

EFFECTS OF CROSSLINKER AND FILLER ON THE MECHANICAL PROPERTIES OF  
1,2,3-TRIAZOLE-POLYMERS AS POTENTIAL ROCKET PROPELLANT BINDERS

By

LING WANG

A THESIS PRESENTED TO THE GRADUATE SCHOOL  
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT  
OF THE REQUIREMENTS FOR THE DEGREE OF  
MASTER OF SCIENCE

UNIVERSITY OF FLORIDA  
2009

© 2009 Ling Wang

To my family

## ACKNOWLEDGMENTS

First, I would like to thank my advisor Randolph. S. Duran for his support and guidance through the past few years. My thanks also go to Dr. Alan R. Katritzky and my group members for NAVY project: especially Yuming Song, Reena Gyanda, and Rajeev Sakhuja for their kindness and helpful discussion. I also thank Dr. David A. Ciaramitaro and Dr. Clifford D. Bedford for their help and guidance. I also appreciate the help from Dr. Anthony B. Brennan's group in Materials Science and Engineering department, especially Dave Jackson, for helping me run mechanical tests. In addition, I would like to thank all the group members in Duran's group for their support.

Lastly, I wish to thank my parents and my husband for their selfless love. They never stopped encouraging and supporting me during my most difficult times.

## TABLE OF CONTENTS

	<u>page</u>
ACKNOWLEDGMENTS.....	4
LIST OF TABLES.....	7
LIST OF FIGURES .....	8
ABSTRACT .....	11
<b>CHAPTER</b>	
1    INTRODUCTION.....	12
Solid Composite Propellant Binders .....	12
Triazole polymers.....	13
Factors that affect mechanical properties of rocket propellants.....	16
Effect of filler.....	16
Effect of crosslinking of binder .....	20
Thesis overview.....	24
2    EXPERIMENTAL AND OPTIMIZATION OF POLYMERIZATION .....	25
Experimental.....	25
General .....	25
Method of manual testing strain and modulus.....	26
General procedures for preparation of unfilled linear triazole polymer mini samples....	26
General procedures for preparation of crosslinked triazole polymer mini samples.....	27
General procedures for preparation of dogbone samples .....	29
Optimization of polymerization .....	29
Selection of monomers.....	29
Stoichiometry effect on the mechanical properties of triazole polymers.....	30
Summary .....	31
3    EFFECT OF CROSSLINKER ON THE MECHANICAL PROPERTIES OF UNFILLED TRIAZOLE POLYMERS .....	33
Effect of crosslinker concentration .....	33
Effect of crosslinker functionality .....	36
Conclusion .....	38
4    EFFECT OF FILLER ON THE MECHANICAL PROPERTIES OF TRIAZOLE POLYMERS .....	43
Effect of filler type .....	43
Effect of aluminum filler content .....	45

Conclusion .....	51
<b>5 SUMMARY AND FUTURE WORK .....</b>	<b>53</b>
Summary .....	53
Future work.....	54
Optimization of filler's size and composition.....	54
Optimization of plasticizers .....	54
Preparation and characterization of high filled triazole polymers.....	54
<b>LIST OF REFERENCES .....</b>	<b>56</b>
<b>BIOGRAPHICAL SKETCH .....</b>	<b>59</b>

## LIST OF TABLES

<u>Table</u>		<u>page</u>
2-1	Effect of stoichiometry on the mechanical properties of triazole polymers (data from mini samples).....	32
3-1	Strain and modulus of unfilled triazole polymers (data from dogbone samples) .....	35
3-2	Strain and modulus values of crosslinked triazole polymers having different crosslink functionality (data from dogbone samples) .....	41
4-1	Triazole polymers with different fillers (mini samples) .....	43
4-2	Effect of Al filler content on the mechanical properties of triazole polymers (Strain and modulus data from dogbone samples) .....	46
4-3	Strain and modulus of filled triazole polymers (43wt% Al, data from dogbone samples) .....	48
4-4	Experimental and predicted values of the modulus of filled triazole polymers (27 vol% Al).....	51

