

Preparation and Properties of a Novel Polytriazole Resin

Liqliang Wan,^{1,2} Yonghong Luo,^{1,2} Lian Xue,^{1,2} Jianjun Tian,^{1,2} Yanhong Hu,^{1,2} Huimin Qi,^{1,2} Xuening Shen,^{1,2} Farong Huang,^{1,2} Lei Du,³ Xiangbao Chen⁴

¹Key Laboratory for Ultrafine, Materials of Ministry of Education, Shanghai, People's Republic of China

²School of Material Science and Engineering, East China University of Science and Technology, Shanghai 200237, People's Republic of China

³Shanghai Bureau of Astronautics, Shanghai 200233, People's Republic of China

⁴Beijing Institute of Aeronautical Materials, Beijing 100095, People's Republic of China

Received 1 March 2006; accepted 2 May 2006

DOI 10.1002/app.24849

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A novel polytriazole resin prepared from *p*-xylylene diazide (XDA) and *N,N,N',N'*-tetrapropargyl-*p,p'*-diaminodiphenylmethane (TPDDM) was synthesized and characterized. The resin is soluble in common solvents like acetone. The results show that the polytriazole resin can be cured at 70°C. The glass transition temperature and thermal decomposition temperature of the cured resin are 218 and 350°C, respectively. The tensile and flexural strengths of the cured resin achieve 99.0 and 200 MPa, respectively.

It is potential as a low cost and easy processing thermal resistant polymer matrix for advanced composite applications. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1038–1042, 2007

Key words: *p*-xylylene diazide; *N,N,N',N'*-tetra propargyl-*p,p'*-diamino diphenyl methane; 1,3-dipolar cycloaddition polymerization; polytriazole resin; low-temperature molding resin; thermally stable polymer

INTRODUCTION

Recently, advanced composites have found wide applications in the field of aviation and aerospace as structural materials. However, the high cost of advanced composites limits their applications. Thus, developing low-cost advanced composites becomes necessary. One approach is to develop low-temperature molding composites to cut down the manufacturing cost through employing cheaper molds and other processing materials.^{1,2} The ACG Corporation (UK) and the Air Tech Corporation (USA) started the exploration of low-temperature molding (LTM) materials in 1970s and had developed a series of LTM products.³

Huisgen 1,3-dipolar cycloaddition is an exergonic fusion process that combines two unsaturated reactants.⁴ This reaction provides fast access to an enormous variety of five-member heterocycles.^{5,6} The cycloaddition of azides and alkynes to give triazoles is arguably the most useful member of this family.⁷ As shown in Scheme 1, the reaction is highly exothermic reaction and usually occurs at low temperatures even at room temperature. In 1960s, Johnson et al. prepared

polytriazoles from 4-azido-1-butyne, 3-azido-1-propyne, 2-propynyl azidoacetate, and *p*-azidophenyl acetylene and characterized their structure and properties.^{8,9} The obtained polytriazoles with low molecular weights are in solid form and are soluble only in conc. H₂SO₄. These polytriazole polymers were not useful as expected. Since then, no further work has been reported. To further explore the potential of polytriazoles, we synthesized a new series of polytriazoles with good processability from diazides or multiazides and alkynes or multialkynes.^{10–13} In this paper, a new diazide and a tetrapropargyl compound were synthesized and used to prepare a novel polytriazole resin with good processability and high performance. The curing reaction and properties of the developed polytriazole resin were characterized.

EXPERIMENTAL

Raw materials

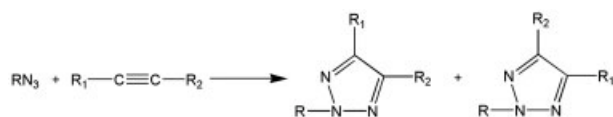
p-Xylylene dichloride and *p,p'*-diamino-diphenylmethane (DDM) were recrystallized from methanol before use. Propargyl bromide was distilled before use. Dimethylformide (analytical reagent grade), benzene (analytical reagent grade), dichloroethane (analytical reagent grade), sodium azide (chemical purity), potassium carbonate (anhydrous, analytical reagent grade), magnesium sulfate (anhydrous, analytical reagent grade), and tetrabutyl-ammonium bromide (analytical reagent grade) were used as received.

