

Effect of the Crosslink Functionality on the Mechanical Properties of Crosslinked 1,2,3-Triazole Polymers as Potential Binders for Rocket Propellants

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ABSTRACT: The mechanical properties of crosslinked polymers depend on their structural features, one of which is the functionality of the crosslinks in a polymer network. To study the effect of crosslink functionality (Φ) on the mechanical properties of 1,2,3-triazole polymers for potential application as rocket propellant binders, crosslinkers with different Φ 's (3, 4, 6, 16, 32, and 64) were used in the polymerization. As the percentage of acetylenic groups provided by crosslinker was kept constant and the functionality of the crosslinker increased, the resulting polymer

showed a higher modulus but a lower strain. Compared to traditional polyurethane binders, 1,2,3-triazole polymers showed comparable mechanical properties, although the stress and modulus tended to be lower and the strain capability tended to be greater for the triazole-linked rubbers. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 473–478, 2010

Key words: crosslinking; mechanical properties; modulus; polyurethanes; strain

INTRODUCTION

Crosslinked polymers are widely used in the biological sciences, synthetic chemistry, the elastomer industry, and generally in new materials development. The properties of such materials strongly depend on the crosslink density in the network or, analogously at the molecular scale, on the average molecular weight between junction points.^{1,2} The relationship between crosslink density and mechanical properties has been studied extensively for various polymers, such as polyurethanes,³ hydrogels,^{4,5} and acrylate networks.^{6,7} In contrast, fewer studies have been conducted on the dependence of the elastomeric properties of a network, that is, the elastic modulus or elongation, on the functionality of its junction points. One of the few such studies was the pioneering work by Mark and coworkers,^{8–11} who did a series of studies on the effect of the crosslink functionality (Φ) on the elas-

tomeric properties of end-linked polydimethylsiloxane. Their experimental results were in agreement with Flory's theory.

The 1,3-dipolar cycloaddition of azides and acetylenes, the model reaction of click chemistry, has drawn increasing attention from researchers because of its mild reaction conditions, compatibility with different functional groups, excellent chemoselectivity and stereoselectivity, reliable procedures for the preparation of reactants, and stable, low-toxicity precursors (i.e., no isocyanates).^{12–14} The 1,2,3-triazole heterocycles themselves show unique chemical, biological, and electronic properties and could be applied in synthetic chemistry, pharmaceutical chemistry, and material science.¹⁵ To date, the work on triazole polymers has focused mainly on polymer synthesis rather than on characterization. The relationship between the structures of triazole polymers and their mechanical properties has not been systematically studied.^{12–14,16,17} In this study, we used a good and flexible methodology to systematically vary the Φ of crosslinks and monitor the effect of these changes on the tensile properties.

Recently, 1,2,3-triazole polymers have been studied as novel binders for high-energy explosive and propellant materials to replace traditional urethane-based binders. This is because polyurethanes and

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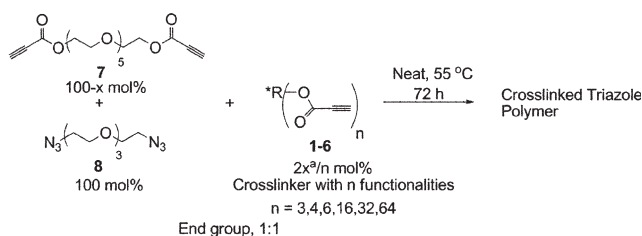
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their curatives are susceptible to undesirable side reactions, which can decrease the mechanical properties of the binders, and have poor compatibility with some of the high-energy ingredients in propellant formulations.^{18–21} The original thrust of this research into triazole curing for polymers was that the curing itself was robust and appeared to proceed in the presence of chemical compounds that tended to interfere with state-of-the-art urethane curing. At that time, we expected that new high-energy materials would become available, some of which, such as hydrazine nitroform, might be incompatible with the polyisocyanates used in the urethane curing reaction. Thus, this triazole cure was developed as an alternate binder linkage for composite solid propellants. As part of our continuing efforts in the development of novel rocket propellant binders with 1,3-dipolar cycloaddition,^{20,22} we report herein the preparation of crosslinked triazole polymers with excellent mechanical properties in one step under extremely mild conditions without any heavy-metal catalyst. In particular, the effects of Φ on the mechanical properties in terms of the strain (percentage elongation at break) and elastic modulus were studied. The mechanical properties of the resulting polymers were comparable to those of polyurethanes. However, the stress tended to be lower and the strain capability tended to be higher in triazole-linked polymers than in urethane-linked polymers, although the backbones of the prepolymers were otherwise the same.

