

Surface Modification of Aromatic Polyamide Film by Plasma Graft Copolymerization of Glycidylmethacrylate for Epoxy Adhesion

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ABSTRACT: The graft copolymerization of glycidyl methacrylate, GMA, onto poly(*p*-phenylene terephthalamide), PPTA, film surfaces was investigated to improve adhesion between the PPTA film and epoxy adhesives. The graft copolymerization of GMA was carried out in two steps; a peroxide formation by a combination of argon plasma irradiation and air exposure, and the polymerization reactions of GMA. XPS analyses showed the graft copolymerization of GMA on the PPTA film surface, and only 31–40% of the PPTA film surface was covered with the GMA graft polymers. The graft copolymerization of GMA improved the adhesion between the PPTA film and the epoxy adhesive. The adhesion strength was improved 2.7 times by the graft copolymerization. The failure from the adhesive joint occurred in the epoxy adhesive layer rather than at the interface between the PPTA film and the epoxy adhesive layer. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1179–1185, 1998

Key words: aromatic polyamide film; plasma graft copolymerization; glycidylmethacrylate; epoxy adhesion

INTRODUCTION

Poly(*p*-phenylene terephthalamide), PPTA, is an excellent material in mechanical and chemical properties. It is widely used in a fiber form for applications such as composites, armor goods, ropes and cables, and pulps for papers.¹ In these applications, the PPTA fiber-reinforced composite is one of the most important usages of PPTA. Thermosetting and thermoplastic resins are used as matrices for PPTA fiber-reinforced composites. The thermosetting resins contain epoxy, rubbers, polyurethanes, polyvinyl esters, unsaturated polyesters; and the thermoplastic resins contain nylon, polyesters, acrylonitrile–butadiene–styrene polymer, polyethylene, polypropylene, and polycarbonate.¹ In the application of PPTA fiber-

reinforced composites, poor adhesion between the PPTA fiber and polymer matrices is a serious problem to be solved. Many investigators have investigated the improvement of the adhesion between the PPTA fiber and epoxy resin and reported some methods of the improvement, which include the graft copolymerization of nitrogen-counteracting monomers,² substitution of hydrogen in amide groups,^{3,4} and plasma treatment.^{5,6}

In this study, plasma graft copolymerization of glycidyl methacrylate, GMA, was investigated to improve adhesion between the PPTA fiber and epoxy resin. The PPTA film, Aramika[®], which was commercially supplied by Asahi Chemical Ind. Co. Ltd.,⁷ was used in stead of the PPTA fiber. The usage of Aramika relieves difficulties in the XPS analysis experiments of the graft-copolymerized surfaces and adhesion experiments. Our interest is how the PPTA film surface is modified by the plasma graft copolymerization, and how effective the surface modification by the

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plasma graft copolymerization is with respect to the adhesion improvement.

EXPERIMENTAL

Materials

Aramika was generously provided in film form (500 mm wide and 25 μm thick) by Asahi Chemical Ind. Co. Ltd., and was used as the PPTA sample. The PPTA film was washed with acetone in an ultrasonic washer prior to the surface modification experiments. Glycidyl methacrylate, GMA, which was purchased from Tokyo Kasei Kogyo Co., and whose purity was more than 95% (determined by gas chromatography), was used as a monomer for the graft copolymerization.

Plasma Graft Copolymerization

The plasma graft copolymerization of GMA on the PPTA film surface was carried out in two steps: the PPTA film surface was exposed for 30–600 s to an argon plasma that was operated at a power of 25–100 W at 13.56 MHz frequency at an argon pressure of 13.3 Pa to generate radicals, and subsequently exposed to air for 5 min to modify the radicals into the corresponding hydroperoxides that were able to initiate the graft copolymerization. The apparatus used for the argon plasma irradiation was a home-made, glass-tubular reactor (170 mm diameter, 300 mm long), which contained a micrometering valve for an argon gas inlet (Whitey Co., USA, model SS-22RS4), a pressure gauge (Datametrics Co., USA, capacitance manometer type, model 622), and a vacuum system (Daia Vacuum Engineering Co. Ltd., model DSSO-422) composed of a combination of diffusion (150 L/s) and rotary pumps (200 L/min). The electric power at 13.56 MHz for generating a glow discharge was supplied from a generator (Samco International Inc., Japan, model FRG-200) into the reactor through a capacitively coupled system with electrodes wound on the outside of the glass reactor.

