Synthesis and Properties of Thermosetting Modified Polyphenylene Ether

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Summary

A novel method for preparing thermosetting modified Poly(2,6-dimethyl-1,4-phenylene ether) (PPE) was developed by introducing allyl groups into PPE. It was successfully prepared from the reaction between brominated PPE and a Grignand reagent. The effects of substitution of bromine on methyl group and dosage of allylated Grignard reagent on the substitution value of allyl group were studied. The structure of the resulting allylated PPE (A-PPE) was characterized by ^{1}H-NMR and FT-IR spectroscopy. The curing reaction process was researched by differential scanning calorimetry (DSC), and the properties of the cured A-PPE were also investigated. The curing reaction of the A-PPE was first order reaction. The curing reaction activation energy obtained by Kissinger equation was 121.7kJ/mol. The cured A-PPE resin is excellent not only in solvent resistance and dielectric properties, but also in thermal properties, moisture absorption and adhesion with glass fiber. The dielectric constant (ε) and dissipation factor (tanδ) of A-PPE composites reinforced with E-glass cloth at 1 MHz were measured as 2.84 and 2.65$\times$10^{-3}, respectively. In addition, A-PPE was very easy to form into films.

Introduction

In recent years, with the rapid development of the computer and communication technique, dielectric materials with excellent dielectric properties (such as a low dielectric constant and a low dielectric dissipation factor, and almost constant with the variety of temperature and frequency), a relatively good heat resistance and dimensional stability have been strongly desired in application. For example, a copper-clad laminate (CCL) made of a substrate containing a thermosetting resin has been widely used as a high speed and high frequency printed circuit boards (PCB). Poly(2,6-dimethyl-1,4-phenylene ether) (PPE) has low dielectric constant (ε), low dissipation factor (tanδ), high glass transition temperature (Tg), low water absorption, excellent flame resistance and dimensional stability[1]. It has been attracting attention as a new material, and it has been attempted to apply PPE to a high performance CCL. However, when conventional PPE is used as a material for PCB substrate, it is unlikely to undergo high temperatures in soldering and solvent resistance against

halogenated hydrocarbons and aromatic hydrocarbons used to rinse oil stain on the substrate, which are caused by its thermoplasticity [2, 3].

For overcoming the above-mentioned drawback, PPE is necessarily modified from thermoplasticity to thermosetting. There were two ways to obtain thermosetting: introducing a crosslinkable "active" radical to PPE chain; and introducing another thermosetting resin by blending or interpenetrating networks to form compatible thermosetting resins system. Many researches on the second way have been widely reported in the literature [4-14]. However, study on the first way has been seldom introduced [15, 16]. An interesting achievement of introduced crosslinking "active" radical is the preparation of allylated PPE (A-PPE). This article proposes a new way to synthesize thermosetting PPE containing allyl groups from thermoplastic PPE and introduces the curing dynamics and properties of allylated PPE.

Experimental

Materials

Poly(2,6-dimethyl-1,4-phenylene ether) (PPE) was obtained from the GE Plastics Company (Mn=1.23×10^4; Mw=4.72×10^4). Chlorobenzene, methanol, benzoyl peroxide (BPO), and dicumyl peroxide (DCP) were purchased from Shanghai Lingfeng Chemical Reagent Co. Ltd (China). Tetrahydrofuran (THF) and allyl bromide were bought from Shanghai Chemical Reagent Co. Ltd (China). N-bromosuccinimide (NBS) and magnesium powder were received from Shanghai Guoyao Chemical Reagent Co. Ltd (China) and from Shanghai Runjie Chemical Reagent Co. Ltd (China), respectively.

