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Preparation and properties of a new polytriazole resin made from dialkyne and triazide compounds and its composite

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Summary

A new kind of polytriazole resins were prepared from a triazide and a dialkyne compounds and characterized. These resins can be cured at 80°C. The curing process for a resin was traced by FT-IR. The glass transition temperature T_g and thermal decomposition temperature T_{d5} of the cured resin with the molar ratio of azide group to alkyne group [a]/[b]=1.0:1.0 reach 216°C and 360°C, respectively. The flexural strength of the cured resin and its glass fiber reinforced composite arrive at 183.6 MPa and 963.4 MPa, respectively. The resin would be a good candidate for the matrices of advanced composites.

Keywords

Thermosetting polytriazole resin, Low temperature curing, Polymer synthesis, Thermal and mechanical properties

Introduction

The resin matrices for advanced composite materials are usually cured at high temperature such as 180°C. This would result in high manufacturing cost of the composite materials. Therefore, developing a resin matrix cured at low temperature has become one of important research directions for advanced composite materials. Up to now, a series of resins cured at low temperature have been developed [1-3].

In 1966, a linear polymer was synthesized at 70°C by the polycondensation of a monomer with azide group and alkyne group and the obtained polymer had good thermal stability [4-5]. However, the polymer was not useful as expected. Since then, no futher work has been reported. Because the addition of azide group with alkyne group can easily take place, the reaction (so called click chemistry) has been using widely for the synthesis of various compounds and polymers [6-7].

In resent years, our lab was engaged in developing novel polytriazole resins with low temperature curing and heat-resistance [8-12]. Although a polytriazole resin with T_g of 324°C was prepared from a triazide and a tetraalkyne compound, its mechnical properties were poor [11]. Here, a new polytriazole resin and its glass fiber composites with good mechanical properties were prepared and characterized.

Experimental

Raw materials

Mesitylene (Chemical Purity), paraformaldehyde, toluene, N, N-dimethylformamide, glacial acetic acid, sulfuric acid, sodium bromide, sodium azide, bisphenol A, benzyltriethylammonium chloride (all analytical reagent grade) were purchased from Sinopharm Chemical Reagent Co. Ltd and used as received. Propargyl bromide was purchased from KeLiDa Chemical Factory and distilled before use. The glass fabric SW-160 was purchased from Nanjing Fiberglass Research & Design Institute.

Instruments

The melting temperature was measured on X-4 melting-point apparatus with a microscope (Shanghai precision & scientific instrument Co. Ltd.). Proton nuclear magnetic resonance (^{1}H NMR) analyses were conducted on the BRUKER AVANCE 500 (500MHz) and tetramethylsilane (TMS) was used as an internal standard. FT-IR spectra was recorded on a Nicolet 550 (TA, U.S.). Differential scanning calorimetry was carried out on the Diamond DSC (PE, U.S.) analyser under nitrogen at the heating rates of 20°C/min. Dynamic Mechanical Analysis (DMA) was carried out on the Rheogel-E4000 (UBM, Japan) analyser operating in the tension mode under nitrogen at the frequency of 11Hz with a programmed heating rate of 3°C/min. Thermogravimetry (TG) analysis was conducted on the Pyris Diamond TG/DTA (PE, U.S.) at the heating rate of 10°C/min. Scanning electron microscope (SEM) analysis was performed on JSM-6360LV (JEOL, Japan). The mechanical properties of the cured resin and its composite were measured according to the national standard of China GB 2568-1995 and GB 1449-2005 on the DXLL-5000 electronic pulling tester (Shanghai D&G machinery equipment Co. Ltd.), respectively.

Preparation of a polytriazole resin

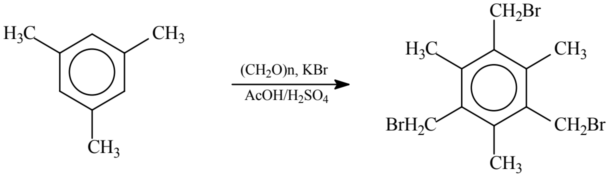
Synthesis of 1, 3, 5-tris(azidomethyl)-2, 4, 6-trimethyl-benzene (A_3)

Preparation of 1, 3, 5-tris(bromomethyl)-2, 4, 6-trimethyl-benzene [13]

