhesive. Their thermal properties, adhesive properties, electrical properties, and chemical resistance were measured and compared.

Scheme 2.



Scheme 3.



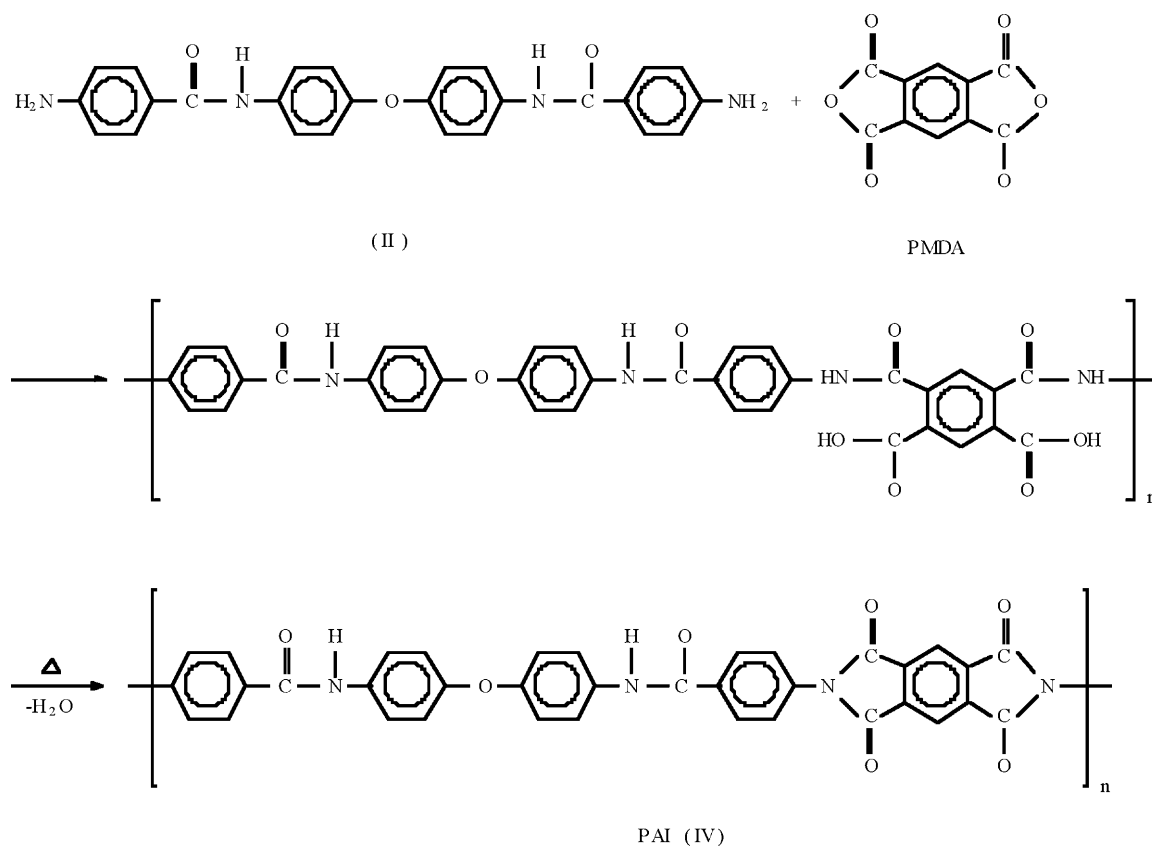
The temperature was increased to 40 °C and held for 3 h, whereupon an amine-terminated polyurea-amide (III) solution was obtained.

(4) Synthesis of poly(amic acid) solution

The equation for the synthesis is shown in Scheme 4.

0.03 mol of precursor (II) were dissolved in 120 ml of NMP. After stirring, 0.03 mol of PMDA was added to the solution and the mixture was stirred under a nitrogen blanket at 5 °C for 4 h. Then the temperature was increased to 40 °C and held for 6 h, and a poly(amic acid) solution was obtained. The inherent viscosity of the polymer was 0.68 dL/g, measured in NMP at 30 °C.

Scheme 4.



(5) Synthesis of poly(urea-amic acid) solution

The equation for the synthesis is shown in Scheme 5.

The temperature of the 0.02 mol precursor (III) solution was reduced from 40 °C to 25 °C. Then, 0.02 mol of BTDA were added to the solution, nitrogen was again introduced, and the mixture was stirred. The temperature was maintained at 25 °C for 6 h, then a poly(urea-amic acid) solution was obtained. The inherent viscosity of the polymer was 0.93 dL/g, measured in NMP at 30 °C.

2.3 Preparation of PAI and PUA Films

To prepare the films, the poly(amic acid) or the poly(urea-amic acid) solution was poured into a glass Petri dish of 9 cm in diameter. The dishes were placed in a vacuum oven at 50 °C for 12 h, 70 °C for 2 h, 90 °C for 2 h, 110 °C for 2 h, 150 °C for 2 h, 180 °C for 2 h, and 230 °C for 1 h, to remove the solvent. Then the dishes were immersed for 24 h in distilled water after at room temperature. The films were stripped from the glass substrate and

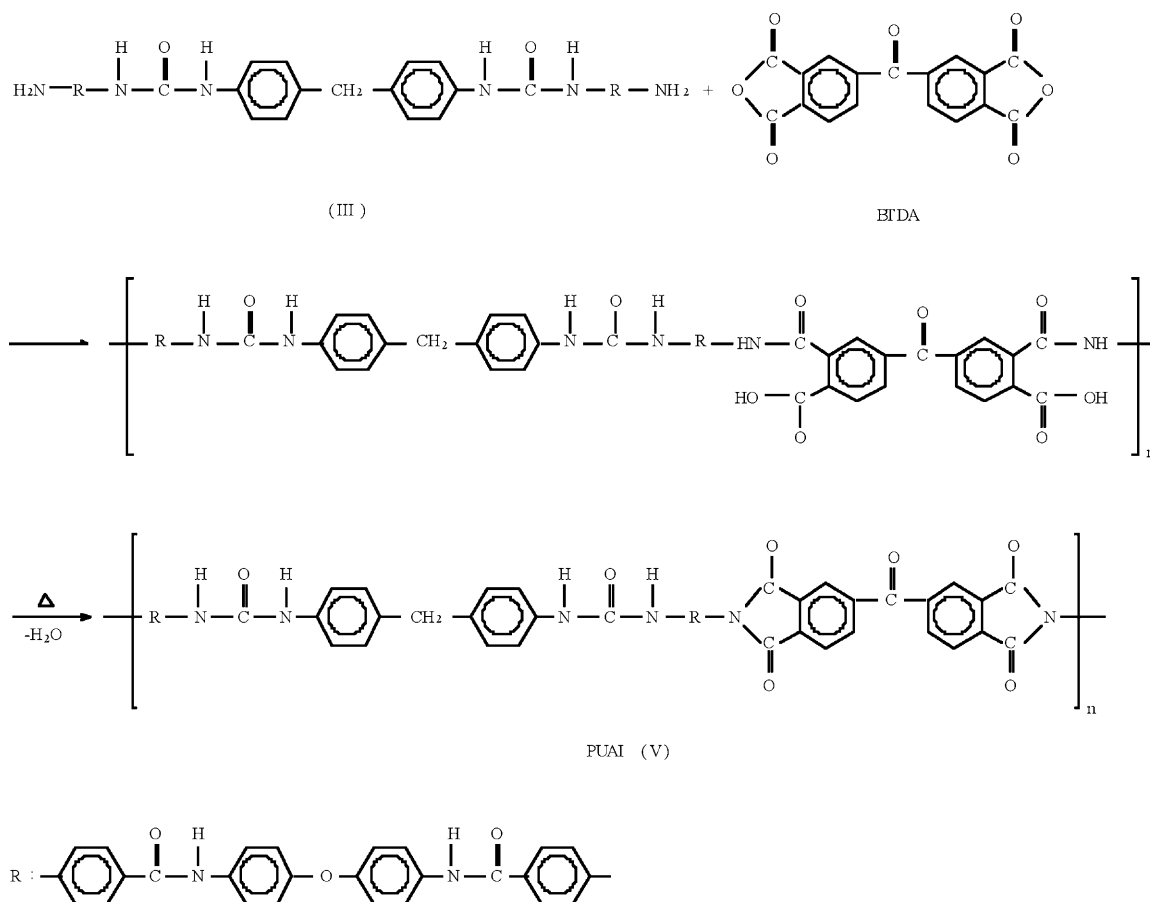
dried at 100 °C for 1 h. The thickness of the films was about 0.03 mm.