Synthesis of allylated PPE (A-PPE)

Owing to stability of PPE, it is very difficult to directly introduce allyl functional groups to the backbone of PPE. So it is necessary to functionalize PPE by introducing "active" site. The most common and simple functionalization method is halogenation [17]. In addition, Grignard reagent is known for its simple preparation technique and high efficiency reaction activation [18, 19], for which it is widely used to synthesize C-C bond in organic synthesis. The present novel technique of thermosetting modification for PPE is as follows: the PPE reacts with halide reagent; then the resultant reacts with allylated Grignard reagent, and allylated PPE (A-PPE) is gained.
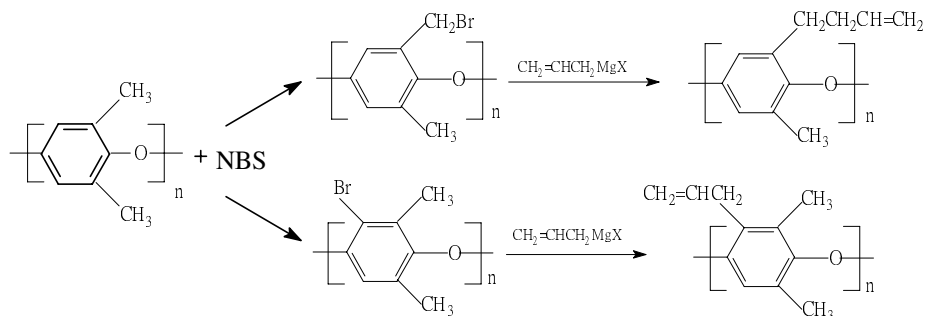
Scheme 1. The mechanism for allylation of PPE

The scheme for modification is shown below:

brominated reagent   allylated Grignard reagent

PPE ⟶ brominated PPE ⟶ A-PPE

The bromine in the brominated PPE is substituted for the active allylated Grignard reagent, and at the same time the allyl functional groups are introduced to PPE. The mechanism for allylation of PPE is shown in Scheme 1.

Synthesis of brominated PPE. When NBS is used as brominating agent, bromination of the methyl group of PPE takes place in the mechanism of free radical reaction [17]. If a peroxide initiator (BPO or DCP) during bromination is not used, it is difficult for the bromination of the methyl group of PPE to occur. After PPE (20g) was dissolved in chlorobenzene (250ml) in a four-necked flask at 110°C, BPO (2g) and NBS (30g) were added. The mixture was agitated under nitrogen gas for at least 1 h. Then a large volume of methanol was poured into the flask and a polymer precipitated. The mixture was filtered, and the precipitate was washed with methanol for several times. The washed polymer was dried in the oven at 80°C for 12 h, and a yellow polymer powder could be obtained. By controlling the amount of NBS, single substituted brominated PPE was synthesized.

Synthesis of allylated Grignard Reagent. A round-bottom flask equipped with a reflux condenser was charged with 10g of magnesium, a little iodine and 30ml of purified THF. The system was agitated under the nitrogen gas and a solution of 30ml of allyl bromide in THF (100ml) was dropwise added to the above flask. Then the reaction lasted for about 1 hour and allylated Grignard Reagent was obtained.

Synthesis of A-PPE. After 20g of brominated PPE was dissolved in THF (250ml) in a 500ml round-bottom flask, allylated Grignard Reagent (120ml) was added and the system was heated by an oil-bath to keep the constant temperature (40°C) for an hour. After the reaction was finished, a large volume of methanol was poured into the system, and a polymer was precipitated. The polymer was filtered and washed with methanol for several times. The washed polymer was dried in the oven at 60°C for 12 h, and a white polymer powder was obtained. The product yield was 86%.

Cure of A-PPE and preparation of the laminate based on the A-PPE

The powder of A-PPE sample was mixed with peroxide (3 wt. %, DCP) in toluene, and then the solution was poured into a flat vessel. After the toluene in the solution was volatilized at 30°C under vacuum for 24h, several sheets of films obtained were put in the presser and cured at 200°C for 2 h by a hot-press curing.
The mixed resin solution above was poured into a clean plastic-plate, conducting impregnating with E-glass fiber cloth as reinforcement for 1 min. The prepreg was prepared after the impregnated cloth was dried in the oven at 100°C for 10-20 min. The laminate (GF/A-PPE composite) based on the A-PPE can be made with the prepreg by hot-press curing at 200°C for 2 h.