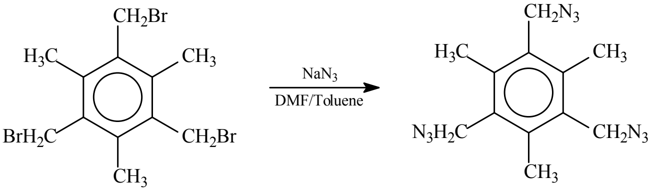
Mesitylene (0.288 mol), paraformaldehyde (1.320 mol), sodium bromide (1.720 mol) and glacial acetic acid (280 mL) were added into a 1L three-neck round bottom flask. To the flask, a mixture of 120 mL concentrated sulfuric acid and 120 mL glacial acetic acid was added dropwise under agitation at 40°C for 2 hours. Then the mixture was heated to 90-95°C and kept at the temperature for 8 hours. The product was washed with deionized water several times and the yellow solid was obtained. Then the crude product was recrystallized from acetone to obtain the white solid product. Yield: 70%, m.p. 187-189°C (186°C reported by van der Made *et al* [14], 188-189°C by Závada *et al* [15]). ^{1}H NMR ($CDCl_3$, TMS) δ: 4.50 (s, 6H, CH_2), 2.45 (s, 9H, CH_3). The schematic synthesis of 1, 3, 5-tris(bromomethyl)-2, 4, 6-trimethyl-benzene is shown in Scheme 1.

Preparation of 1, 3, 5-tris(azidomethyl)-2, 4, 6-trimethyl-benzene

1, 3, 5-tris(bromomethyl)-2, 4, 6-trimethyl-benzene (0.40 mol) and sodium azide (1.44 mol) were charged into a 1L flask with 250 mL toluene and 250 mL N, N-dimethylformamide (DMF). The mixture was heated to 75°C and stirred at this temperature for 5 hours. Thereafter, the mixture was washed with deionized water several times to remove the excessive NaN_3, DMF and NaCl formed during the reaction. The toluene layer with a product was obtained. Then the toluene was removed by using an evaporator and a white crystalline product was obtained. Yield: 83%, mp: 60-62°C. ^1H NMR ($CDCl_3$, TMS): δ 4.50 (s, 6H, CH_2), 2.45 (s, 9H, CH_3). FT-IR(KBr, ν, cm^{-1}): 2089 ($-N_3$). The reaction for the synthesis of 1, 3, 5-tris(azidomethyl)-2, 4, 6-trimethyl-benzene is shown in Scheme 2.



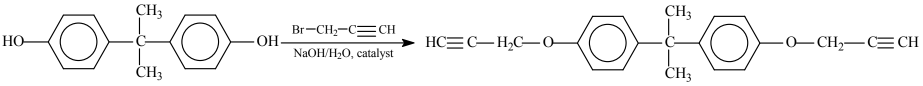
Scheme 1. Synthesis of 1, 3, 5-tris(bromomethyl)-2, 4, 6-trimethyl-benzene