2.4 Fabrication of PAI/CU and PUA/CU Composites

The PAI and PUA films were cut into appropriate sizes. The surface was cleaned with acetone and dried at 100 °C for 30 min. The copper foil/PAI film/copper foil laminate was placed in a flat panel mould and mounted on a hot press. The temperature was increased to 200 °C. When the temperature reached 200 °C, the pressure was increased to 0.49 MPa. The temperature and pressure were maintained for 10 min. Then the temperature was increased to 380 °C at a heating rate of 6 °C/min and the pressure was increased to 4.9 MPa. The temperature and pressure were maintained for 40 min, after which the pressure was gradually reduced to 0.98 MPa and the temperature was reduced to 120 °C. The mould was taken out of the press after cooling to room temperature.

The copper foil/PUAI film/copper foil laminates were placed in flat panel mould and mounted on a

Scheme 5.



hot press. The temperature was increased to 100 °C. When the temperature reached 100 °C, the pressure was increased to 0.49 MPa, and the temperature and pressure were held for 10 min. Then the temperature was increased to 250 °C at a heating rate of 6 °C/min and the pressure was increased to 4.90 MPa. The temperature and pressure were held for 40 min, after which the pressure was gradually reduced to 0.98 MPa while the temperature was lowered to 100 °C. The mould was taken out of the press after cooling to room temperature.

2.5 Characterization

- (1) Elemental analyses (EA) were performed on the monomer and the synthesized polymer using a Perkin Elmer 2400 elemental analyses.
- (2) A Fourier transform infrared spectrometer (FTIR) (SPC-3200, Bio-Rad) was employed to measure the infrared spectra.
- (3) ^1H NMR spectra were measured using a Bruker DMX-500 MHz FT-NMR.
- (4) Differential scanning calorimetry (DSC) analyses were performed using a Perkin-Elmer Diamond

DSC controller in a flowing nitrogen stream (50 cm³/min) at a heating rate of 5 °C/min.

- (5) Thermogravimetric analyses (TGA) were conducted using a TA Instrument 5100 System in flowing nitrogen (60 cm³/min) at a heating rate of 10 °C/min.
- (6) Dynamic mechanical analyses (DMA) were performed using a TA Instrument 5100 at a heating rate of 5 °C/min.
- (7) A solubility test was carried out. At room temperature, 0.5 g of sample was added to a sealed glass bottle containing 4.5 g of solution before stirring. It was observed for 3 h to see whether the sample was fully dissolved. If not, the solution was heated up to 80 °C before another observation was made.

2.6 Composite Properties

- (1) The dielectric constant and dissipation factor were measured according to the CNS 10555 standard for testing copper foil laminate printed circuit boards, using an impedance analytical instrument.

- (2) Peel strength was determined by means of a T-peel strength test in accordance with ASTM D1876-01.
- (3) Heat resistance was determined by placing the samples in ovens at 100 °C, 150 °C, 200 °C, 250 °C, and 300 °C for 24 h before testing their peel strengths and comparing with the values before heat treatment.
- (4) Chemical resistance tests were carried out according to CNS 5609 and the peel strength again determined after immersion of ten samples in 10% sulfuric acid or 10% sodium hydroxide solution at 70 °C for various times. The specimen dimensions were 25 × 305 × 0.1 mm³, but only approximately 241 mm of the length were bonded. The peel strength retention was calculate as follows:

$$R = 100(Y/X)$$

where R is the peel strength retention in%, X is the untreated peel strength, and Y is the treated peel strength.

- (5) Water absorption ratio was determined according to CNS 10555. Each test sample was maintained at 50 °C in a thermostat for 24 h. The samples were then moved to a dryer and cooled to 20 °C. Samples were accurately

weighed before placing in a bath of distilled water at 23 °C for 24 h. They were then wiped clean with a dry gauze and re-weighed. The water absorption was calculate as follows:

$$A(\%) = \frac{(W_2 - W_1)}{W_1} \times 100\%$$

where A is the water absorption in %, W_1 is the sample weight before treatment, and W_2 is the sample weight after treatment.

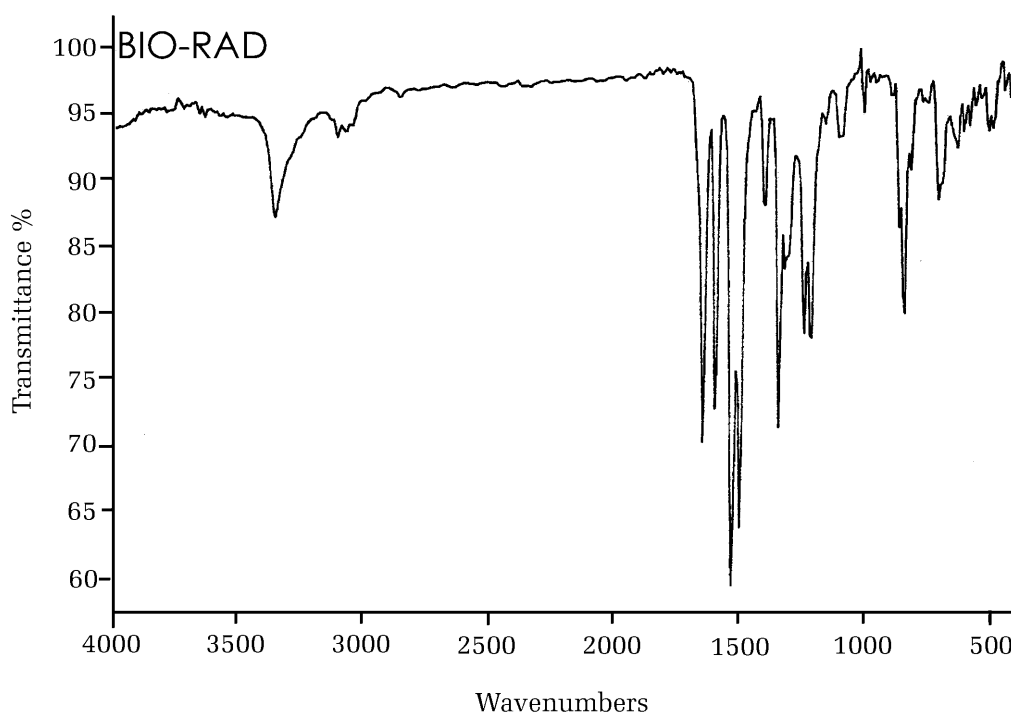
3. RESULTS AND DISCUSSION

3.1 Functional Group Structural Analyses

(1) *N-N'*(oxydi-4,1-phenylene)bis(4-nitrobenzamide) (I)

The IR spectrum in Figure 1 shows that the characteristic absorption peaks of –NH and C=O appeared at 3350 cm⁻¹ and 1630 cm⁻¹, respectively. Thus the existence of the amide group was confirmed. The characteristic absorption peaks of –NO₂ appeared at 1335~1385 cm⁻¹ and 1510~1570 cm⁻¹. In addition, a para-benzene ring peak occurred near 800~860 cm⁻¹. The results were consistent with the chemical structure of *N-N'*(oxydi-4,1-phenylene)bis(4-nitrobenzamide).