Instruments

The bromination value of brominated PPE and substitution value of allyl groups were calculated on the basis of the integral of proton in benzene of PPE and double bond in

allyl group from the ^{1}H-NMR spectra, which were taken on a DRX500 spectrometer with CDCl$_3$ as solvent at 25°C and a frequency of 500MHz. Infrared spectra were recorded on a Nicolet Magna-IR550 FTIR spectrophotometer to analyze the chemical structure of A-PPE. Dynamic mechanical analysis (DMA) of samples was performed on a DMA2980 in tensile mode at a heating rate of 3°C /min and a frequency of 11Hz. Thermogravimetric analysis (TGA) of the specimen was taken on a Dupont 1060 at a heating rate of 10°C /min. DSC analyses were carried out on a Modulated DSC2910 differential scanning calorimeter at heating rate of 5°C /min, 10°C /min, 15°C /min, and 20°C /min under nitrogen gas, respectively. The ε and tanδ of both the cured A-PPE and the laminate were measured by using Broadband Dielectric Spectrometer (Novocontrol Concept 40, Germany), respectively. The morphology of fracture surface of the laminate samples was observed under a scanning electron microscope (JSM-6360LV, JEOL) after gold coating and the Barcol hardness of the sample surfaces was determined according to ASTM D2583 with an Hba-1 Barcol sclerometer.

Results and Discussion

Characterization

^{1}H-NMR spectroscopy has been used to characterize the chemical structure of the products. The ^{1}H-NMR spectrum of A-PPE is shown in Fig. 1. It is found that the chemical shifts match those of the chemical structure of the desired product [20, 21]. It is concluded that the allyl was introduced into PPE.
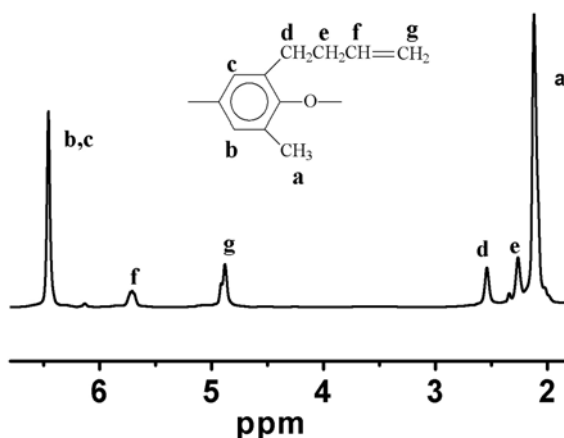

Figure 1. The ^{1}H-NMR spectrum of A-PPE in CDCl$_3$ solvent

The FT-IR of allylated PPE and unmodified PPE are shown in Fig. 2. It is observed that there are an out-of-plane bending vibration peak of the vinyl group at 912cm^{-1} and a stretching vibration peak of the vinyl group at 1640 cm^{-1} in FT-IR spectrum of A-PPE, implying the existence of the allyl group in PPE. Therefore it could be concluded from the combination with the ^{1}H-NMR analysis result mentioned above that A-PPE was successfully synthesized.

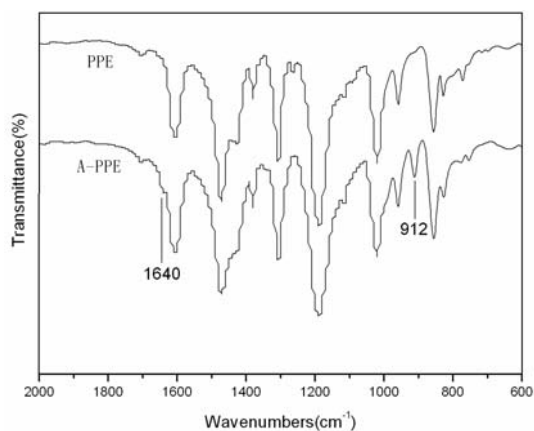**Figure 2.** FT-IR spectra of PPE and A-PPE in 600-2000cm^{-1}