## LIST OF FIGURES

<u>Figure</u>		<u>page</u>
1-1	Urethane linkage and polyurethane formation .....	13
1-2	Triazole linkage and 1,2,3-triazole polymer formation .....	14
1-3	Crosslinked triazole polymer formation in Reed's group.....	15
1-4	Crosslinked triazole polymer formation in Manzara's group.....	15
1-5	Variation trend of elongation at break of HDPE-A1 composite versus volume percent of Al .....	19
1-6	The variation trend of modulus of elasticity of HDPE-A1 composite versus volume percent of Al .....	19
1-7	Formation of crosslinking .....	20
1-8	Variation trend of modulus of the HTPB-based polyurethane elastomer with increasing triol concentration .....	21
1-9	Variation trend of elongation at break of the HTPB-based polyurethane elastomer with increasing triol concentration .....	21
1-10	Scheme of a hexafunctional network formation.....	23
1-11	Tensile stress-strain curves for the three different functionalities .....	24
2-1	Dimension of dogbone mold .....	25
2-2	Method of manual testing strain.....	26
2-3	Method of manual testing modulus.....	27
2-4	Formation of crosslinked triazole polymers with different crosslinkers .....	28
2-5	Formation of different triazole polymers and their properties .....	28
2-6	Dogbone mold with unfilled and filled samples .....	29
2-7	Triazole polymer formation at different stoichiometry .....	30
2-8	Reaction of pure acetylene.....	32
2-9	Reaction of diacetylene and diazide at 1:1 ratio.....	32
3-1	Formation of triazole polymers with varied crosslinker concentration .....	33

3-2	TGA curve of unfilled crosslinked triazole polymer (with 16mol% tetra- propoiolate) .....	33
3-3	Effect of crosslinker concentration on the mechanical properties of unfilled triazole polymers (data from mini samples).....	34
3-4	Effect of crosslinker concentration on the mechanical properties of unfilled triazole polymers (data from dogbone samples).....	35
3-5	Crosslinkers with different functionality $f$ ( $f=3, 4, 6, 16, 32, 64$ ) .....	36
3-6	Formation of unfilled triazole polymers with different crosslinkers.. .....	37
3-7	Effect of crosslinker functionality on the strain of triazole polymers (data from mini samples) .....	39
3-8	Effect of crosslinker functionality on the modulus of triazole polymers (data from mini samples).....	39
3-9	Effect of crosslinker functionality on the strain of triazole polymers (data from dogbone samples).....	40
3-10	Effect of crosslinker functionality on the modulus of triazole polymers (data from dogbone samples).....	40
3-11	Stress-strain curves of the polymers having different crosslink functionality (data from dogbone samples).....	41
4-1	Formation of triazole polymers with different fillers.....	43
4-2	Mini samples of triazole polymers filled with $\text{NH}_4\text{NO}_3$ with and without degassing .....	44
4-3	Triazole polymers filled with different content of aluminum powder.....	45
4-4	Formation of triazole polymers with different aluminum content .....	45
4-5	Stress-strain curves of triazole polymers with different aluminum content .....	46
4-6	Formation of filled triazole polymers with different crosslinker concentration .....	47
4-7	Effect of crosslinker concentration on the mechanical properties of filled triazole polymers (43wt% Al, data from mini samples) .....	48
4-8	Effect of crosslinker concentration on the mechanical properties of filled triazole polymers (43wt% Al, data from dogbone samples).....	49
4-9	Stress-strain curves of filled triazole polymers with increasing crosslinker concentration (4mol%-14mol%) .....	49

4-10	Comparison of mechanical properties of unfilled and filled (with 43% Al) triazole polymers (data from dogbone samples).....	50
4-11	Comparison of predicted modulus and experimental modulus.....	52

Abstract of Thesis Presented to the Graduate School  
of the University of Florida in Partial Fulfillment of the  
Requirements for the Degree of Master of Science

**EFFECTS OF CROSSLINKER AND FILLER ON THE MECHANICAL PROPERTIES OF  
1,2,3-TRIAZOLE-POLYMERS AS POTENTIAL ROCKET PROPELLANT BINDERS**