Correspondence to: F. Huang (fhuanglab@ecust.edu.cn).

Contract grant sponsor: National High Technology Research and Development Program of China; contract grant number: 2002AA305103.

Contract grant sponsor: National Basic Research Program; contract grant number: 5131101.

Journal of Applied Polymer Science, Vol. 104, 1038–1042 (2007)
© 2007 Wiley Periodicals, Inc.



Scheme 1 1,3-dipolar cycloaddition reaction of azides and alkynes.

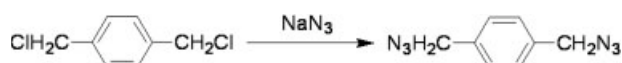
Instrumentation

$^1\text{H-NMR}$ spectrum was recorded on a Bruker Avance 500(500 MHz) nuclear magnetic resonance spectrometer. CDCl_3 was used as the solvent and chemical shifts were reported in ppm. FTIR was performed on a Nicolet 550 and solid samples were pressed into pellets with KBr. Thermal analysis was performed on a differential scanning calorimeter(DSC, Universal V2.3 TA Instruments 2910 modulated system) with the heating rate of $10^\circ\text{C}/\text{min}$. Thermogravimetric analysis(TGA), was conducted on a Mettler TGA/SDTA 851 in nitrogen with the heating rate of $10^\circ\text{C}/\text{min}$. Rheological behavior was traced on a RheoStress RS600 Rheometer with the heating rate of $0.33^\circ\text{C}/\text{min}$, and the shear rate of 0.1 s^{-1} . Dynamic mechanical analysis(DMA) was carried out on a Rheogel-E4000 operating in the tension mode at the temperatures from 30 to 300°C at the frequency of 11 Hz with a programmed heating rate of $3^\circ\text{C}/\text{min}$. The flexural property of the cured resin was measured according to ASTM 790. The sample dimension was $80 \times 15 \times 4\text{ mm}^3$, and the crosshead speed was $2\text{ mm}/\text{min}$. The tensile property was measured according to ASTM 638. Standard dumbbell specimens with a $60 \times 10 \times 4\text{ mm}^3$ neck were made. The flexural and tensile properties were measured with a Shimadzu AG-50kNE universal tester.

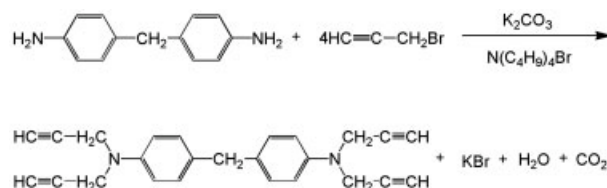
Preparation of polytriazole resin

Synthesis of monomers

p-Xylylene diazide¹⁴. *p*-Xylylene dichloride, XDA (4.38 g; 0.025 mol), sodium azide (6.50 g; 0.100 mol), 20 mL dimethylformide, and 20 mL benzene were added into a three-neck round bottom flask. The reaction mixture was slowly heated to 75°C and kept at this temperature for 6 h. Then it was poured into a beaker with 200 mL deionized water. The organic benzene layer was separated and the aqueous layer was extracted with 20 mL benzene three times. All the benzene layers were combined and dried by anhydrous magnesium sulfate. The benzene was then distilled out and a liquid product of 3.93 g was obtained. Yield: 90%, mp: $27.5\text{--}29.0^\circ\text{C}$; FTIR: 2098 cm^{-1} (azide);



Scheme 2 Synthesis of *p*-xylylene diazide.



Scheme 3 Synthesis of *N,N,N',N'*-tetra propargyl-*p,p'*-diamino diphenyl methane.

$^1\text{H-NMR}$ (CDCl_3 , TMS): δ 7.33 (s, 4H, Ar-H), 4.35 (s, 4H, Ar- CH_2N_3). The reaction was shown in Scheme 2.