EXPERIMENTAL

Materials

Commercially obtained reagents were used without further purification. Boltorn series H20, H30, and H40 polyols were supplied by Perstorp AB (Perstorp, Sweden). Monomers **7** and **8** were prepared following procedures reported elsewhere (see Scheme 1, presented later, for the compounds).²⁰ Solvents were distilled by standard methods. ¹³C-NMR and ¹H-NMR spectra were recorded at 75 and



Scheme 1 Preparation of the triazole polymers with different crosslinkers. $^a x$ = Number of acetylene groups provided by crosslinker/Total number of acetylene groups provided by the crosslinker and diacetylene.

300 MHz with tetramethylsilane as an internal standard. Elemental analysis was performed by the analytical laboratory, Department of Chemistry, University of Florida. In view of the stringent stoichiometry requirements for step polymerization, the monomers were systematically dried by azeotropic distillation and lyophilization. The uniaxial test specimen was a standard microtensile dog bone with dimensions of $0.88 \times 0.19 \times 0.13$ in.²³ Strain (percentage elongation at break) and elastic modulus (Young's modulus) were measured by an Instron universal tensile testing machine (model number 4301) (Instron Worldwide Headquarters, Norwood, MA) with a strain rate of 50 mm/min.²²

General procedure for the preparation of end-functionality propiolates (crosslinkers)

A mixture of polyol ($\Phi = 3, 4, 6, 16, 32, \text{ or } 64$), propiolic acid (1.4 equiv), and *p*-toluenesulfonic acid (10 wt %) in benzene (70 mL) were heated to reflux through a Dean–Stark apparatus for 2–8 days. The course of the reaction was monitored by ¹H-NMR. The reaction mixture was concentrated *in vacuo*, and the residue was diluted with ethyl acetate, neutralized with saturated sodium bicarbonate, and washed with brine. The organic layer was separated, dried over Na_2SO_4 , filtered and concentrated *in vacuo* to yield propiolates **1–6** (Fig. 1). Among all of the propiolates (crosslinkers) synthesized, compound **3** was novel, and we now report the characterization data of that compound, dipentaerythritol hexapropiolate (**3**; yield = 84%):

Pale yellow solid (recrystallized from ether/hexane). mp = 70–75°C. ¹H-NMR (300 MHz, CDCl_3 , δ , ppm): 2.85 (s, 6H), 3.40 (s, 4H), 4.15 (s, 12H). ¹³C-NMR (75 MHz, CDCl_3 , δ , ppm): 42.8, 63.7, 69.3, 73.9, 76.0, 151.9. Anal. Calcd for $\text{C}_{28}\text{H}_{22}\text{O}_{13}$: C, 59.37%; H, 3.91%. Found: C, 59.03%; H, 3.89%.

General procedures for the preparation of the crosslinked triazole polymers

In an aluminum pan, diacetylene (**7**) was weighed, and different concentrations of crosslinker (**1–6**) were added and stirred until it dissolved. The time for dissolution of the crosslinker varied from 30 min to 3 h with increasing Φ . This was followed by the addition of diazide (**8**), which, on stirring, gave a homogeneous mixture. We carried out the reactions on a total scale of 2 g (including the three reactants for each dog-bone sample) in aluminum pans by taking 100 mol % of **8** and calculating the concentrations of **7** and the crosslinker (**1–6**) accordingly, as shown in Scheme 1, keeping the overall end group stoichiometric ratios at 1 : 1. The mixtures were cast into dog-bone molds. The cast mixtures were