By

Ling Wang

May 2009

Chair: Randolph S. Duran

Major: Chemistry

Crosslinked Triazole polymers are potential novel binders for high-energy explosives and rocket propellants. 1,2,3-triazole linkages can be realized by Huisgen 1,3-dipolar cycloaddition of alkynes and azides. The reaction of E300 dipropiolate with diazide from tetraethylene glycol was selected to study the effects of crosslinker and filler on the mechanical properties of resulting triazole polymers. The modulus of the polymers increases while the strain decreases with increasing crosslinker concentration and functionality. However, the effects of crosslinker functionality are getting much less at functionality higher than 6. Addition of filler also increases the modulus but decreases the strain. The increase in elastic modulus of resulting triazole polymers due to the addition of aluminum powder could be well predicted by the equation of Guth and Smallwood. The resulting triazole polymers showed that the desired mechanical properties could be obtained by selecting an appropriate crosslinker and tuning the concentration of the crosslinker and filler. The mechanical properties of these triazole polymers are comparable to typical polyurethane elastomeric matrices for rocket propellants. Thus, the triazole polymers are of potential application as novel rocket propellant binders.

## CHAPTER 1

### INTRODUCTION

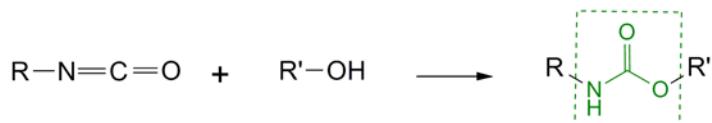
#### **Solid Composite Propellant Binders**

Solid rocket propellants have two types: double-base and composite.<sup>1</sup> Composite solid propellant contains three basic components: (I) a fuel, which is an organic polymer and also serves as a binder; (II) an oxidizer such as ammonium perchlorate or ammonium nitrate; (III) various additives such as metallic filler, plasticizers, wetting agents, and stabilizers, for improving propellant processability, efficiency, or physical properties.<sup>1,2</sup> All solid ingredients are distributed uniformly in a matrix provided by the polymeric binder.

Various organic polymers have been used as binders such as polyesters, polysulphides, polyurethanes, polybutadienes, polyvinyl chloride, synthetic rubbers, epoxy resins and acrylates.<sup>1</sup> Polyurethane binders are widely used in modern rocket propellants due to their excellent mechanical properties, shrink free, low-temperature controlled cure and acceptable compatibility with metal powders and oxides.<sup>3</sup> Polyurethanes are organic polymers with urethane linkages, which are formed from the reaction of di- or multifunctional isocyanates with polymeric diols. (Figure 1-1) However, they have several drawbacks: First, isocyanate is toxic. Second, both reactants are moisture sensitive: isocyanate can react with water, and hydroxyl groups including even trace amount of moisture in the binder or other ingredients.<sup>4</sup> Third, polyurethane rocket propellant binders can undergo side reactions during and after polymerization that degrade the mechanical properties of the resulting propellant, e.g., loss of elasticity.<sup>3</sup> Last, the process of preparing polyurethane binders also presents environmental concerns. Their formulations, once mixed, must be cured quickly or side reactions will degrade the ultimate properties of resulting polymer. Excess material cannot be reused and must be disposed of. Consequently, not only the environmental burden is increased but the cost of

disposal these hazardous energetic materials.<sup>4</sup> Therefore, new polymer propellant binders that are effective, economical, environmentally friendly and compatible with other ingredients are desired.<sup>4</sup>