Figure 1. FTIR spectrum of the *N-N'*(oxydi-4,1-phenylene)bis(4-nitrobenzamide)



(2) *N-N'*(oxydi-4,1-phenylene)bis(4-aminobenzamide) (II)

The IR spectrum in Figure 2 shows that the characteristic absorption peaks of -NH_2 and -NH appeared around $3300\text{--}3400\text{ cm}^{-1}$ and that of C=O appeared at 1630 cm^{-1} . However, the characteristic absorption peaks of -NO_2 were not observed. This confirmed that the nitrogroups had been converted into amino groups. These peaks were consistent with the structure of *N-N'* (oxydi-4,1-phenylene)bis(4-aminobenzamide).

(3) Synthesis of polyamide-imide (PAI) (IV)

The IR spectrum in Figure 3 shows that the characteristic absorption peak of -NH appeared at 3350 cm^{-1} . However, the characteristic absorption peaks of -NH_2 were not observed. In addition, the characteristic absorption peaks of C-N and C=O appeared at 1220 cm^{-1} and 1620 cm^{-1} , respectively. Thus the existence of imide groups was confirmed. These results confirmed that PAI had been synthesized.

(4) Synthesis of polyurea-amide-imide (PUAI) (V)

The IR spectrum in Figure 4 shows that the characteristic absorption peak of -NH appeared at

3350 cm^{-1} . However, the characteristic absorption peaks of -NH_2 were not observed. In addition, the characteristic absorption peaks of C-N and C=O appeared at 1220 cm^{-1} and 1620 cm^{-1} , respectively. Thus the existence of imide groups was confirmed. The characteristic absorption peak of NH-CO-NH appeared at 2921 cm^{-1} . Thus the existence of a urea group was confirmed. These results confirmed that polyurea-amide-imide had been synthesized.

3.2 Elemental Analysis

The elemental analyses results are listed in Table 1. The theoretical percentages of the four synthesized compounds are close to their experimental percentages. This indicates that the prepolymers and resins of PAI and PUAI were successfully synthesized from 4,4'-ODA, NBC, MDI, PMDA, and BTDA.

3.3 ^1H NMR Analysis

From Figures 5 and 6, the singlet peaks at 10.59 ppm and 9.77 ppm were assigned to the amide (-NH) protons in the intermediates I and II, respectively. The benzene ring protons in (I) led to the doublet at 7.03–8.38 ppm and those in (II) led to the doublet and triplet at 6.57–7.74 ppm. Because nitro-termination and amino-termination are different, the peak

Figure 2. FTIR spectrum of the *N-N'*(oxydi-4,1-phenylene)bis(4-aminobenzamide)

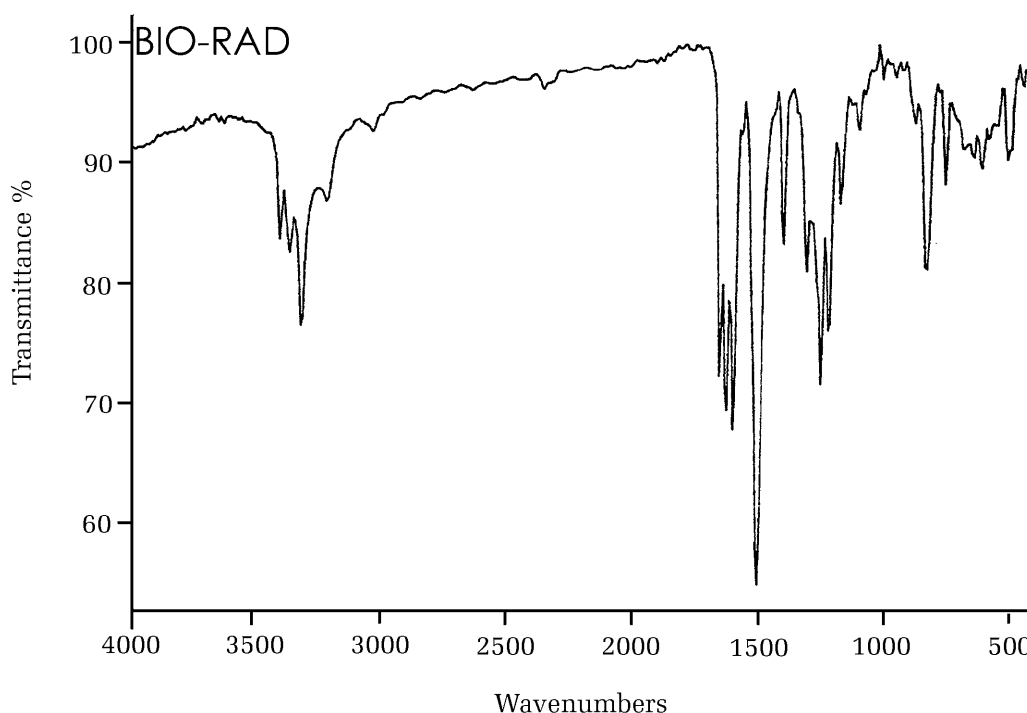


Figure 3. FTIR spectrum of the polyamide-imide

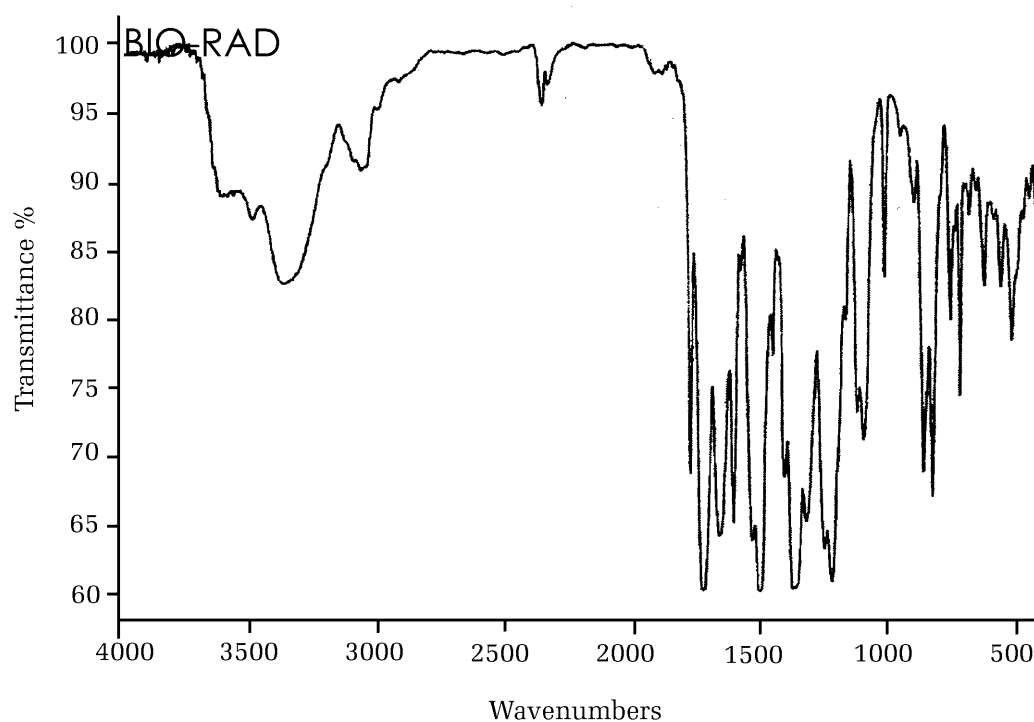
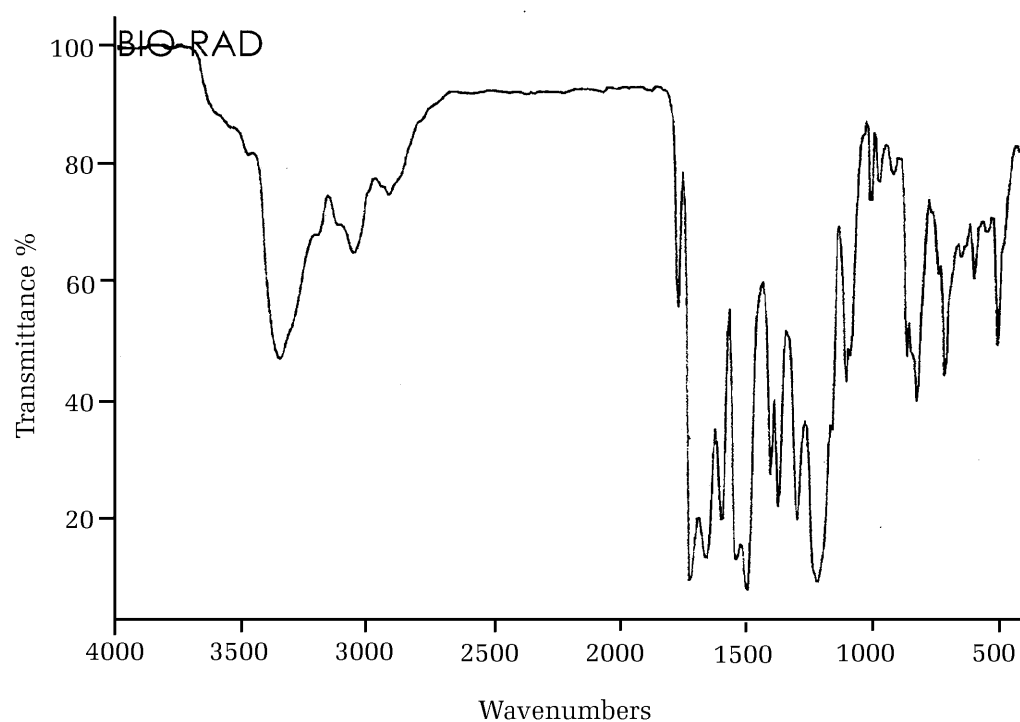