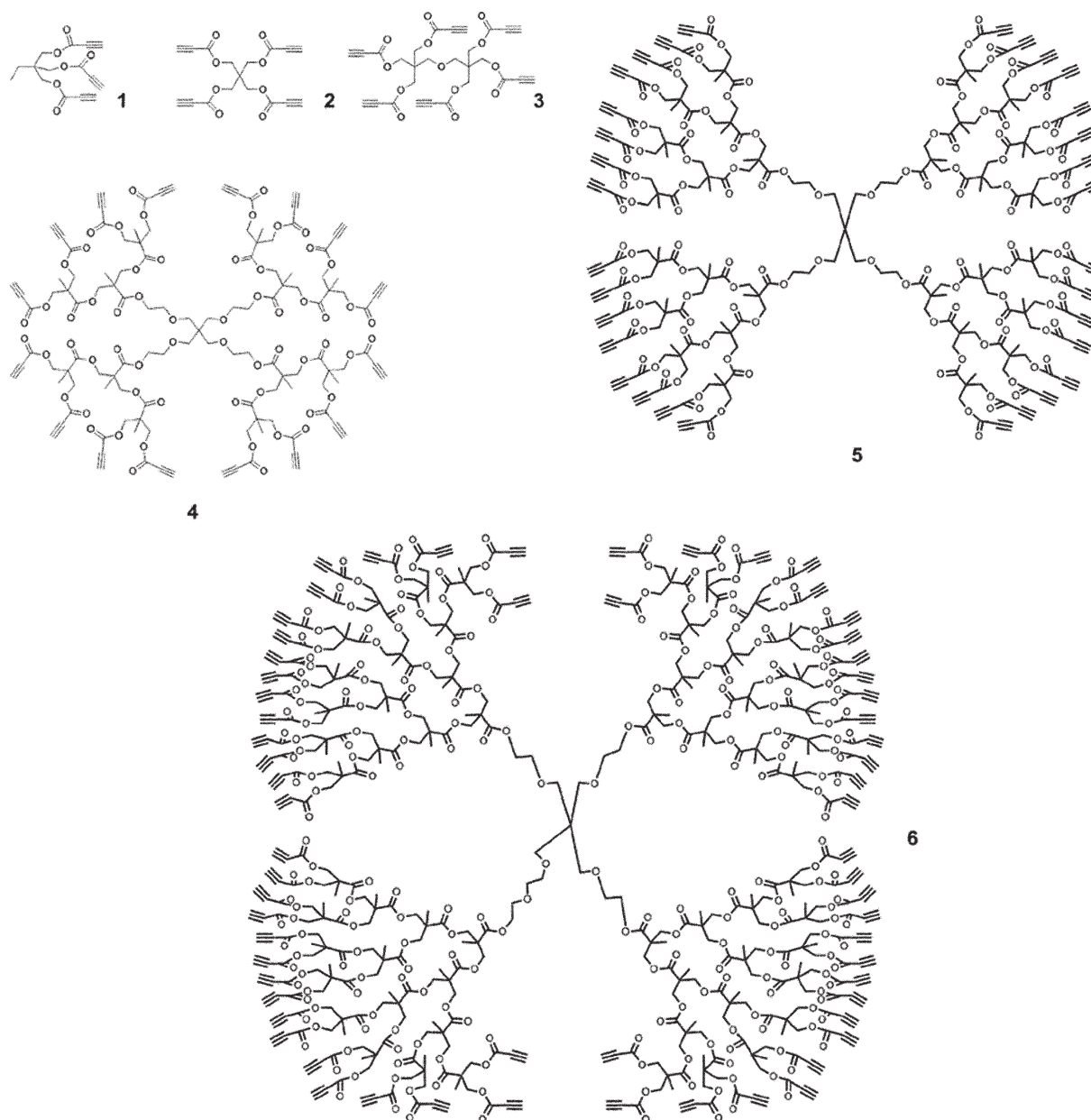


Figure 1 Crosslinkers with different Φ 's: 3, 4, 6, 16, 32, and 64.

degassed *in vacuo* at room temperature for 15 min and left at room temperature for 3–4 h. The curing was then done in a vacuum oven at 55°C for 72 h. The dog-bone samples were carefully removed from the mold. After they cooled, they were tested with the Instron universal tensile testing machine with a 20-lb load cell and a 50 mm/min test speed.

RESULTS AND DISCUSSIONS

In our earlier studies,^{20,22,24} we mainly focused on the synthesis of crosslinked triazole polymers by selecting the reaction between E300 dipropiolate (7) and diazide of tetraethylene glycol (8) as a model reaction with a tetrapropiolate-functionalized

crosslinker ($\Phi = 4$). These investigations showed that the modulus of both unfilled and aluminum-filled polymers increased whereas the elasticity decreased with increasing percentage crosslinker.²² Following the same lines, in this article, we concentrate to further study the effect of Φ on the mechanical properties of the resulting crosslinked triazole polymers. For this purpose, we prepared hyperbranched and dendritic crosslinkers with increasing Φ 's (3, 4, 6, 16, 32, and 64; Fig. 1) from their corresponding polyols following the standard methods.²⁴