The argon-plasma-irradiated PPTA film was immersed in a toluene solution of GMA (10 wt %) from which dissolved air had been removed by a repeated freezing-fusion procedure before the graft copolymerization, and the graft copolymerization reactions were continued under nitrogen atmosphere at 50–70°C for 3 to 24 h. After the graft copolymerization, the PPTA film was washed with

methanol for 24 h using a Soxhlet apparatus to remove the homopolymer of GMA, and dried at 50°C under vacuum.

Hydroperoxide Concentration Generated on PPTA Film Surface

The concentration of hydroperoxides generated on the PPTA film surface by a combination of the argon plasma irradiation and the air exposure was determined by the iodide method.⁸ The plasma-irradiated PPTA film was reacted with sodium iodide in a mixture of 2-propanol and benzene (6 : 1 volume ratio) containing a trace of ferric chloride (1 ppm) at 60°C for 10 min. The concentration of hydroperoxide in the PPTA film was determined from the absorption intensity of the mixture solution at 360 nm.

X-ray Photoelectron Spectroscopy

XPS spectra of the plasma-graft-copolymerized PPTA films were obtained on a Shimadzu ESCA K1 using a nonmonochromatic MgK_{α} photon source. The anode voltage was 12 kV, the anode current 20 mA, and the background pressure in the analytical chamber 1.5×10^{-6} Pa. The size of the X-ray spot was 2 mm diameter, and the take-off angle of photoelectrons was 90° with respect to the sample surface. The XPS spectra were referenced with respect to the 285.0 eV carbon 1s level observed for hydrocarbon to eliminate the charge effect. The spectra were not smoothed. The C_{1s} , O_{1s} , and N_{1s} spectra were decomposed by fitting a Gaussian-Lorentzian mixture function (80 : 20 mixture ratio) to an experimental curve using a nonlinear least-squares curve-fitting program, ESCAPAC, supplied by Shimadzu. The sensitivity factors (S) for the core levels were $S(\text{C}_{1s}) = 1.00$, $S(\text{O}_{1s}) = 2.85$, and $S(\text{N}_{1s}) = 1.77$.

Adhesive Joint Between PPTA Film and Epoxy Adhesive and Peel Strength

The PPTA film surface was joined with a sand-blasted aluminum sheet using an epoxy adhesive that was composed of a mixture of Epicoat 828 and Tomide 235S (100 : 70 weight ratio). The jointing area was 10 mm wide \times 40 mm long, and was pressed at 11.76 N/m^2 (1.2 kgf/m^2) at 22°C for 24 h for curing the epoxy adhesive.

The 90° type peel strength (10 mm wide) of the adhesive joints between the PPTA film and the epoxy adhesive was evaluated at a peel rate of 10

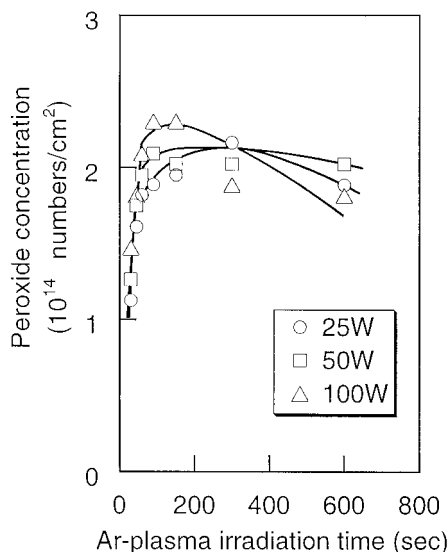


Figure 1 Peroxide concentration formed by Ar plasma irradiation as functions of the irradiation time and electric power for Ar plasma.

mm/min using an Instron-type tensile strength tester (Shimadzu AGS100-A). The peel strength was determined from an average of 10 specimens.

RESULTS AND DISCUSSION

Peroxide Formation and Graft Copolymerization of GMA

A combination of the Ar plasma irradiation and air exposure formed peroxide groups on the surface of the PPTA film. The peroxide concentration depended on the Ar plasma irradiation time, and the electric power for the Ar plasma. Figure 1 shows peroxide concentrations as functions of the Ar plasma irradiation time and the electric power. Most formation of the peroxide groups occurs within short Ar plasma irradiation times (90–150 s), and afterwards, the peroxide formation becomes insignificant. A maximum formation of the peroxide groups appears at irradiation times of 90–150 s. Table I shows the maximum peroxide concentration, which is in the range of $1.95\text{--}2.30 \times 10^{14}$ numbers/cm 2 . From these results, we used in this study Ar plasma irradiation at 100 W for 90 s for generating the peroxide groups on the PPTA film surface.