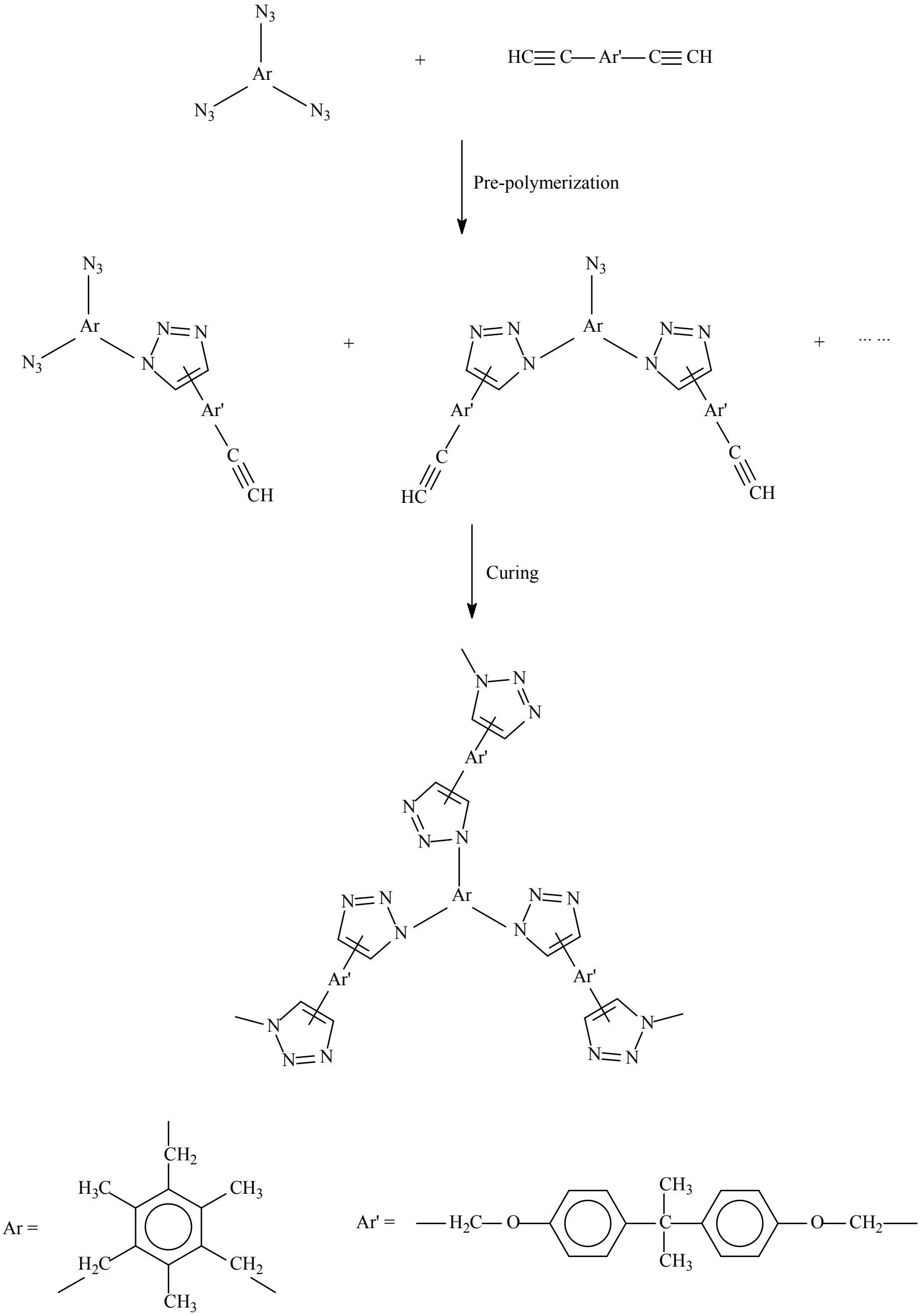
Scheme 2. Synthesis of 1, 3, 5-tris(azidomethyl)-2, 4, 6-trimethyl-benzene

Synthesis of bis propargyl ether of bisphenol A (B_2) [8, 16]

Bisphenol A (0.05 mol), sodium hydroxide (0.15 mol), and benzyltriethylammonium chloride (0.2g) were dissolved in 30 mL deionized water in a three-necked round bottom flask equipped with a condenser, a dropping funnel and a stirrer. To the flask, 0.125 mol propargyl bromide was added dropwise under drastic agitation at 60°C for 2 hours. Then the mixture was kept at this temperature for 6 hours. The product was isolated by pouring the mixture into 1L of deionized water and washed with deionized water several times to remove benzyltriethylammonium chloride and the salt formed during the reaction. The crude product was recrystallized from methanol twice to obtain a pale-yellow crystalline monomer. Yield: 70%. m.p. 79-80°C; ^1H-NMR ($CDCl_3$, TMS) δ: 1.62 (s, 6H, $-CH_3$), 2.50 (tr, 2H, ≡CH), 4.65 (d, 4H, $-CH_2$), 6.86 (m, 4H, -O-Ar-H), 7.15 (m, 4H, -C-Ar-H); FT-IR (KBr): 3286cm^{-1}, 3260cm^{-1}(≡CH), 2110cm^{-1}(C≡C); Elemental analysis for $C_{21}H_{20}O_2$, Found (Calcd) (%): C 82.19 (82.87), H 6.63 (6.62), O 11.18 (10.51). Synthesis of bis propargyl ether of bisphenol A is shown in Scheme 3.



Scheme 3. Synthesis of bis propargyl ether of bisphenol A



Scheme 4. The preparation and curing reaction of A_3B_2 resin

Preparation of a polytriazole resin (A_3B_2)

A_3 and B_2 with the molar ratio of azide group to alkyne group [a]/[b]=1.0:1.0, 1.0:1.1 and 1.0:1.2 were mixed and stirred at 80°C till homogeneous liquid products occurred.