### 1. Urethane formation



### 2. Polyurethane formation

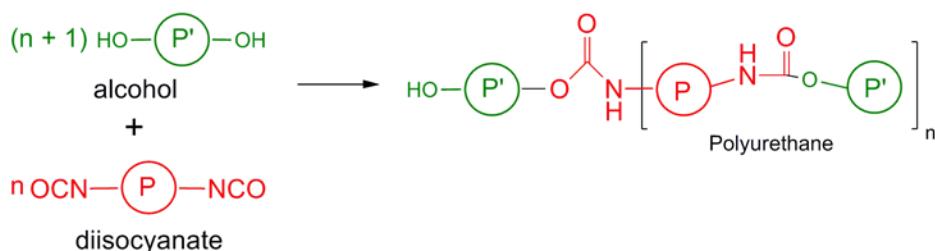
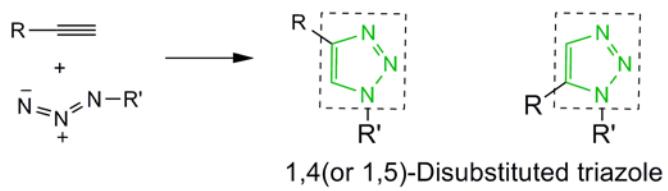


Figure 1-1. Urethane linkage and polyurethane formation

## Triazole polymers

Triazole polymers are novel macromolecules that have received growing interest in the areas of polymer, material, and surface science.<sup>5,6</sup> They can be used as high energy binders for explosives or rocket propellants, destructible adhesives, or other high energy and destructible products.<sup>7</sup> The triazole linkage can be synthesized by 1,3-dipolar cycloaddition of azides with terminal alkynes following ‘Click’ Chemistry (Figure 1-2), which has been explored as an efficient tool for the synthesis of functionalized monomers<sup>8</sup>, polymers<sup>9</sup> and post-polymerization modification of polymers,<sup>5,10</sup> such as the synthesis of dendrimers, dendronized polymers,<sup>11,12</sup> biohybrid amphiphiles,<sup>13</sup> chromophores,<sup>14</sup> conjugated polymers,<sup>15</sup> block copolymers<sup>16,17</sup>, glyco-polymers,<sup>18</sup> macrocyclic polymers,<sup>19</sup> and adhesives.<sup>20</sup>

### 1. Triazole formation



## 2. Triazole polymer formation

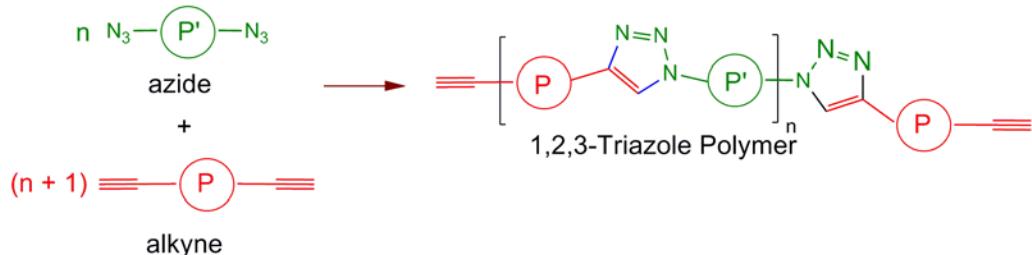


Figure 1-2. Triazole linkage and 1,2,3-triazole polymer formation

1,2,3-triazole-polymers have been studied recently as novel binders for explosives and high energy propellants.<sup>3,21,22</sup> Compared to polyurethane linkages, polymerization through thermally and chemically stable triazole linkages proceeds readily and the components of the triazole cure (ethynyl groups and azido groups) react preferentially with each other<sup>3</sup>, which largely avoids the possibility of side reactions. The reaction between acetylenes and azides is insensitive to moisture, and no special precautions are needed for preventing moisture from air or other ingredients.<sup>7</sup> The reactions of certain azides and acetylenes, such as acetylenes having long carbon chains between end groups, proceed slowly at the temperature between 100-140°F ((38-60°C)), temperatures below which the mixture of acetylenes and azides can sit at least one week without significant reaction. One desirable consequence of this is that excess mixed starting materials can be stored at ambient temperature (about 77 °F (25°C)) and reused the next day, which reduces the cost and environmental contamination.<sup>4</sup>

Reed's group reported the synthesis of crosslinked triazole polymers as energetic binders with improved mechanical properties and stability. The triazole polymers are formed from azido

and azido nitrato polyether prepolymers crosslinked by diacetylenes without a catalyst. (Figure 1-3) The resulting triazole binder is soluble in energetic plasticizers and has excellent mechanical properties, like polyurethanes, but has improved compatibility with other propellant ingredients.<sup>3</sup>