The PPTA films, with the peroxide groups formed by the Ar plasma irradiation, were immersed in a toluene solution of GMA (10 wt %), and the graft copolymerization was carried out at

temperatures of 50–70°C for 3–24 h. Figures 2 and 3 show typical results of the graft copolymerization of GMA. The PPTA film weight, as shown in Figure 2, increases, and the weight increase is a linear function of the graft copolymerization time and copolymerization temperature (Fig. 3). From these kinetic data, an apparent activation energy for the graft copolymerization of GMA is estimated to be 27.8 kJ/mol, which almost corresponds to the activation energy for propagation of methacrylates (methyl ester, 29.1 kJ/mol; ethyl ester, 27.0 kJ/mol).⁹

Surface Composition of Graft-Copolymerized PPTA Film Surfaces

The PPTA film surfaces graft copolymerized with GMA were analyzed by XPS. Table II shows typical results regarding the atomic composition of the graft-copolymerized PPTA film surfaces. The graft-copolymerized PPTA film surfaces show increases in the O/C atomic ratio from 0.14 to 0.18–0.22, but change in the N/C atomic ratio is negligible. If GMA was graft copolymerized onto the PPTA film surface and the graft polymers covered completely all the surface of the PPTA film, the O/C and N/C atomic ratios should change from 0.14 (repeating unit of PPTA, $C_{14}H_{10}N_2O_2$) to 0.43 and from 0.14 to 0.00, respectively, which corresponds to the repeating unit of GMA ($C_7H_{10}O_3$). The estimated O/C atomic ratio (0.18–0.22) for the graft-copolymerized PPTA films is higher than 0.14, but lower than 0.43. Therefore, we believe that GMA may be graft copolymerized onto the PPTA film surface. The graft polymers do not cover all the PPTA film surface, only a part of the film surface. However, we cannot explain why an apparent decrease does not appear in the N/C atomic ratio.

The C_{1s} and O_{1s} core level spectra for the graft-copolymerized PPTA films were decomposed into special components to investigate the chemical composition of the film surfaces. Figure 4 compares typical C_{1s} and O_{1s} core level spectra between the original PPTA and the GMA graft-copolymerized PPTA film that was graft copolymerized with GMA (20 wt %) at 70°C for 24 h. We could observe some differences in the C_{1s} and O_{1s} spectra between the graft-copolymerized PPTA and the original PPTA films. The C_{1s} spectrum for the original PPTA film, as illustrated by dotted lines in Figure 4, is decomposed into five components that appear at 285.0 (CH groups), 286.2 (C–N groups), 288.0 (C=O groups), 289.0

Table I Maximum Concentration of Peroxide Groups Formed on PPTA Film Surface by Ar Plasma Irradiation

Ar Plasma Irradiation Conditions		
Electric Power (W)	Irradiation Time (s)	Peroxide Concentration ($\times 10^{14}$ Numbers/cm ²)
25	150	1.95
50	90	2.10
100	90	2.30

(C(O)O groups), and 291.0 eV ($\pi-\pi^*$ shakeup satellite),¹⁰ and whose relative concentration is 73, 13, 11, and 3%, respectively. The component due to $\pi-\pi^*$ shakeup satellite is eliminated from estimating the relative concentration. On the other hand, the C_{1s} spectrum for the graft-copolymerized PPTA film is decomposed into five components. They are the CH groups at 285.0 eV (65%), C—O groups at 286.1 eV (12%), epoxy groups at 287.0 eV (9%), C=O groups at 288.2 eV (12%), and $\pi-\pi^*$ shakeup satellite at 291.2 eV. The comparison shows that the large differences are due to the appearance of a new component due to the epoxy group and the decrease of the CH component.