Thus the A_3B_2 resins were obtained. The schematic polymerization of A_3 and B_2 is shown in Scheme 4. Samples of resin castings for flexural property tests were made in following: an obtained liquid resin was poured into a mold. Then the resin with the mold was together put into a vacuum oven for removing air embedded. Thereafter, the resin with the mold was transferred into another oven for being cured at 80°C for 12h. Then, the cured samples with the size of $80\times15\times5$ mm^3 were demolded and were postcured on the following procedure: 120°C/2h + 150°C/2h + 180°C/2h + 200°C/2h. The flexural tests were carried out at room temperature. The cured resins for other analyses were prepared on the same curing procedure as above.

Preparation of a glass fiber reinforced A_3B_2 resin composite

The glass fabric SW-160 was used as a reinforcing material for composites. A_3 and B_2 were weighed and dissolved in acetone ([a]/[b]=1.0:1.2). Then the mixed solution was stirred at 65°C for 3h to get a polytriazole resin solution (50wt%). The glass fabric was impregnated with the solution and dried under air. A prepreg with resin content about 37-38% was obtained and then pressed on a pressure machine under a pressure of 2 MPa at 80°C for 12h. Then the composite laminate was transferred into an oven and postcured at 120°C for 2h, 150°C 2h, 180°C 2h and 200°C 2h. Finally, the composite laminate with resin content of 32% was obtained. The samples with the dimension of $60\times15\times2$ mm^3 for the flexural tests were made of the laminate.

Results and Discussion

Curing behavior of A_3B_2 resin

Figure 1 shows the DSC curve of A_3B_2 resin. As shown in Figure 1, the endothermic peak in the range of 50°C to 70°C is ascribed to the melting peak of the resin. The peak in the range of 80°C to 250°C is attributed to the exothermic peak of the curing reaction for the resin. The exothermic reaction heat of A_3B_2 resin reaches 931 J g^{-1} which is much higher than that of other thermosetting resins like modified bismaleimide resin (398 J g^{-1}) [17] but lower than that of A_3B_4 resin [11]. Thereby,

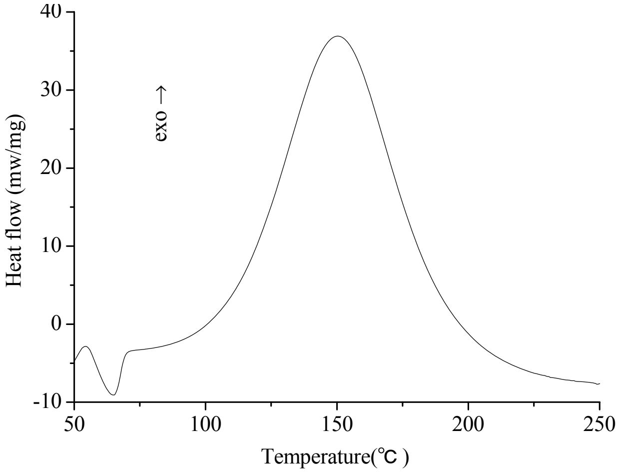


Figure 1. DSC curve of A_3B_2 resin ([a]/[b]=1.0:1.0, heating rate 20°C/min, nitrogen).

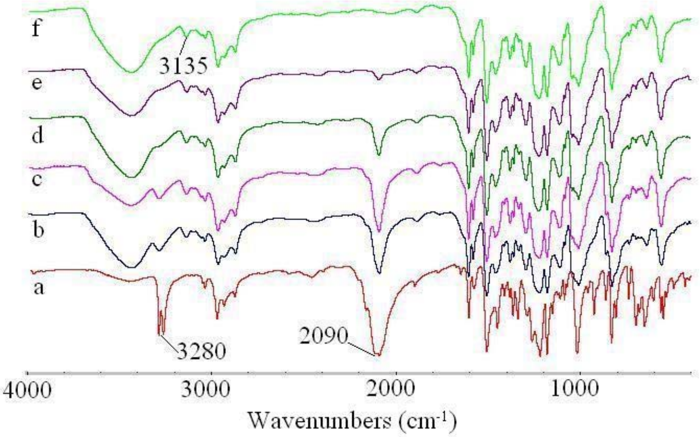


Figure 2. FT-IR spectra of A_3B_2 resin (a) and the resin (b-f) at different stages of curing process: b. 80°C/12h; c. 80°C/12h+120°C/2h; d. 80°C/12h+120°C/2h+150°C/2h; e. 80°C/12h+120°C/2h+150°C/2h+180°C/2h; f. 80°C/12h+120°C/2h+150°C/2h+180°C/2h+200°C/2h ([a]/[b]=1.0:1.0).

the curing reaction of A_3B_2 resin can take place at a temperature in the range of 80°C to 250°C.