Factors affecting the substitution value of allyl group

Brominated PPE with different substitution of Br and different dosage of Grignard reagent were used to prepare A-PPE with different substitution value (shown in Fig. 3 and Fig. 4). It could be concluded from Fig. 3 and Fig. 4 that, under the same reaction condition, the substitution value of allyl group increased with the increment of the bromination value of PPE and the dosage of Grignard reagent. During the reaction process, the bromine on methyl group and the bromine on benzene ring of the brominated PPE were replaced continuously by allyl groups. If the dosage of Grignard reagent was less than 10ml (the mol concentration was 1.5mol/l), the allylated reaction hardly carried out. However, if the dosage of Grignard reagent exceeded 25ml, the substitution value of allyl group almost did not vary with the dosage of Grignard reagent.
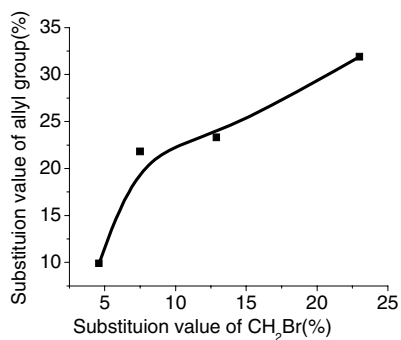

Figure 3. Effect of substitution of bromine on methyl group on substitution value of allyl group reagent
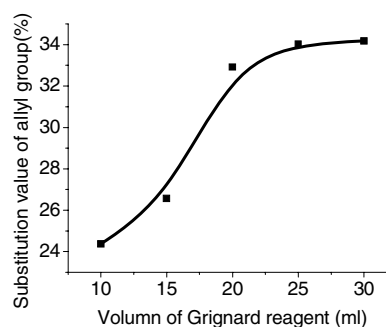

Figure 4. Effect of dosage of Grignard reagent on substitution value of allyl group

The analysis of curing dynamics of allylated PPE system

Fig. 5 shows the curing curves of the A-PPE sample (the substitution value of allyl group is 12%) containing 3%DCP initiator at different heating rates and the results are collected in Table 1. From Table 1, it could be observed that the beginning

temperature, the terminating temperature and the peak temperature of curing reaction increased with the heating rate.
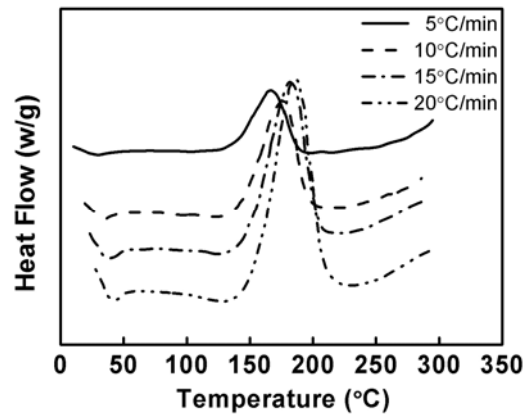

Figure 5. The dynamic DSC curves of A-PPE resin systems

Table 1. The Dynamic DSC Results of A-PPE Resin

ϕ (K/min)	T_{onset} (°C)	T_m (°C)	T_{final} (°C)	ΔH (J/g)
5	151.3	180.1	201.0	74.14
10	152.9	188.8	209.8	67.79
15	155.8	194.3	217.0	68.54
20	159.4	198.0	223.4	69.44

T_{onset}—The starting temperature of curing reaction; T_m—The temperature of exothermic peak; T_{final}—The terminating temperature of reaction; ϕ—The heating rate; ΔH—The residual heat.