The strain and modulus values obtained by variation of the concentrations of the crosslinker, with the overall end group stoichiometric ratios kept at 1 : 1, are listed in Table I. The variation in trends of the

TABLE I
Strain and Modulus Values of Crosslinked Triazole
Polymers with Different Φ 's

Entry	Φ	Diacetylene 7 (mol %)	x (mol %)	Modulus (MPa) ^a	Strain (%) ^b
1	3	68	32	0.87	113
2		64	36	1.14	99
3		60	40	1.36	92
4		56	44	2.01	71
5		52	48	2.04	66
6		48	52	2.16	78
7	4	88	12	0.18	488
8		84	16	0.43	207
9		80	20	0.72	166
10		76	24	1.20	116
11		72	28	1.57	85
12		68	32	1.99	65
13	6	88	12	0.29	298
14		84	16	0.61	171
15		80	20	0.97	128
16		76	24	1.69	82
17		72	28	2.03	88
18		68	32	2.73	72
19	16	92	8	0.17	270
20		88	12	0.47	155
21		84	16	0.48	108
22		80	20	0.82	73
23		76	24	0.90	74
24	32	92	8	0.064	269
25		88	12	0.21	124
26		84	16	0.38	95
27		80	20	0.51	75
28		76	24	0.98	59
29	64	92	8	0.074	242
30		88	12	0.18	126
31		84	16	0.46	89
32		80	20	0.57	77

^a Elastic modulus or Young's modulus.

^b Percentage elongation at break.

strain and modulus with increasing concentrations of crosslinkers with different functionalities are illustrated in Figures 2 and 3.

As expected, for each crosslinker, as the concentration increased, the strain decreased, whereas modulus increased via a subsequent increase in crosslink density, which was consistent with our previous studies.²² Figure 4 compares the stress-strain curves of the crosslinked triazole polymers for one specific example with $x = 32$ mol %, where x is the percentage of acetylenic groups provided by the crosslinker, for the trifunctionalized, tetrafunctionalized, and hexafunctionalized crosslinkers used.

With x kept constant, polymers containing more functionalized crosslinker showed a higher modulus but a lower strain. For example, at 68 mol % diacetylene ($x = 32$ mol %), as Φ increased from 3 to 6, the corresponding modulus of the resulting triazole polymers also increased from 0.87 to 2.73 MPa, whereas the failure strain decreased from 113 to 72%, respectively (Table I, Fig. 4). Junctions of higher

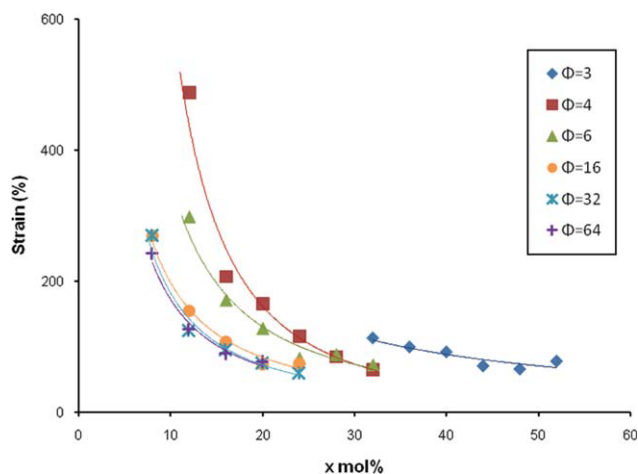


Figure 2 Effect of Φ on the strain of the triazole polymers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

functionality will be more firmly embedded within a polymer network. With higher Φ , more polymer chains extend from each crosslink, which should also introduce more entanglements and steric hindrance. Therefore, such networks should be stiffer and less flexible and thus have a higher modulus and lower strain.⁸ However, for the crosslinkers with higher average functionalities of 16, 32, and 64 end groups (4, 5, and 6), such trends were not obvious. In fact, the modulus versus functionality appeared to level off. The falling off of the stress despite the continuing increase in the number of functions in the dendrimeric curatives suggested that the ends of the polymers were having trouble to be fully end capped in polymer framework. However, higher concentrations of the trifunctional and tetrafunctional curatives always increased the stress,