Figure 4. FTIR spectrum of the polyurea-amide-imide



numbers were different. In addition, the amino ($-\text{NH}_2$) protons appeared as a singlet at 5.74 ppm in Figure 6. These results confirmed the formation of these intermediates in the reaction.

Table 1. Elemental analyses of intermediates I, II, PAI, and PUAI			
N-N'(oxydi-4,1-phenylene)bis(4-nitrobenzamide): $\text{C}_{26}\text{H}_{18}\text{N}_4\text{O}_7$			
Theoretical value	C:62.65%	H:3.64%	N:11.24%
Experiment value	C:62.47%	H:3.76%	N:11.14%
N-N'(oxydi-4,1-phenylene)bis(4-aminobenzamide): $\text{C}_{26}\text{H}_{22}\text{N}_4\text{O}_3$			
Theoretical value	C:71.22%	H:5.06%	N:12.78%
Experiment value	C:70.96%	H:4.99%	N:12.95%
Polyamide-imide (PAI): $\text{C}_{43}\text{H}_{24}\text{N}_4\text{O}_8$			
Theoretical value	C:76.78%	H:2.67%	N:6.25%
Experiment value	C:76.42%	H:2.76%	N:6.02%
Polyurea-amide-imide (PUAI): $\text{C}_{84}\text{H}_{48}\text{N}_{10}\text{O}_{13}$			
Theoretical value	C:71.38%	H:3.96%	N:9.91%
Experiment value	C:71.23%	H:4.01%	N:9.86%

3.4 DSC Analysis

Figure 7 shows the DSC curves of the (I) and (II). The melting point (T_m) of the (I) and (II) occurred at around 275 °C and 282 °C, respectively.

3.5 TGA Analysis

The thermal stability was studied by thermogravimetric analysis (TGA). As shown in Figure 8, for (I) in nitrogen, 5% and 10% weight loss occurred at approximately 378 °C and 393 °C, respectively. As shown in Figure 9, for (II) in nitrogen, 5% and 10% weight loss occurred at approximately 394 °C and 410 °C, respectively. This is because the bond energy of $\text{C}-\text{NO}_2$ (251 kJ mol⁻¹) is less than that of $\text{C}-\text{NH}_2$ (356 kJ mol⁻¹) [20]. As shown in Figure 10, for PAI films in nitrogen, 5% and 10% weight loss occurred at approximately 433 °C and 481 °C, respectively. As shown in Figure 11, for PUAI films in nitrogen, 5% and 10% weight loss occurred at approximately 358 °C and 420 °C, respectively. Benzene rings and imide groups are stable, so imide-containing polymers must have had higher heat resistance. The PAI films had a higher operating temperature than the PUAI ones because the amide group had better heat resistance than the urea group.

Figure 5. ^1H -NMR spectrum of the N-N'(oxydi-4,1-phenylene)bis(4-nitrobenzamide)

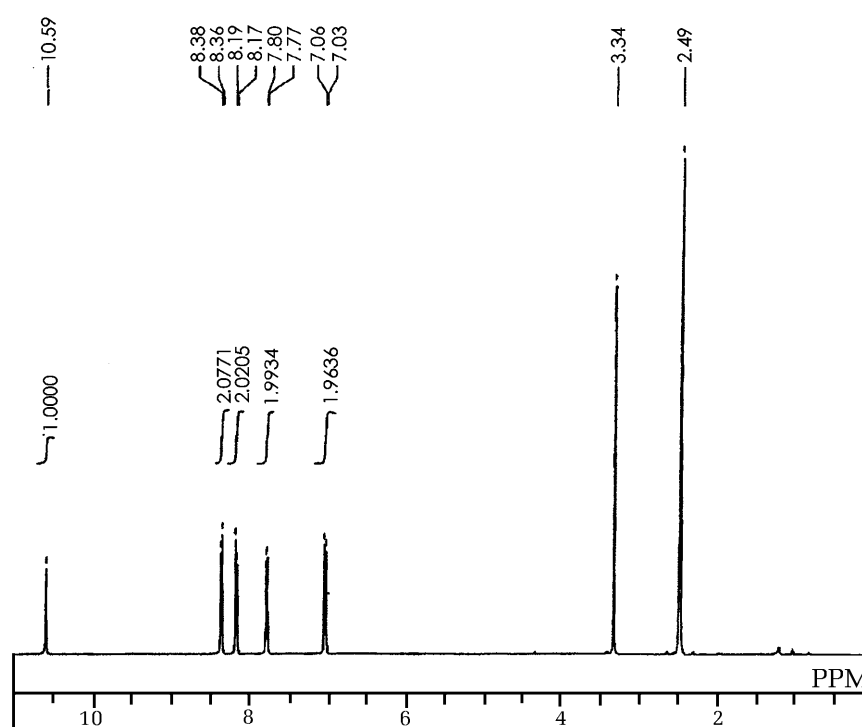


Figure 6. ^1H -NMR spectrum of the N-N'(oxydi-4,1-phenylene)bis(4-aminobenzamide)