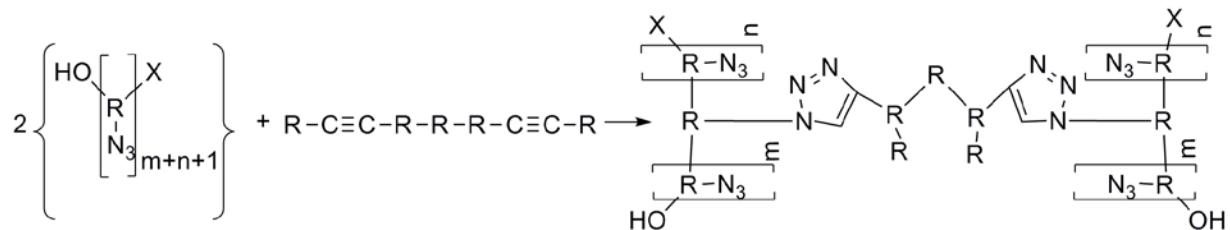


Figure 1-3. Crosslinked triazole polymer formation in Reed's group (adapted from reference 3)

Crosslinked triazole polymers were also prepared as rocket propellant binders in Manzara's group by crosslinking azido polymers with a multifunctional dipolarophile having a reactive group selected from acrylic and acetylenic esters or amides (Figure 1-4), which enhanced the burn rate of the crosslinked polymer.<sup>7</sup>

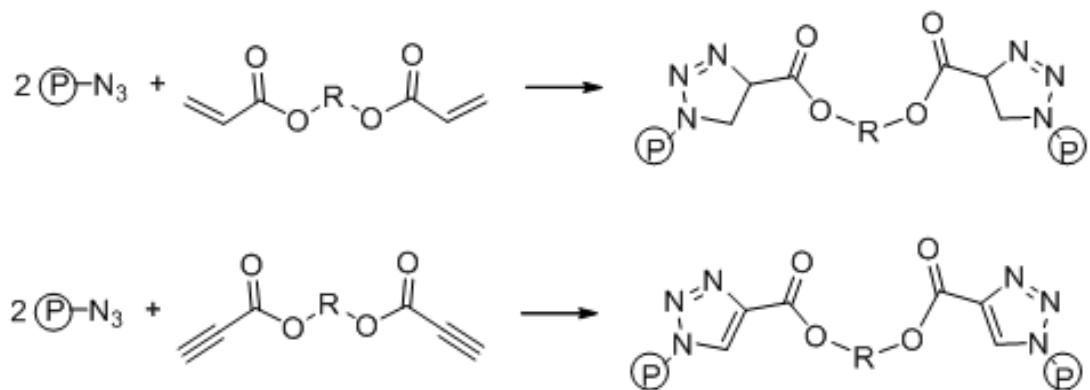


Figure 1-4. Crosslinked triazole polymer formation in Manzara's group (adapted from reference 7)

Huang's group synthesized and characterized a series of novel low-temperature curing and heat-resistant polytriazole resins by the 1,3-dipolar cycloaddition reaction of various acetylenes and azides as advanced composites. The curing reactions and the properties of developed

polytriazole resins such as decomposition temperature, tensile strength, modulus and elongation at break were characterized.<sup>23-25</sup>

Previous work in our group developed strategies for low-temperature synthesis of oligo-triazoles as binder ingredients.<sup>26</sup> Triazole-cured polymers were prepared with various alkynes and azides without any solvent or copper catalysts under mild conditions near room temperature. The resulting triazole polymers were characterized by NMR spectroscopy, elemental analysis, and gel permeation chromatography. Five triazole polymers were selected as potential rocket propellant binders for future work.<sup>21</sup> However; the mechanical properties of those triazole polymers were not quantified.