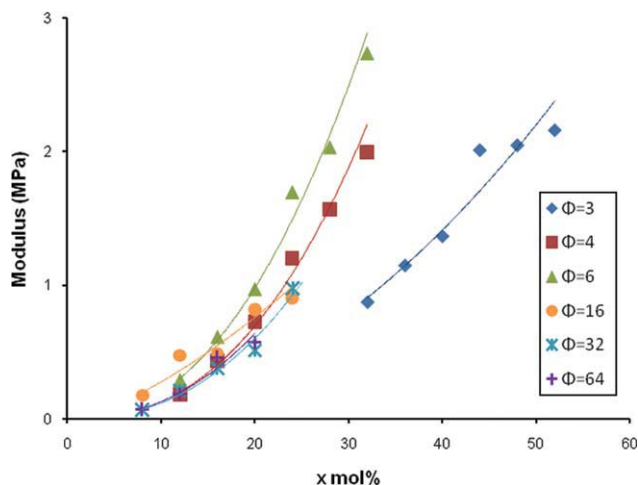


Figure 3 Effect of Φ on the modulus of the triazole polymers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

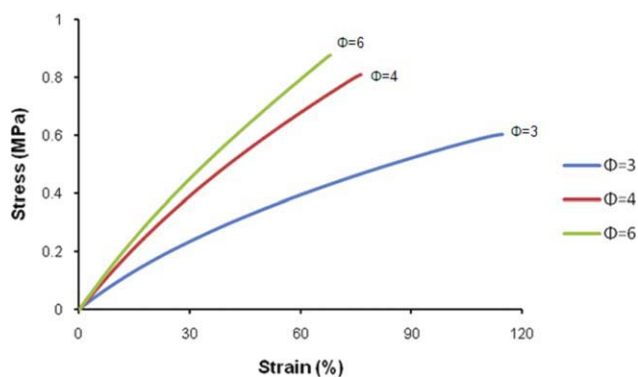


Figure 4 Stress-strain curves of the polymers with different Φ 's ($x = 32$ mol %). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

to the extent, on occasion, of brittleness, and decreased the strain accordingly.

This behavior may be explained by the following reasons. Qualitatively, one might imagine the effect of dendrimer-shaped junction points on the mechanical properties as being limited by the number of nearest neighbors possible in a close-packed arrangement, which would maximize near the 14 possible neighbors of a face-centered cubic structure (Fig. 5). Quantitatively, Barr-Howell and Peppas²⁵ established a modified theoretical model for the determination of the average molecular weight between crosslinks (M_c) of highly crosslinked polymers that also includes functionality. M_c showed a strong dependence on the junction functionality (Φ). As Φ increased from 2 to 20, M_c underwent the greatest variation near $\Phi = 4$. M_c leveled off when Φ was increased further. In addition, the highest Φ could have introduced possible steric difficulties in terms of many chains terminating within a relatively small volume, which may have caused an incomplete

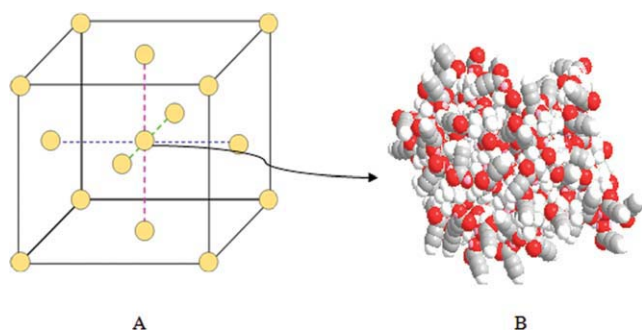


Figure 5 Schematic view of multifunctional crosslinkers arranged in a face-centered cubic arrangement. (A) Multifunctional crosslinkers are arranged in face-centered cubic arrangement. This arrangement gives the maximum number of nearest neighbors, which is equal to 14. This is in qualitative agreement with the observed mechanical properties. (B) The spherical structure of the crosslinker Boltorn H40 ($\Phi = 64$). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