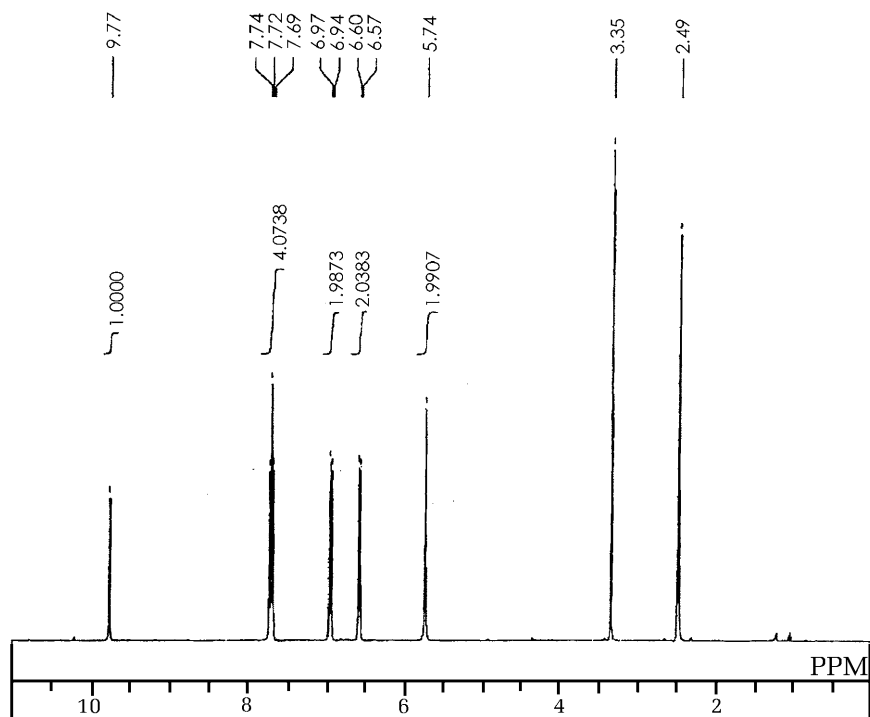


Figure 7. DSC spectrum of the N-N'(oxydi-4,1-phenylene)bis(4-nitrobenzamide) and N-N'(oxydi-4,1-phenylene)bis(4-aminobenzamide)

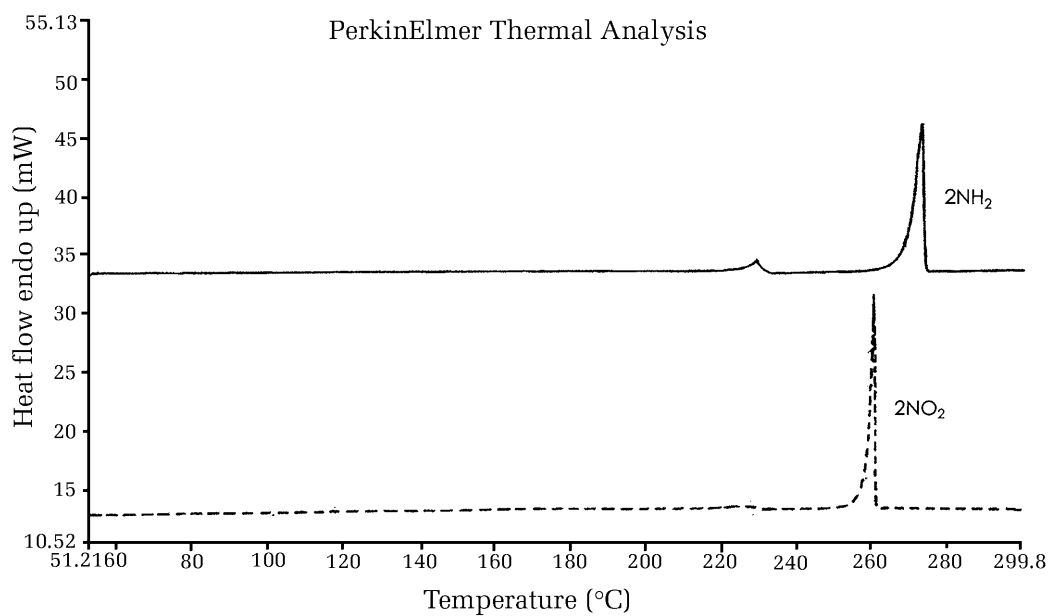


Figure 8. TGA spectrum of the N-N'(oxydi-4,1-phenylene)bis(4-nitrobenzamide)

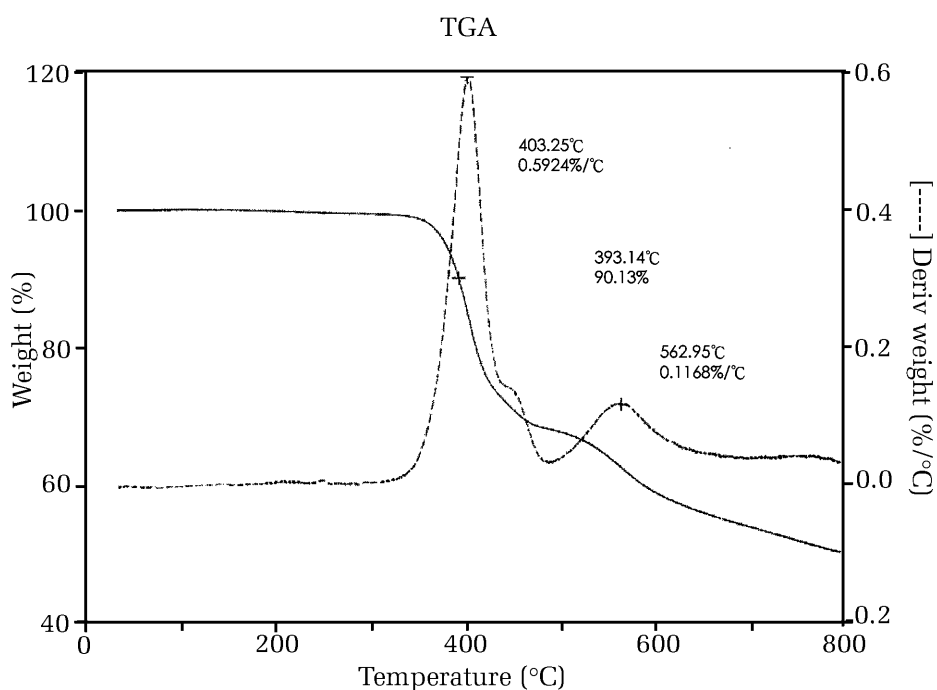


Figure 9. TGA spectrum of the N-N'(oxydi-4,1-phenylene)bis(4-aminobenzamide)