The O_{1s} spectra for the original PPTA and the graft-copolymerized PPTA films, as shown in Figure 4, are decomposed into two components, O=C groups at 531.5–531.8 eV, and O—C groups at 533.5–533.6 eV.¹⁰ The main difference between the original and graft-copolymerized PPTA films

is the relative composition of the two O=C and O—C components. For the original PPTA films, the O=C component (81%) is a main ingredient and the O—C component (19%) is a minor ingredient. On the other hand, for the graft-copolymerized PPTA film, the O=C and O—C components are competitive elements whose relative concentrations are 48 and 52%, respectively. Therefore, the graft copolymerization leads to a decrease of the O=C component from 81–48%, and an increase of the O—C component from 19–52%. The increase of the O—C component and the decrease of the O=C component may be due to the coverage of the PPTA film surface with the GMA graft polymers, because the O=C and O—C components in the GMA polymers are 33 and 67%, respectively.

From the C_{1s} and O_{1s} spectra analyses, we conclude that GMA is graft copolymerized onto the PPTA film surface. However, the graft polymers do not cover all the PPTA film surface, only a part of the film surface. The coverage of the PPTA film

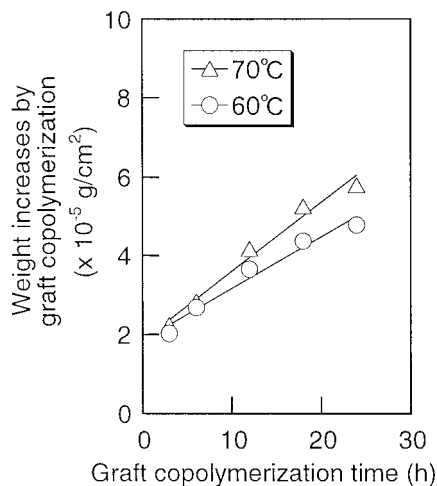
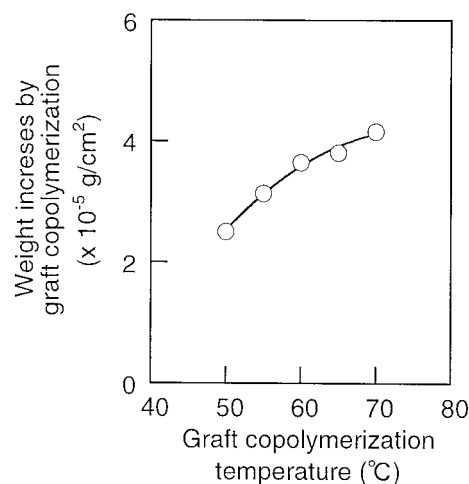
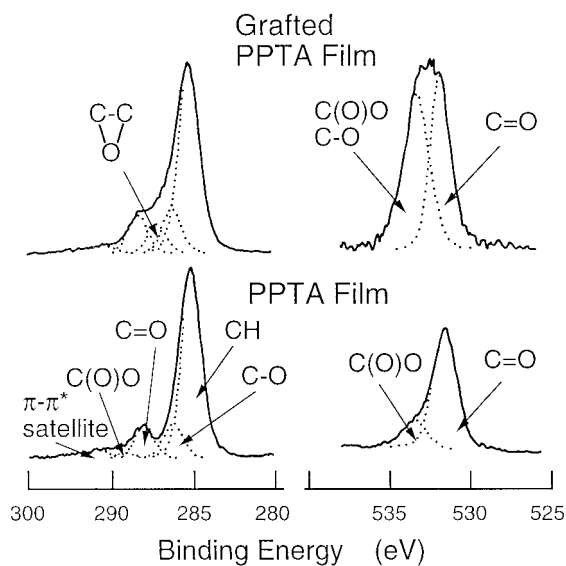
**Figure 2** Weight increase by graft copolymerization as functions of graft copolymerization time and temperature.**Figure 3** Weight increase by graft copolymerization as a function of graft copolymerization temperature.