FT-IR spectra of A_3B_2 resin at different stages of curing process are shown in Figure 2. As shown in Figure 2, absorption peaks of ≡CH (3280 cm^{-1}) and $-N_3$ (2090 cm^{-1}) decrease gradually for the resin with the increasing of the postcured temperature and time, while the peak at 3135 cm^{-1} occurs for the characteristic absorption of C-H on the triazole ring. This implies that the cycloaddition reaction between azide and alkyne groups had taken place and poly(1, 2, 3-trizaole) had formed [9]. After the resin was cured at 80°C for 12h, 120°C 2h, 150°C 2h, 180°C 2h and 200°C 2h, absorption peaks of ≡CH (3280 cm^{-1}) and $-N_3$ (2090 cm^{-1}) totally disappear, which means that the curing reaction of A_3B_2 resin has completed.

Thermal properties of the cured resin

The DMA curves of the cured A_3B_2 resin with different molar ratio of azide group to alkyne group are shown in Figure 3 and the results are listed in Table 1. As shown in Table 1, the glass transition temperature T_g of the cured resin drops from 216°C to 170°C when the molar ratio of azide group to alkyne group decreases from 1.0:1.0 to 1.0:1.2. When the molar ratio of azide group to alkyne group decreases, the propargyl group increases and becomes excessive. It was reported that the alkyne group would polymerize obviously with itself at the temperature higher than 200°C [18-19]. Therefore the excessive alkyne group would keep un-reacted. There are some freely flexible propargyl group in the formed crosslinking structure. In addition, when the content of B_2 in the cured resin increases, the flexible -O- and $-C(CH_3)_2-$ groups in the resin structure also increase. Therefore, T_g of the cured resin decreases with the increase of alkyne group.

Figure 4 shows thermogravimetric diagrams of the cured A_3B_2 resin under air and nitrogen atmosphere. The thermogravimetric results are tabulated in Table 1. As shown in Figure 4, the decomposition process for the cured resin takes place in one stage under nitrogen but in two stages under air. The decomposition temperature T_{d5}

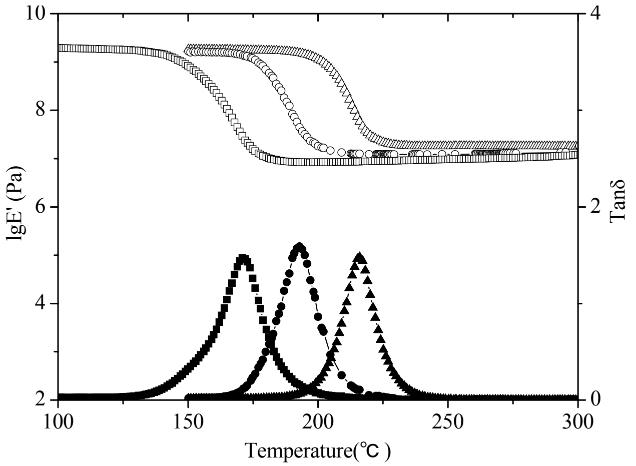


Figure 3. Logarithm of the storage modulus (lgE') and Tanδ as a function of temperature for the cured resins with different molar ratios of azide to alkyne group [a]/[b]=1.0:1.0 (△, ▲); 1.0:1.1 (○, ●); 1.0:1.2 (□, ■).

Table 1. Thermal properties of the polytriazole resins

[a]/[b]	T_g (°C)	T_{d5} (°C)		Residue (%)	
		Air	Nitrogen	Air	Nitrogen
1.0:1.0	216	360	361	32.5	0.7
1.0:1.1	193				
1.0:1.2	170				

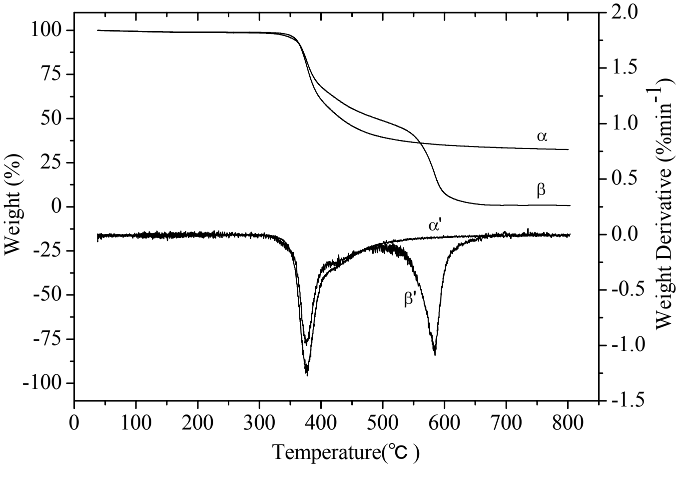


Figure 4. TG and DTG thermograms of the cured resin under nitrogen (α and α') and air (β and β') (heating rate 10°C/min, [a]/[b]=1.0:1.0).