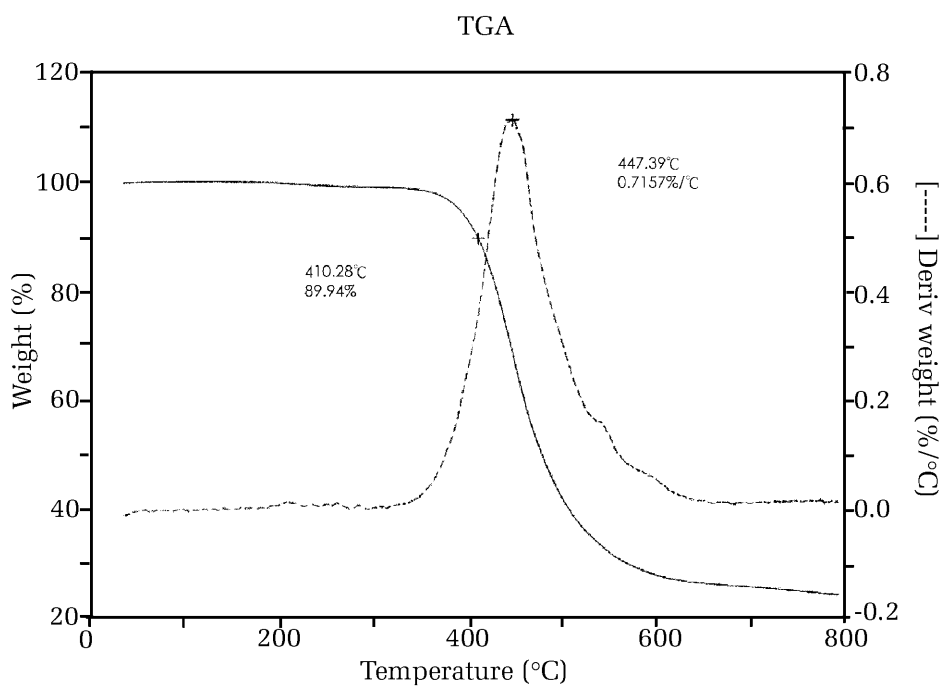


Figure 10. TGA spectrum of the polyamide-imide

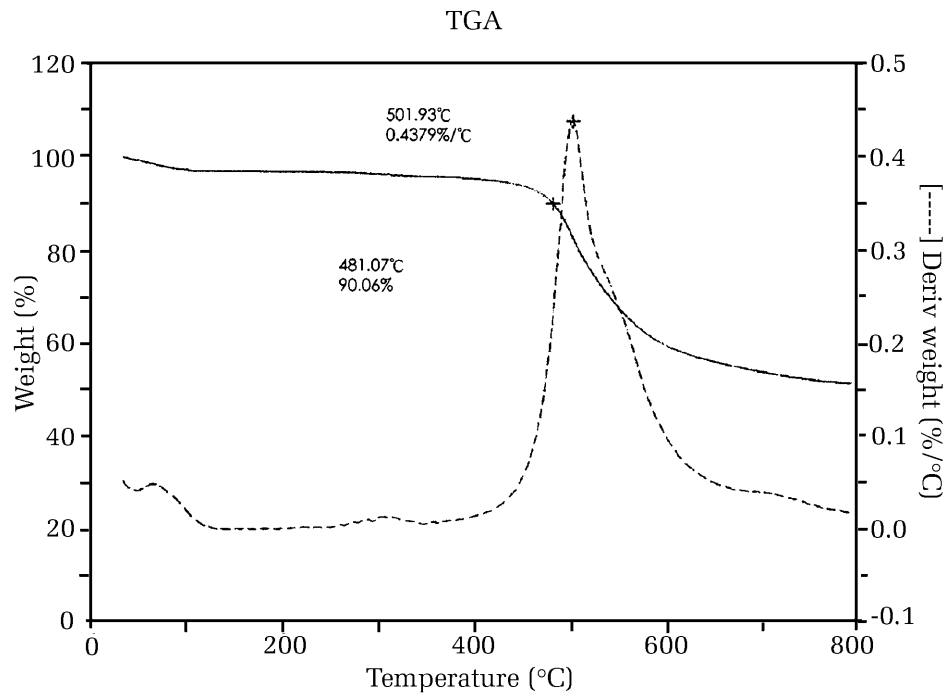
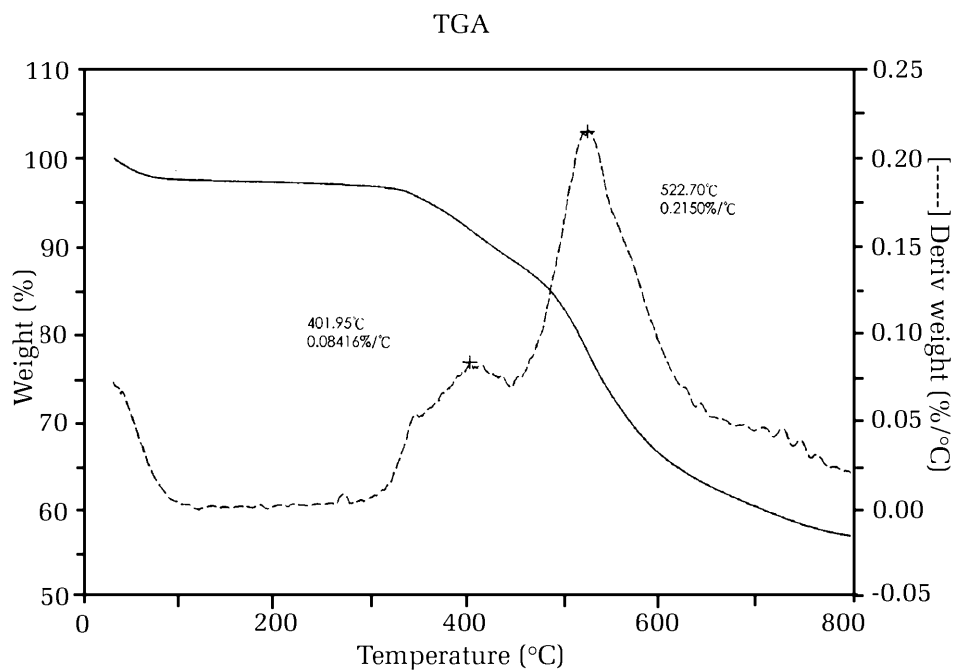


Figure 11. TGA spectrum of the polyurea-amide-imide



3.6 DMA Analysis

The thermal behaviour can be deduced from the dynamic mechanical measurements. Figures 12 and 13 show the DMA curves of the PAI and PUAI films, respectively. The glass transition temperatures (T_g) of the PAI and PUAI films occurred at approximately 360 °C and 229 °C, respectively. The reason why the PAI film had a higher T_g than the PUAI one is because that the amide (-NHCO-) group of PAI is shorter than the urea (-NHCONH-) group of PUAI.

3.7 Solubility

In Table 2, at room temperature, it is recorded that the two films were insoluble in NMP, DMF, DMAc and DMSO because these solvents did not have enough energy to reduce the intermolecular bonding. After heating to 80 °C, the PAI and PUAI films were both partially soluble in NMP and DMAc. Because urea groups are more polar than amide groups, the PUAI film was partially soluble in DMF and DMSO, while PAI film was insoluble. If a polar group were to be introduced into the molecular chain to reduce the intermolecular bonding strength, the polymer would become easier to dissolve in an organic solvent.

3.8 Electrical Properties

Table 3 shows that the dielectric constants of PAI and PUAI films were 2.86 and 3.17, respectively.

Table 2. Solvent test for PAI and PUAI films

Temperature / Solubility / Solvent	Room temperature (21 °C)		Heated up to 80 °C	
	PAI	PUAI	PAI	PUAI
NMP	I	I	PS	PS
DMF	I	I	I	PS
DMAc	I	I	PS	PS
DMSO	I	I	I	PS
H ₂ SO ₄	S	S	S	S
Pyridine	I	I	I	I
TPP	I	I	I	I
THF	I	I	I	I
Acetone	I	I	I	I

S = Soluble, PS = Partial Soluble, I = Insoluble
NMP = N-Methyl-2-Pyrrolidone
DMAc = N,N-Dimethylacetamide
DMF = N,N-Dimethylformamide
DMSO = Dimethyl Sulfoxide

The dissipation factors of PAI and PUAI films were 0.0122 and 0.0139, respectively. So the dielectric constant and dissipation factor of PAI films were better than those of PUAI films. The electrical properties of the polymers were closely related to