Table II Atomic Composition of Graft-Copolymerized PPTA Film Surfaces

Films	Graft Copolymerization		Atomic Ratio of PPTA Film Surface	
	GMA Conc. (%)	Polym. Time (h)	O/C	N/C
Original PPTA			0.14	0.14
Graft-copolymerized PPTA	10	24	0.18	0.15
	10	48	0.21	0.12
	20	24	0.22	0.14

surface with the graft polymers can be estimated from the relative concentration of the epoxy groups or that of the CH groups in the C_{1s} spectra. The estimation is 31% from the relative concentration of the epoxy groups, and is 40% from the relative concentration of the CH groups. We believe that the graft-copolymerized PPTA film surface is a mixture of the graft-polymer-covered surface (31–40%) and the uncovered PPTA film surface (69–60%). It is not so unusual a phenomenon that polymer chains graft copolymerized on the polymer film surfaces are not homogeneously distributed on the film surfaces, but are heterogeneously distributed in an island-sea structure. Such island-sea structure has been observed in the graft polymers of vinylimidazole onto polyimide films¹¹ and the graft polymers of sodium vinylsulfonate onto polytetrafluoroethylene films.¹²

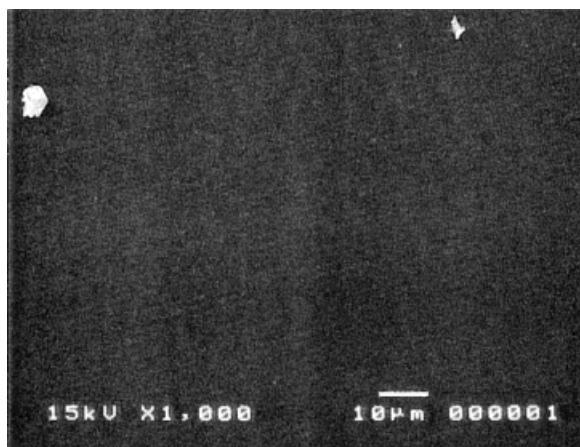
**Figure 4** XPS (C_{1s} and O_{1s}) spectra for GMA graft-copolymerized PPTA film surfaces.

Adhesion Between Graft-Copolymerized PPTA Film and Epoxy Adhesive

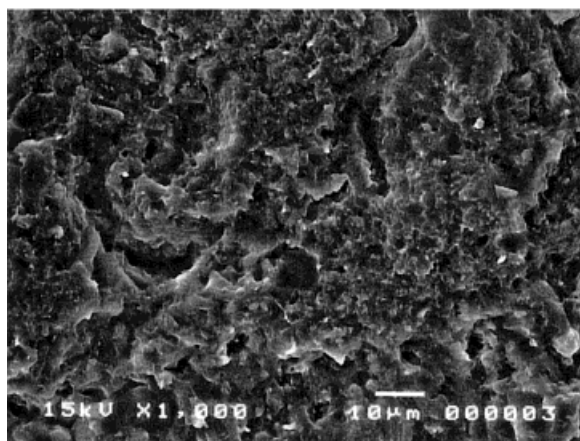
The PPTA films graft copolymerized at 70°C for 24 h were used as specimens for adhesion experiments. The graft-polymerized PPTA films adhered to the sandblasted aluminum plate using the epoxy adhesive that was a mixture of Epicoat 828 and Tomide 235S. The adhesive joints were pressed at a pressure of 11.76 N/m² (1.2 kg f/m²) at 22°C for 24 h for curing the epoxy adhesive, and the adhesion between the graft-polymerized PPTA film and epoxy adhesive was evaluated by 90° type peel strength of the adhesive joint at a peeling rate of 10 mm/min (Table III). The peel strength of the original PPTA/epoxy adhesive joint was 1.23 N/10 mm, and the Ar plasma treatment showed no improvement on the adhesion (the peel strength was 1.32 N/10 mm). On the other hand, the graft copolymerization showed large improvement. The peel strength of the graft-polymerized PPTA/epoxy adhesive joint, as shown in Table III, is improved from 1.23 to 3.33 N/10 mm (2.7 times higher) by the graft copolymerization. Therefore, we conclude that the graft copolymerization of GMA is effective in improving the adhesion between the PPTA film and epoxy adhesive.

Table III Peel Strength for Adhesive Joint Between PPTA Film/Epoxy Adhesive

Structure of Adhesion Joint	Peel Strength (N/10 mm)
Original PPTA film/epoxy adhesive/A1 sheet	1.23 ± 0.11
GMA-grafted PPTA film/epoxy adhesive/A1 sheet	3.33 ± 0.14



(a)



(b)

Figure 5 SEM pictures of the PPTA film surfaces peeled off from adhesive joints (a) between the original PPTA film and epoxy adhesive and (b) between the GMA graft-copolymerized PPTA film and epoxy adhesive.