Generally the A-PPE resin is cured in the mold at a constant temperature, while thermal analysis was conducted in DSC non-isothermally. Therefore, there is a difference between the two cases. The extrapolation is used to calculate the reference curing condition of the system in order to eliminate that difference. The extrapolation procedure is as follows: the curves of the beginning temperature of curing reaction (T_{onset}), the temperature of exothermic peak (T_m) and the terminating temperature of
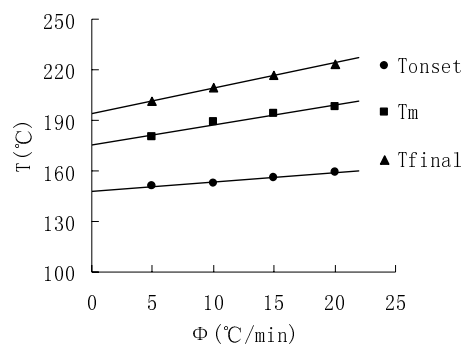

Figure 6. T vs. ϕ curves of A-PPE resin system

the reaction (T_{final}) vs. the DSC heating rates (ϕ) are plotted, respectively (Fig. 6); by extrapolating the heating rate of the three curves to zero, the corresponding temperatures obtained are named respectively: the gelling temperature T_{gel}=148°C, the curing temperature T_{cure}=176°C, the postcure temperature T_{post}=194°C.

The apparent activation energy (ΔE) of the curing reaction of the A-PPE resin is calculated by Kissinger equation [22]:

$$\frac{d(\ln(\phi/T_m^2))}{d(1/T_m)} = -\frac{\Delta E}{R} \tag{1}$$

where ϕ—the heating rate, °C·min^{-1}; T_m—the temperature of exothermic peak of DSC curves, K; ΔE—the apparent activation energy, J·mol^{-1}; R—the gas constant, 8.3144 J·K^{-1}·mol^{-1}.

According to the results of Table 1, a line of $\ln(\phi/T_m^2)$ vs. $1/T_m$ (see Fig. 7) could be plotted. ΔE of the curing system calculated by the slope of the line is 121.7kJ/mol.
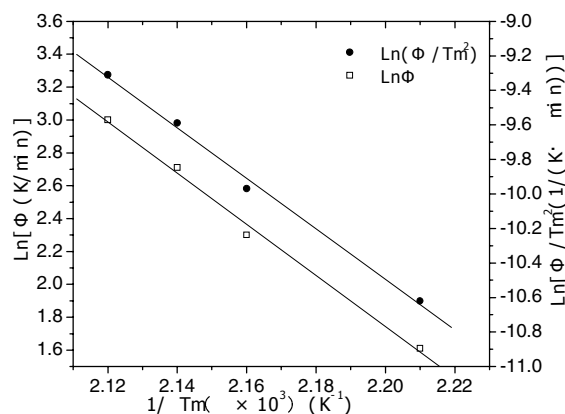

Figure 7. Kissinger plot of $\ln(\phi/T_m^2)$ vs. $1/T_m$ and Crane plot of $\ln\phi$ vs. $1/T_m$

The curing reaction order of the A-PPE resin can be calculated by Crane equation [23]:

$$\frac{d\ln\phi}{d(1/T_m)} = -(\frac{\Delta E}{nR} + 2T_m) \tag{2}$$

The $2T_m$ can be ignored when $\Delta E/nR \gg 2T_m$. A line of $\ln\phi$ versus $1/T_m$ (see Fig. 7) could be plotted. The curing reaction order (n) calculated according to the slope of the line is 0.94, so it can be concluded that the curing reaction of the A-PPE resin is the first order reaction.

Properties of cured A-PPE

Solvent Resistance. After immersion in chloroform at 23°C for 12 h, the uncured A-PPE (the substitution value of allyl group in A-PPE remains 15% in the following discussions of properties of cured A-PPE) was dissolved while the solubility of the cured A-PPE partly depended on the curing period of time. The content of chloroform extractable A-PPE cured at 200°C for 1 h was only 0.82 wt%. When the curing time exceeded 2 h, the fully cured A-PPE was insoluble in chloroform.