Figure 12. DMA spectrum of the polyamide-imide

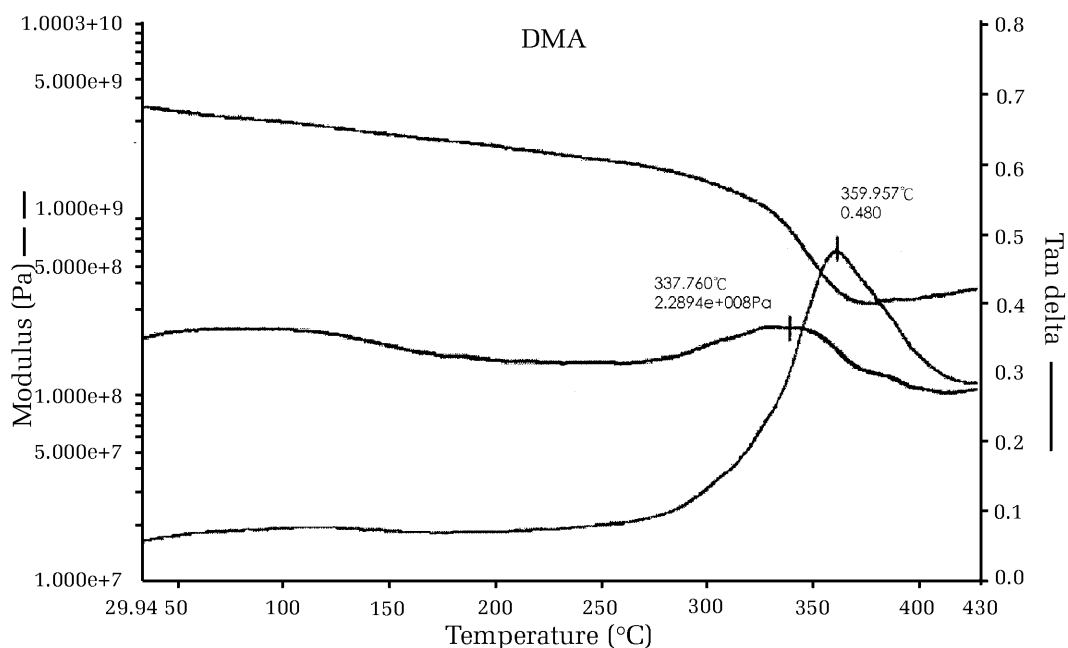
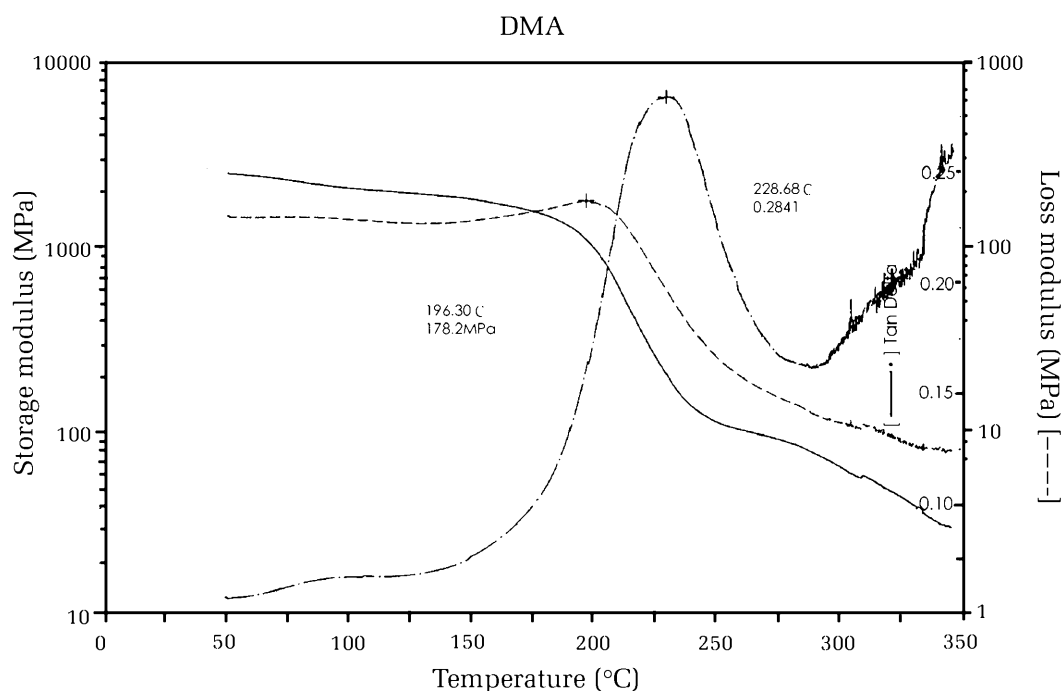


Figure 13. DMA spectrum of the polyurea-amide-imide



their molecular structure, especially to that of the polar molecules. It was predictable that the PUAI, which had a relatively high polarity, would have a higher dielectric constant and dissipation factor. The dielectric constants of PAI/CU and PUAI/CU composites were 2.90 and 3.19, respectively. The dissipation factors of PAI/CU and PUAI/CU composites were 0.0143 and 0.0152, respectively. In general, for phenolic or epoxy/CU composites under normal circumstances, the dielectric constant should be below 5.5 and the dissipation factor should be below 0.035. Apparently, the PAI/CU and PUAI/CU composites in this study did meet these requirements.

Table 3. The dielectric constant and dissipation factor of PAI and PUAI films and PAI/CU and PUAI/CU composites. (measurements at 1 MHz)

Films or composites	Electrical properties	
	Dielectric Constant	Dissipation Factor
PAI film	2.86	0.0122
PUAI film	3.17	0.0139
PAI/CU composite	2.90	0.0143
PUAI/CU composite	3.19	0.0152

3.9 Process Conditions of Copper Foil Composites

The adhesive bond strength of polymer films to copper foil can be enhanced by applying pressure and heating in a press. Figures 14 and 15 show the peel strengths of PAI/CU and PUAI/CU composites under various temperature and pressure conditions. The maximum peel strength of PAI/CU composites (approximately 2.60 kN/m) was obtained at 380 °C (the T_g of PAI was 360 °C) and 4.90 MPa. Similarly, the maximum peel strength of PUAI/CU composite (approximately 2.41 kN/m) was obtained at 250 °C (the T_g of PUAI was 229 °C) and 4.90 MPa. Higher temperatures and pressures did not increase the peel strength further. Once the pressure exceeded 4.90 MPa the adhesive bond strength decreased, perhaps due to a “hungry” joint caused by excess pressure.

3.10 Heat Resistance

Two kinds of composites were kept separately at 100 °C, 150 °C, 200 °C, 250 °C, and 300 °C for 1 h to test the peel strength retention after heating. Table 4 shows that the PAI/CU composites had higher heat resistance, measured by peel strength retention, than PUAI/CU composites. This is because amide

Figure 14. The peel strength of PAI/CU composites with various molding pressures and temperatures

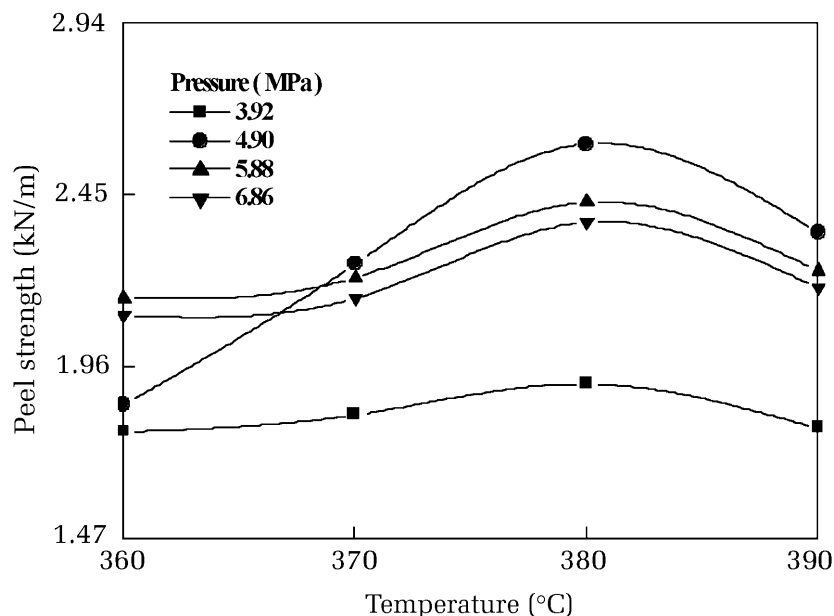
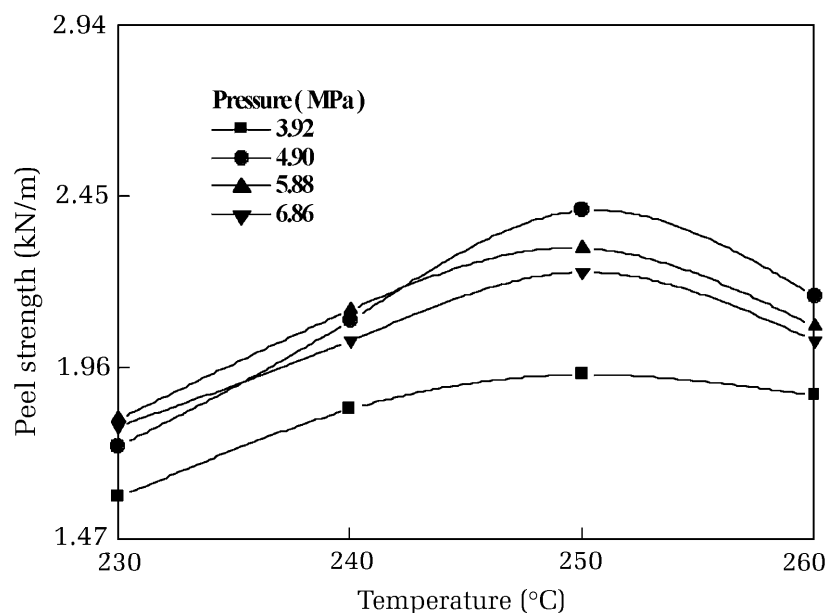