N,N,N',N'-Tetra propargyl-*p,p'*-diaminodiphenyl methane¹⁵. DDM (4.90 g; 0.025 mol), anhydrous potassium carbonate (10.35 g; 0.075 mol), 15 g deionized water, 15 g dichloroethane, and 0.40 g tetrabutyl-ammonium bromide were poured into a 250-mL three-neck bottom flask with a nitrogen gas inlet tube. Propargyl bromide (20.80 g; 0.175 mol) was then added dropwise at 70°C within 3 h while stirring intensively. The reaction mixture was continuously stirred at 70°C for 6 h. Thereafter, the dichloroethane layer was separated from aqueous layer and washed with deionized water three times. It was then distilled and the crude solid product was obtained. The product was purified by the recrystallization with 50 mL petroleum ether and then with 50 mL methanol three times. A yellow solid powder of 7.44 g was obtained. Yield: 85%, mp: $50\text{--}51^\circ\text{C}$; FTIR: 3286 cm^{-1} ($\equiv\text{C-H}$), 2110 cm^{-1} ($\text{C}\equiv\text{C}$); $^1\text{H-NMR}$ (CDCl_3 , TMS): δ 2.20 (s, 4H, $\equiv\text{CH}$), 3.80 (s, 2H, Ar- $\text{CH}_2\text{-Ar}$), 4.10 (d, 8H, $\text{CH}_2\text{-C}\equiv\text{C}$), 6.80 (d, 4H, N-Ar-H), 7.10 (d, 4H, $\text{CH}_2\text{-Ar-H}$). The synthetic reaction was shown in Scheme 3.

Synthesis of polytriazole resins

The monomers, XDA and TPDDM, well-proportioned with the molar ratio of 2.0 : 1.0, were mixed in a 250-mL

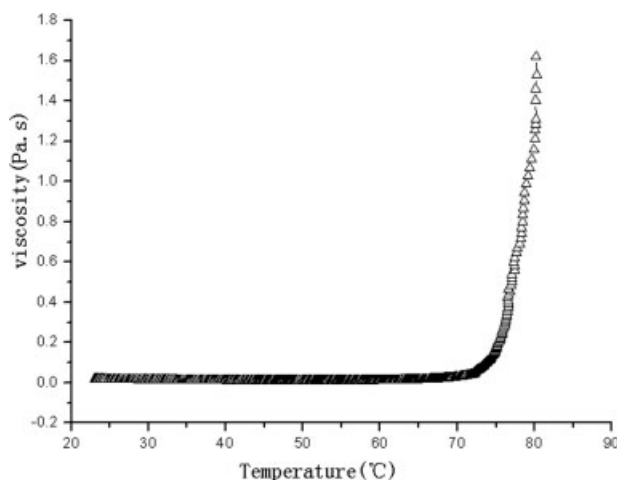


Figure 1 Viscosity of the polytriazole resin against temperature (heating rate $0.33^\circ\text{C}/\text{min}$).

TABLE I
Solubility of the Polytriazole Resin

Solvent	Solubility	Solvent	Solubility
Ethyl Ether	×	Toluene	+
Ethyl acetate	×	Chloroform	+
Petroleum ether	×	Dichloromethane	+
Ethanol	×	1,2-Dichloroethane	+
Tetrahydrofuran	+	Dimethylacetamide	+
Methyl Ethyl Ketone	+	Dimethyl sulfoxide	+
acetone	+	Dimethylformide	+

+, soluble; ×, insoluble.

three-neck bottom flask equipped with a stirrer, a cooling condenser, and a thermometer. The monomer mixture was heated with an oil bath to 50°C, and stirred continuously at 50°C for 10 min. A transparent and viscous liquid polytriazole resin was obtained.

Sample preparation

The polytriazole resin prepared above was poured into an aluminum pan or a mold and then the pan or mold was put into a vacuum oven for curing. The polytriazole resin was heated to 70°C and cured at 70°C for 12 h. Thereafter, the solid samples were demolded and were postcured at: 120, 150, 180, and 200°C each for 2 h. The obtained cured polytriazole samples were used for subsequent property characterization.