When GF/A-PPE composites were used as the substrate of PCB, oil stain on the substrate must be rinsed by trichloroethylene, so trichloroethylene resistance was very important to the substrate. After GF/PPE composite was immerged into trichloroethylene for one day, it was softened, dissolved and corroded seriously, while the surface of GF/A-PPE composite was still smooth when it was immerged into trichloroethylene for three days according to ASTM C581. At that time, the changing rate of the GF/A-PPE composites' weight was -3.13%/3 days and the retention rate of Barcol hardness was 95.6%/3 days. Thus, the trichloroethylene resistance of the A-PPE was much better than that of unmodified PPE. Table 2 shows the resistance of the GF/A-PPE composites to the other solvent.

Table 2. The solvent resistance of GF/A-PPE composites in some solvents for 24 hours (25°C)

Solvent	Trichloroethylene	Acetone	Toluene	Chlorobenzene	Benzene
Changing rate of weight (%)	1.22	3.84	5.34	5.19	2.03
Barcol hardness	52	50	41	36	35

The Film-forming Properties. To compare the film-forming property of A-PPE with that of PPE, the specimens were dissolved in a matched amount toluene, then the solutions were dumped into molds. Put them in a fuming cupboard for12h and resin film would be formed after the solvent was volatilized. The film-forming property of PPE before and after modification is obviously different. The obtained films of conventional PPE are the ivory-white brittle fragments, which shows the film-forming property of unmodified PPE is extremely poor, while the film-forming property of A-PPE is improved by the introduction of allyl groups. After the allyl group is grafted in PPE, the obtained film is transparent, tenacious and smooth.

Dielectric property. Curves of dielectric constant (ε) vs. frequency and dielectric dissipation factor ($\tan\delta$) vs. frequency of the laminate based on the A-PPE are shown in Fig. 8. The ε and $\tan\delta$ at 1 MHz are determined as 2.84 and 2.65×10^{-3}, respectively. The ε have small fluctuation with frequency in the range from 10^2 to 10^6 Hz. The dielectric properties of the laminate based on the A-PPE and the other typical systems available from literatures [24] are listed in Table 3 to conduct a comparison. It indicates that the laminate based on the A-PPE has the excellent dielectric properties and good stability. It is obvious that A-PPE is suitable to be used as a new high performance thermosetting resin for PCB substrate.

Table 3. Dielectric properties of the laminate based on the A-PPE and the comparison other typical systems [24]

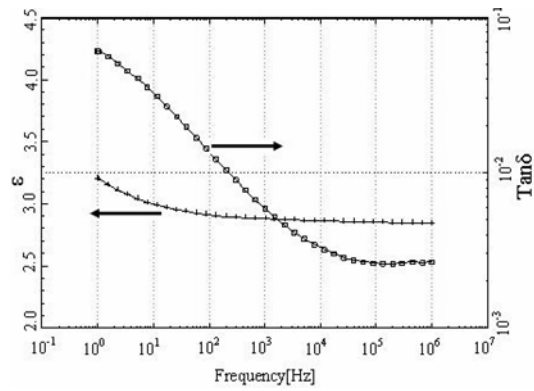| Types of resins of the laminates	Dielectric constant (ε)	Dissipation factor ($\tan\delta$)
A-PPE	2.84	2.65×10^{-3}
Bromized epoxy (FR-4)	4.66	1.5×10^{-2}
High-performance FR-4	3.92	1.1×10^{-2}
Bismadeimide Triazine (BT)	4.20	6.0×10^{-3}
Polyimides (PI)	4.20	8.0×10^{-3}
Cyanate Ester Resin (CE)	3.80	6.0×10^{-3}
Polytetrafluoroethylene (PTFE)	2.60	1.0×10^{-3}

Figure 8. Curves of ε vs. frequency and tanδ vs. frequency for laminate based on the A-PPE