(the temperature of decomposition at 5% weight loss) under air and nitrogen reaches 360°C and 361°C, respectively. Two T_{d5} values are almost the same. This indicates that thermal oxidative decomposition is not a main process for the decomposition of the cured resin in the initial stage and the cleavage of weak bonds in the cured resin should be a main decomposition mechanism [10]. In addition, the weight loss of the cured resin in the range of 400-550°C under air is lower than that under nitrogen. Oxygen might take part in the decomposition reactions of the cured resin. The uptake of oxygen would increase the weight. The decomposition would be faster when the temperature rise further (>550°C).

Mechanical properties of the cured resin

The A_3B_2 resins with different molar ratios of functional groups were prepared. The experimental results for mechanical properties are tabulated in Table 2. As shown in Table 2, when the molar ratio of azide group to alkyne group changes from 1.0:1.0 to 1.0:1.2, the flexural strength and modulus of the cured resins increases a little although the crosslinking density would decrease a bit. With the increase of B_2 in resin, the content of polar oxygen atom increases. This would increase the interaction between molecular segments in the cured resin. As a result, the properties increases slightly. This indicates that the ratio of azide group to alkyne group in the range of 1.0:1.0 and 1.0:1.2 do not affect the mechanical properties of the resins obviously.

Table 2. Mechanical properties of the cured resin

[a]/[b]	Flexural strength (MPa)	Flexural modulus (GPa)
1.0:1.0	168.3±3.9	3.6±0.1
1.0:1.1	183.2±3.9	3.7±0.1
1.0:1.2	183.6±3.6	4.1±0.1

Mechanical properties of a glass fiber reinforced A_3B_2 resin composite

The A_3B_2 resin/glass fiber composite shows excellent mechanical properties. The flexural strength and modulus reach 963.4 MPa and 28.1 GPa, respectively, which is much higher than those of other glass fiber reinforced composites like epoxy/glass fiber composite (735MPa) [20]. This illustrates that the polytriazole resin is an excellent resin matrix for glass fiber reinforced composites.

Figure 5 shows the fractured cross section micrographs of a sample of the polytiazole resin/glass fiber composite. As shown in Figure 5, a rough surface of glass fiber and a few evidence of fiber pullout are observed. The glass fibers are well embedded in the polytriazole resin. This indicates that there is good interface adhesion between the polytriazole resin and glass fibers.

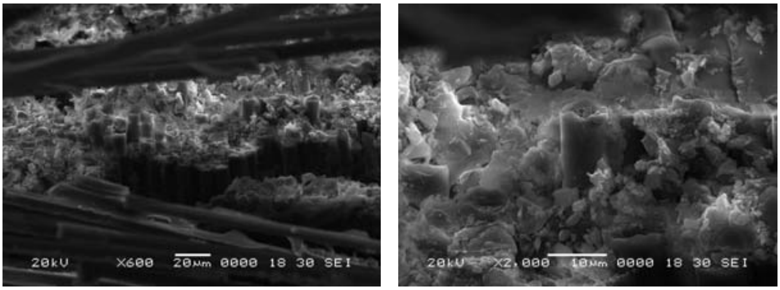


Figure 5. The micrographs of fractured surface of the polytiazole resin/glass fiber composite.

Conclusion

A new polytriazole resin made from a triazide and a dialkyne compounds could be cured at 80°C. The curing process for the resin was traced by FT-IR. The structure of triazole ring is confirmed by FT-IR. The glass transition temperature T_g and the thermal decomposition temperature T_{d5} of the cured resin with [a]/[b]=1.0:1.0 reaches 216°C and 360°C, respectively. DMA results shows T_g of the resin decreases as the molar ratio of azide group to alkyne group dereases. The flexural strength and modulus of the cured resin change a bit with the molar ratio of azide group to alkyne group between 1.0:1.0 and 1.0:1.2 and arrive at 183.6MPa and 4.1GPa. The flexural strength of polytriazole resin/glass fiber composite arrives at 963.4 MPa. The SEM results show that the adhesion between the polytriazole resin and the glass fibers is good. The polytriazole resin would be a potential matrix for advanced composite materials.

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