RESULTS AND DISCUSSION

The properties of polytriazole resin

Rheology

The polytriazole resin prepared from XDA and TPDDM is a homogenous and transparent yellow liquid at room temperature. Rheology of the resin was measured by a rheometer. The viscosity response of

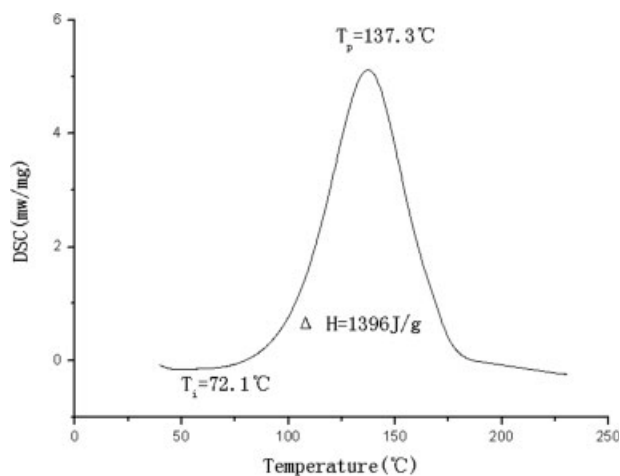


Figure 2 DSC trace of the polytriazole resin (heating rate 10°C/min N²).

the resin to the temperature ramping at heating rate of 0.33°C/min was shown in Figure 1. The results show that the resin viscosity is low at the low-temperature region (< 70°C). The low resin viscosity was suitable for composite fabrication. On the other hand, resin viscosity starts to rapid increase around 73°C, indicating that the 1,3-dipolar cycloaddition polymerization of the resin can take place at about 73°C and the rate of polymerization increases quickly with further increase in the temperature.

Solubility

The solubility of the polytriazole resin was shown in Table I. The resin can be dissolved in many common solvents, such as acetone, methyl ethyl ketone, etc. The viscosity of the resin solution in acetone was not changed for 2 months at room temperature (25°C). This solution can be directly used to prepare the prepreg for composite fabrication.

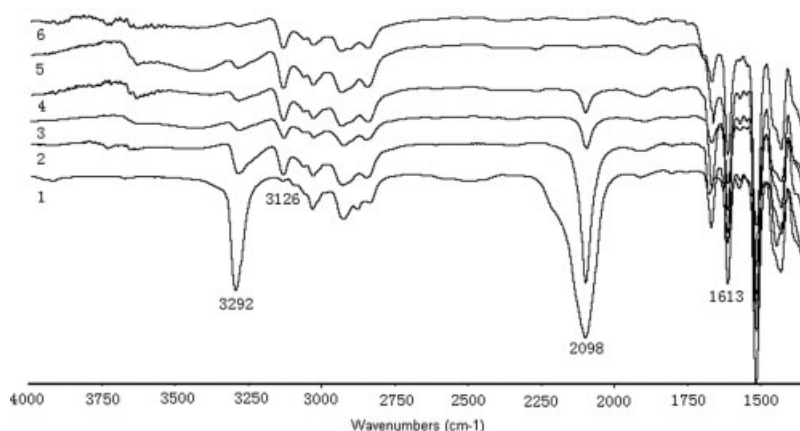


Figure 3 FTIR spectra of the resin at different stages of the curing: 1. at beginning; 2. 70°C/12 h; 3. 70°C/12 h + 120°C/2 h; 4. 70°C/12 h + 120°C/2 h + 150°C/2 h; 5. 70°C/12 h + 120°C/2 h + 150°C/2 h + 180°C/2 h; 6. 70°C/12 h + 120°C/2 h + 150°C/2 h + 180°C/2 h + 200°C/2 h.

TABLE II
FTIR Analysis Results of the Specimens at Different Stages of the Curing

The stage of the curing	Area of the peak (<i>a</i>) at 2098 cm ⁻¹ /that of 1613 cm ⁻¹	Degree of cure (<i>p</i>) (%)
At beginning	12.25	0
70°C/12 h	3.04	75.2
70°C/12 h + 120°C/2 h	1.13	90.8
70°C/12 h + 120°C/2 h + 150°C/2 h	0.37	96.9

Curing behavior

1,3-Dipolar cycloaddition of azide and propargyl groups in the resin was traced by DSC technique. As shown in Figure 2, the initial and peak temperature of the exothermal peak corresponding to the 1,3-dipolar cycloaddition of the resin are 72 and 137.3°C, respectively. The exothermic heat is 1396 J/g. These results indicate that the cycloaddition polymerization take place at about 72°C and is highly exothermic. Thereby, the curing rate should be controlled to avoid the violent polymerization, i.e., the curing heat should be dissipated during curing. For this reason, the initial curing of the resin is better carried out at the temperature of 70°C for a long period of time so that most active groups of monomers would react with each other before the curing continued at higher temperature.