Thermal properties. Dynamic mechanical analysis curves of the cured A-PPE resin are shown in Fig. 9. It is obvious from the Fig. 9 that the glass transition temperature determined by loss peak is about 217°C. The TG curve of the cured A-PPE is shown in Fig. 10. From the Fig. 10, the thermal decomposition temperature is about 400°C. It shows the cured A-PPE possesses good thermal stability.
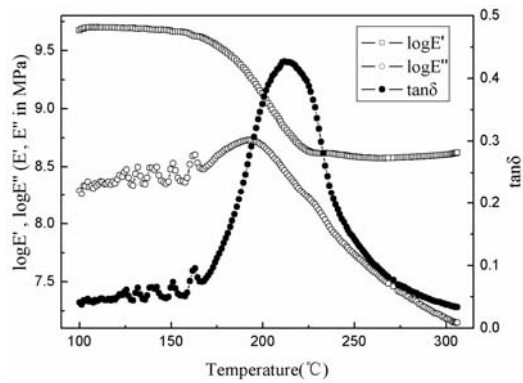

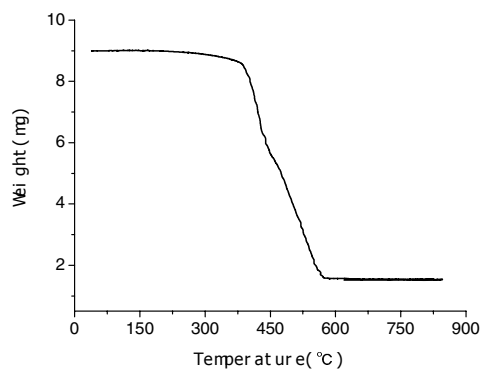**Figure 9.** Dynamic mechanical analysis curves of the cured A-PPE resin

Figure 10. TG trace of the cured A-PPE resin

Low temperature resistance. After GF/A-PPE composite samples were immersed in liquid nitrogen (-196°C) for 6 h, 12h, and 24h, the appearance and Barcol hardness of them almost did not change.

Water absorption. Water, as a common polar impurity, directly affects dielectric properties of the cured A-PPE. The water absorption of the cured A-PPE samples immerged in water for 24 h at 25°C is determined according to ASTM D570 (Table 4). The water absorption of A-PPE of different substitution values of allyl is lower than that of unmodified PPE.

Table 4. Water absorption of the cured A-PPE immerged in water for 24 h at 25°C

Substitution value of allyl groups (%)	Water absorption (%)
0	4.0×10^{-2}
9	3.0×10^{-2}
10	3.0×10^{-2}
12	3.0×10^{-2}
19	2.0×10^{-2}

SEM micrographs of GF / A-PPE composites. SEM micrograph (Fig.11) of tensile fracture surface of GF/A-PPE composite shows that the interface of glass fiber and A-PPE resin are adhered tightly. A lot of resin is coated on the surface of the fiber drawn, which proves that allylated PPE has good adhesion to glass fiber.
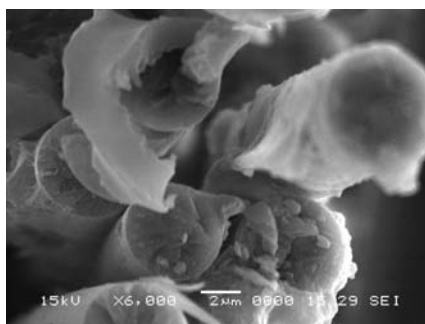

Figure 11. SEM micrograph of tensile fracture surface of the GF / A-PPE composite

Conclusions

In this study, the curable PPE was successfully prepared by the reaction of brominated PPE and allyled Grignard Reagent. It was confirmed by ^{1}H-NMR and FT-IR analysis. The substitution value of allyl could be controlled by both the dosage of allyled Grignard Reagent and the substitution value of Br of brominated PPE. The curing reaction of the A-PPE is first order reaction. The curing reaction activation energy obtained by Kissinger equation is 121.7kJ/mol. The cured A-PPE resin has low water absorption (< 0.04 wt. %), a superior glass transition temperature (217°C), high thermal stability, and fine solvent resistance. The GF/A-PPE composite has a low dielectric constant (2.84), a low dissipation factor (2.65×10^{-3}), and excellent adhesion to fiberglass. In addition, A-PPE shows a good film-forming property in toluene.

Therefore, A-PPE is suitable to be used as a high performance thermosetting resin matrix for high-speed and high frequency multilayer PCB substrate.

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