Location of the failure of the adhesive joint was investigated using SEM and XPS of the peeled off PPTA film surfaces. The failure of the adhesive joints gave two peeled-off surfaces: the PPTA film side, and the aluminum plate side. The surfaces of the PPTA film side were surveyed by SEM (Fig. 5). The SEM [Fig. 5(a)] for the surface of the PPTA film side peeled off from the adhesive joints between the original PPTA and the epoxy adhesive is a smooth surface like that of the original PPTA film. On the other hand, the SEM [Fig. 5(b)] for the surface peeled off from the adhesive joints between the graft-copolymerized PPTA film and the epoxy adhesive is rough. The surface morphology is essentially different from Figure 5(a).

The C_{1s} and O_{1s} core level spectra for the surface [Fig. 5(b)] peeled off from the adhesive joint between the graft-copolymerized PPTA and the epoxy adhesive gave suggestive evidence regarding where the failure occurred. Figure 6 shows the C_{1s} and O_{1s} core level spectra for the surface [Fig. 5(b)]. The C_{1s} spectrum corresponds not to the original PPTA film but to the epoxy adhesive. Furthermore, the O_{1s} core level spectra for the surface [Fig. 5(b)] also corresponds to the epoxy adhesive. From these spectroscopic results, we conclude that the failure of the adhesive joint occurred in the epoxy adhesive layer rather than at the interface between the PPTA film and the epoxy adhesive layer.

CONCLUSION

The graft copolymerization of GMA onto the PPTA film surfaces was investigated to improve adhesion between the PPTA film and epoxy adhesives. A combination of the argon plasma irradiation and air exposure was used for forming peroxide groups, which were able to initiate the graft copolymerization of GMA, and the graft copoly-

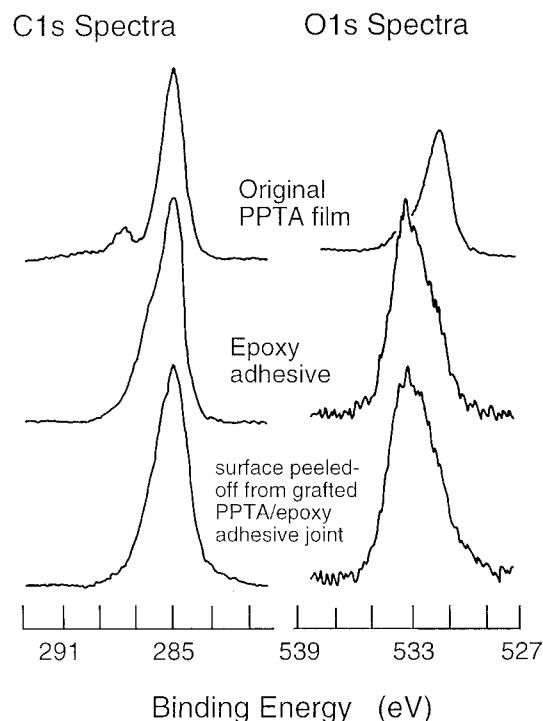


Figure 6 XPS (C_{1s} and O_{1s}) of the the PPTA film surface peeled off from adhesive joint between the GMA graft-copolymerized PPTA film and epoxy adhesive.

merization of GMA was carried out at 50–70°C. The 90° peel strength of the adhesive joint between the GMA graft-copolymerized PPTA film and the epoxy adhesive was used for evaluating the adhesion of the PPTA with the epoxy adhesive. The main results are summarized as follows. (1) A combination of the Ar plasma irradiation and air exposure makes peroxide groups on the PPTA film surfaces. The concentration of the peroxide groups depends on the Ar plasma irradiation time and the rf power, and the maximum concentration of the peroxide groups is 2.30×10^{14} numbers/cm². (2) GMA can be graft copolymerized onto the PPTA film surface from the peroxide groups. The polymers graft copolymerized on the PPTA film surface do not cover all the film surface. The coverage is 31–40% of the PPTA film surface. (3) The graft copolymerization of GMA improves the adhesion between the PPTA film and the epoxy adhesive. The 90° peel strength of the adhesive joint between the modified PPTA film and the epoxy adhesive is improved 2.7 times by the graft copolymerization. The failure from the adhesive join occurs in the epoxy adhesive layer rather than at the interface between the PPTA film and the epoxy adhesive layer.

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