The curing behavior of the polytriazole resin can also be characterized by fourier transform infrared (FTIR) spectroscopy. The FTIR spectra of the resin at different polymerization stages were shown in Figure 3. The characteristic peak at 3292 cm⁻¹ is the absorption of the alkynes(≡C—H) and the peak at 2098 cm⁻¹ corresponds to the absorption of azides(—N=N=N) and alkynes(C≡C). As shown in the Figure 3, the two absorption peaks at 3292 and 2098 cm⁻¹ decrease as the reaction proceeds, clearly showing the gradual consumption of the reactive groups of the cycloaddition reaction. In addition, a new absorption peak at 3126 cm⁻¹ occurred, which was attributed to C—H of triazole ring formed during the polymerization. After the resin was kept at 200°C for 2 h, the absorption peaks at 2098 and 3292 cm⁻¹ nearly disappeared, indicating that all the alkyne and azide groups have taken part in the cycloaddition polymerization.

TABLE III
The Glass Transition Temperature *T_g* of the Cured Products at Different Stages of the Curing

The stage of the curing	<i>T_g</i> of the cured product (°C)
70°C/12 h	119
70°C/12 h + 120°C/2 h	169
70°C/12 h + 120°C/2 h + 150°C/2 h	185
70°C/12 h + 120°C/2 h + 150°C/2 h + 180°C/2 h	218
70°C/12 h + 120°C/2 h + 150°C/2 h + 180°C/2 h + 200°C/2 h	218

FTIR technique can also be used to quantitatively study the curing behavior of the polytriazole resin. The benzene ring absorption peak at 1613 cm⁻¹ was chosen as the internal standard and the azido and propargyl absorption peak at 2098 cm⁻¹ as the variable. The degree of cure was calculated based on the following eq (1):

$$p = 1 - (a_t/a_0) \quad (1)$$

where *a_t* is the ratio of the area of the peak at 2098 cm⁻¹ to the area of peak at 1613 cm⁻¹ at the time *t* and *a₀* is the same ratio at the beginning. As shown in Table II, after the resin reacted for 12 h at 70°C, the degree of curing reached 75.2%. The degree of curing increased with increasing the postcuring temperature. When the resin postcured 150°C for 2 h, the degree of curing reached 96.9%. When further postcuring at 180°C for 2h, the curing reaction was nearly completed.

Properties of the cured polytriazole resin

Glass transition temperature (*T_g*)

Dynamic mechanical analysis (DMA) of the cured polytriazole was carried out under N₂ atmosphere. As shown in Table III, *T_g* of the cured resin increased with increasing the postcuring temperature and reached 218°C, when it was postcured at 180°C for 2 h. When further increasing postcuring temperature to 200°C for

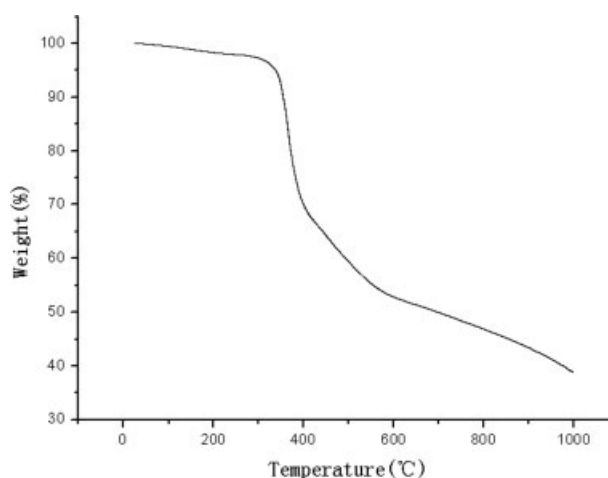


Figure 4 TGA of the cured resin(heating rate 10°C/min, N₂).