Figure 15. The peel strength of PUAI/CU composites with various molding pressures and temperatures



(-NHCO-) groups have higher heat resistance than urea (-NHCONH-) groups.

3.11 Chemical Resistance

Figure 16 shows the peel strength retention variation with time for PAI/CU and PUAI/CU composites treated with 10% H_2SO_4 at 70 °C. After treating for 60 min, the peel strength retentions of PAI/

Table 4. Effect of temperature on the peel strength (kN/m) of PAI/CU and PUAI/CU composites (various temperature for 1 hour)

Composites	Temperature (°C)					
	untreated	100	150	180	250	300
PAI/CU	2.60	2.59	2.58	2.56	2.53	2.49
PUAI/CU	2.41	2.41	2.37	2.34	2.32	2.30

CU and PUAI/CU composites were 95.09% and 94.31%, respectively. Figure 17 shows how the peel strength retention changed with time for PAI/CU and PUAI/CU composites treated with 10% NaOH at 70 °C. After 60 min, the peel strength retentions of PAI/CU and PUAI/CU composites were 95.85%

and 93.09%, respectively. In summary, PAI/CU composites showed higher peel strength retention than PUAI/CU composites. This is because PUAI is more hydrophilic than PAI. The water absorption of PUAI film was 1.62% and that of PAI film was 1.40%.

Figure 16. Effect of 10% H_2SO_4 on the peel strength retention of PAI/CU and PUAI/CU composites (at 70 °C)

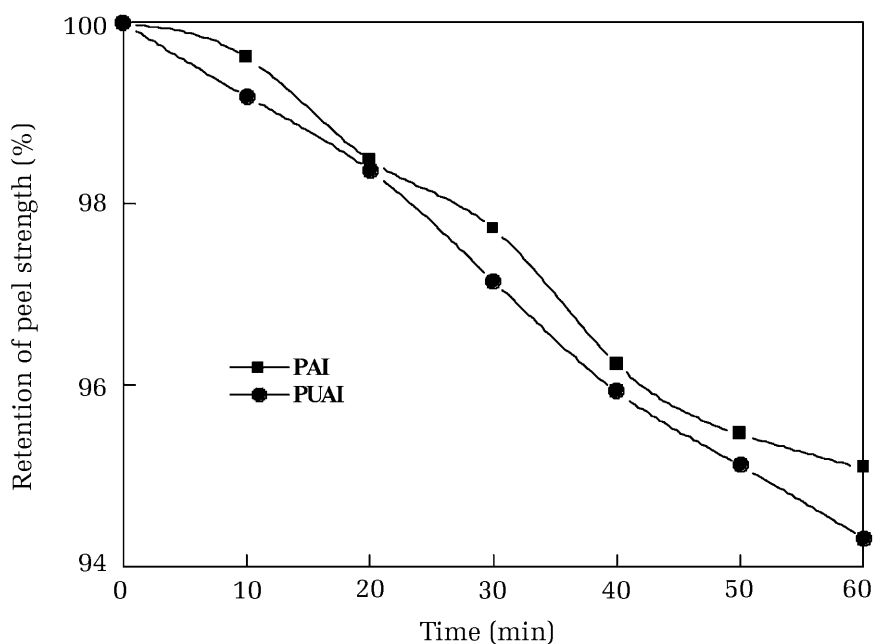
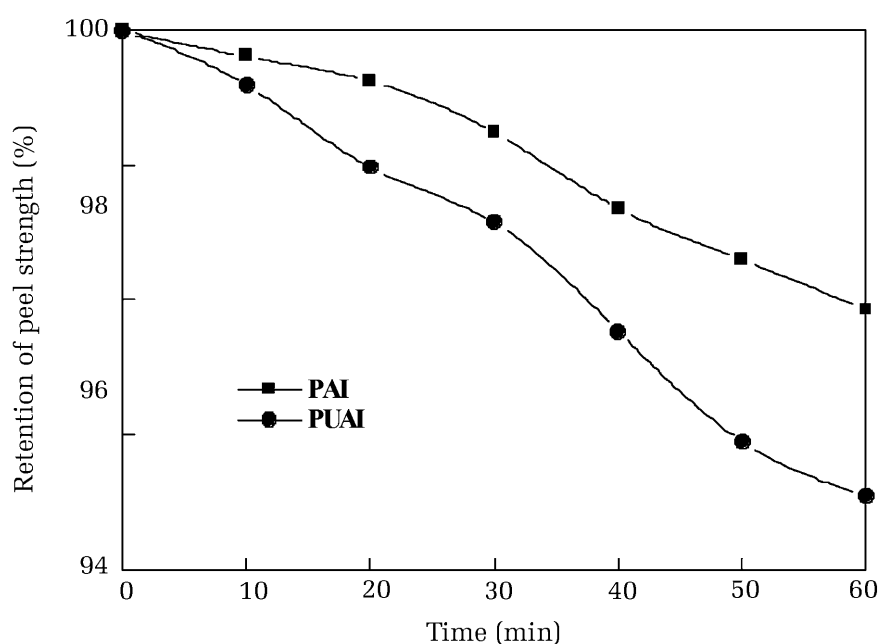


Figure 17. Effect of 10% NaOH on the peel strength retention of PAI/CU and PUAI/CU composites (at 70 °C)



4. CONCLUSIONS

- (1) The maximum peel strength of PAI/CU composites was attained at 380 °C and 4.90 MPa while that of PUAI/CU composites was attained at 250 °C and 4.90 MPa.
- (2) For PAI and PUAI films heated in nitrogen, 10% weight loss occurred at around 481 °C and 420 °C, respectively. The peel strengths of PAI/CU and PUAI/CU composites were 2.49 kN/m and 2.30 kN/m respectively after heating at 300 °C for 1 h.
- (3) The dielectric constant (D_k) and dissipation factor (D_f) of PAI/CU composites ($D_k = 2.90$, $D_f = 0.0143$) were lower than those of PUAI/CU composites ($D_k = 3.19$, $D_f = 0.0152$). Those electrical properties in this study did meet the industrial requirements.
- (4) After treating with either 10% H_2SO_4 or 10% NaOH at 70 °C for 60 min, both PAI/CU and PUAI/CU showed excellent acid and alkali resistance. The peel strength retention of PAI/CU and PUAI/CU composites treated with 10% H_2SO_4 were higher than 95% and 94% respectively and those treated with 10% NaOH were higher than 95% and 93%.

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