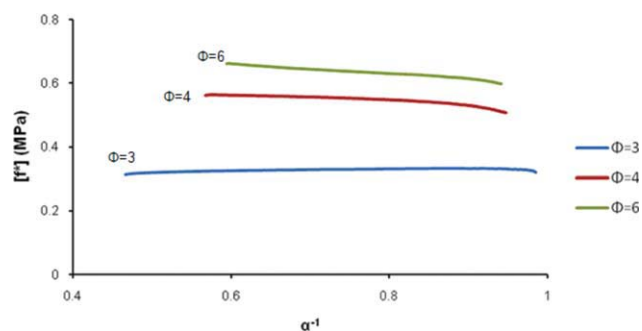


Figure 6 Stress-strain isotherms for the triazole polymers with different Φ 's ($x = 32$ mol %). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

end-link reaction during the polymerization.⁸ Also, the crosslinkers (4, 5, and 6) were derived from commercial available Boltorn polyols, which were, of course, mixtures of highly branched polymers, and the functionality was an average value. All of these factors may have contributed to the uncertainty of the variation trends of strain and modulus observed in our triazole polymers at Φ values higher than 6.

Figure 6 is the plot of the reduced stress ($[f^*]$) versus the reciprocal elongation (α^{-1}). $[f^*]$ is defined as $f/[A(\alpha - \alpha^{-2})]$, where f is the equilibrium elastic force, A is the undeformed cross-sectional area, $\alpha = L/L_i$ is the elongation or relative length of the sample, L is the stretched length, and L_i is initial length.^{8,26} These plots were based on the Mooney-Rivlin equation: $[f^*] = 2C_1 + 2C_2 \alpha^{-1}$ (where $2C_1$ and $2C_2$ are constants independent of α).^{27,28} According to the Flory theory of rubberlike elasticity, $2C_1$, which is the intercept of the plots in Figure 6,

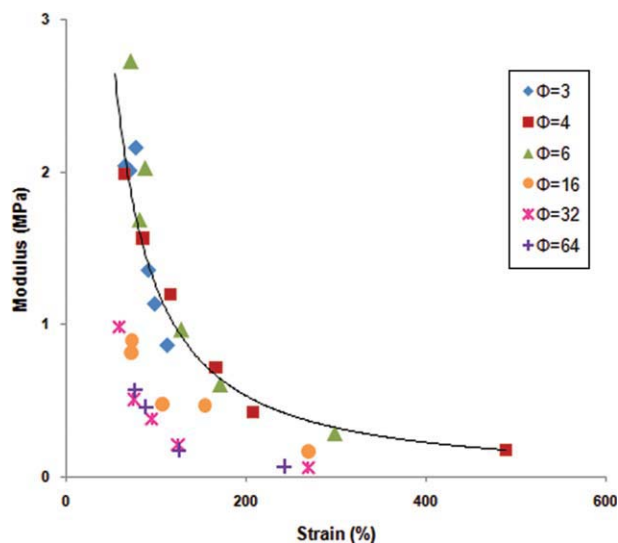


Figure 7 Strain at failure-modulus curves for triazole polymers with different Φ 's: 3, 4, 6, 16, 32, and 64. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

should increase with increasing Φ .⁸ As shown in Figure 6, the stress–strain isotherms for the triazole polymers with Φ values of 3, 4, and 6 were consistent with the Flory theory.

Figure 7 is the plot of strain to failure as a function of the modulus. As the functionality of the crosslinker decreased, the modulus decreased, and the failure strain increased.⁶

CONCLUSIONS

A series of crosslinked triazole polymers were prepared without any catalyst under controlled conditions at 55°C. Compared to the preparation of polyurethanes,¹⁹ both the starting materials and resulting triazole polymers were stable. The effects of Φ on the mechanical properties of the crosslinked triazole polymers were studied systematically. At the same stoichiometry of overall acetylene functionality provided by different crosslinkers (x), higher junction functionality polymers showed lower strain and higher modulus, although the mechanical properties changed much less at functionalities higher than 6. Triazole polymers with mechanical properties suitable for potential rocket propellants could be obtained by the selection of an appropriate crosslinker and the adjustment of the crosslinker concentration with the ratio of azide to acetylene groups kept at 1 : 1 during the polymerization. Compared with the excellent mechanical properties of polyurethane as rocket propellant binders, triazole polymers may obtain comparable or superior mechanical properties.²² In addition, these non-hydrogen-bonded triazole polymers that are weak basic polymers and possess different physical properties than polyurethanes may be more compatible with other high-energy ingredients in rocket propellants. Thus, the triazole polymers described here show promise for applications as rocket propellant binders on basis of their ability to cure in the presence of reactive formulation ingredients and the relative stability of the triazole ring to environmental conditions such as the presence of water.

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