TABLE IV
The Mechanical Properties of the Cured Polytriazole Resin

Tensile strength (MPa)	Tensile modulus (GPa)	Tensile elongation (%)	Flexural strength (MPa)	Flexural modulus (GPa)
99.0	3.60	3.49	200	3.34

2 h, the T_g of the cured resin did not increased further. These results suggest that the suitable postcuring temperatures are 180–200°C to achieve complete cycloaddition.

Thermal stability

The thermal stability of the cured polytriazole resin was determined by TGA. As shown in Figure 4, the thermal decomposition temperature (T_d) of the cured resin arrived at 350°C, showing the good stability of the cured resin. The thermal stability of the cured resin is higher than that of universal epoxy resins and equivalent to that of high performance and some modified BMI resins. However, the degradation temperature of the cured resin is inferior to that of most BMI resins.

Mechanical properties

The mechanical properties of the cured polytriazole resin are listed in Table IV. As shown in the Table IV, the resin has excellent mechanical properties. The tensile and flexural strengths of the polytriazole resin reach 99.0 and 200 MPa, respectively. These property values are higher than those of most thermally cured resins, such as epoxy resins, BMI resins, PMR resins, etc.

CONCLUSIONS

A novel polytriazole resin was obtained by the 1,3-dipolar cycloaddition reaction between XDA and TPDDM. DSC, FTIR, and rheological studies show that

the curing reaction of the polytriazole resin can take place at about 70°C. The resin viscosity is low at room temperature and the resin is soluble in common solvents. The T_g and the T_d of the cured resin are 218 and 350°C, respectively. The cured resin possesses excellent mechanical properties and the corresponding tensile and flexural strengths are 99.0 and 200 MPa, respectively. The developed polytriazole resin is potential for low-temperature molding composite applications.

References

- Doerner, F. J.; Smith, R. M. 41st International Society for the Advancement of Materials and Process Engineering Symposium/ Exhibiton; 1996; p 35.
- Ridgard, C. 41st International Society for the Advancement of Materials and Process Engineering Symposium/Exhibiton; 1996; p 147.
- Ridgard, C. 8th International Conference of the Society for the Advancement of Materials and Process Engineering; 1987; p 18.
- Huisgen, R. 1, 3-Dipolar Cycloaddition Chemistry; Padwa, A., Ed.; Wiley: New York, 1984; Chapter 1, p 1.
- Fan, W. Q.; Comprehensive Heterocyclic Chemistry; Pergamon: Oxford, 1996; Vol. 4, p 101.
- Banert, K. Chem Ber 1989, 122, 911.
- Huisgen, R. Pure Appl Chem 1989, 61, 613.
- Johson, K. E.; Lovinger, J. A.; Parker, C. O.; Baldwin, M. G. J Polym Sci Part B: Polym Lett 1966, 4, 977.
- Baldwin, M. G.; Johson, K. E.; Lovinger, J. A.; Parker, C. O. J Polym Sci Part B: Polym Lett 1967, 5, 803.
- Wan, L. Q.; Hu, Y. H.; Luo, Y. H.; Rong, Z. X.; Zhou, W.; Huang, F. R.; Qi, H. M.; Du, L. In Proceeding of 13th National Conference Composite Materials of China; Chengdu, China, 2004; p 327.
- Luo, Y. H.; Hu, Y. H.; Wan, L. Q.; Zhou, W.; Huang, F. R. In Proceeding of 13th National Conference Composite Materials of China; Chengdu, China, 2004; p 355.
- Hu, Y. H.; Luo, Y. H.; Wan, L. Q.; Qi, H. M.; Huang, F. R. Acta Polym Sinica 2005, 560.
- Luo, Y. H.; Hu, Y. H.; Wan, L. Q.; Xue, L.; Huang, F. R.; Shen, X. N.; Qi, H. M.; Du, L. Chem J Chin Univ 2006, 27, 170.
- Armiger, H.; James, D. J Am Chem Soc 1957, 79, 3491.
- Inbasekaran M, N.; Dirlikov, K. S. U.S. Pat. 4,885,403 (1989).