The above work on triazole polymers was mainly focused on the polymer synthesis rather than characterization. Thus, the properties of novel triazole polymers need to be investigated.<sup>5</sup>

### **Factors that affect mechanical properties of rocket propellants**

Mechanical properties of the propellants are important for rocket motors. Poor mechanical properties such as formation of cracks may lead to unstable combustion and malfunctioning of rocket motors.<sup>1</sup> All the ingredients in the formulation can affect the mechanical properties of final propellant. A good propellant formulation should give a viscous mix that is castable and cures to a rubbery composite. The mechanical properties of rocket propellants can be modified by varying the type and proportion of filler (solids) and plasticizer.<sup>27</sup> The binder polymer's nature and crosslinking degree of binder also affect propellant's properties. To predict the performance of propellants, a knowledge of the mechanical properties of unfilled and filled binder polymers is necessary.<sup>1</sup>

### **Effect of filler**

Fillers are usually used to improve the strength of the polymer matrix, reduce the creep and lower the cost. Generally, fillers have higher elastic modulus than polymer matrix. The size,

shape of filler particles, and the content of filler can affect the mechanical behavior of the resulting filled system.<sup>28</sup> Various mathematical equations have been developed to predict the increase in the modulus of an elastomer resulting from the addition of fillers, most of these relationships originate from the theory of the viscosity of suspensions.<sup>29</sup> The simplest theoretical form is Einstein's well known equation for the viscosity of a suspension.<sup>28,29</sup> (Equation 1-1,  $\eta$ : Viscosity of fluid;  $\eta_0$ : Viscosity of suspension;  $\Phi$ : The volume concentration of suspended particles) This equation can also be used to describe a filler's effect on increasing the rigidity of the polymer matrix by substituting  $\eta$  and  $\eta_0$  with  $E$  and  $E_0$ , respectively. (Equation 1-2,  $E$ : The elastic modulus of filled elastomer;  $E_0$ : The elastic modulus of unfilled elastomer;  $\Phi$ : The volume concentration of filler) The Einstein equation does not consider the interaction of adjacent particles; and assumes that the filler is more rigid than matrix. This expression is valid only at low filler concentration when there is a perfect adhesion between filler particles and polymer. The Einstein equation was developed by Guth and Smallwood to explain rubber reinforcement, which takes account of the interaction between a pair of filler particles. (Equation 1-3)<sup>28,29</sup> Another equation that has been widely used is the empirical Eilers-Van Dijck equation, (Equation 1-4) where  $\Phi_m$  is the maximum volume fraction of filler. (Equation 1-5) The theoretical value of  $\Phi_m$  is 0.74. However,  $\Phi_m$  varied with particle shape and state of agglomeration. Since it is difficult to predict the value of  $\Phi_m$  theoretically,  $\Phi_m$  is generally measured by sedimentation technique and the values range from 0.31 to 0.85.<sup>30</sup>

$$\eta/\eta_0 = (1 + 2.5\Phi) \quad 1-1$$

$$E/E_0 = (1 + 2.5\Phi) \quad 1-2$$

$$E/E_0 = (1 + 2.5\Phi + 14.1\Phi^2) \quad 1-3$$

$$\frac{E}{E_0} = \left(1 + \frac{1.25\phi}{1 - \phi/\phi_m}\right) \quad 1-4$$

$$\phi_m = \frac{\text{true volume of the filler}}{\text{apparent volume occupied by the filler}} \quad 1-5$$

Nicholas and Freudenthal investigated the relationship between mechanical properties of polyurethane elastomers with filler contents from 0 to 50% by volume. An equation was proposed for the increase in modulus due to the addition of filler. (Equation 1-6) Based on Equation 1-4, a more general form (Equation 1-7) was suggested to describe the increase in modulus of an elastomer resulting from the addition of more rigid filler, where  $\Phi_m$  is dependent on each individual material and filler.<sup>29</sup>

$$\frac{E}{E_0} = (1 - 1.20\phi)^{-2.5} \quad 1-6$$

$$\frac{E}{E_0} = \left(1 - \frac{\phi}{\Phi_m}\right)^{-2.5} \quad 1-7$$

The above equations (1-1 to 1-6) generally do not agree with experimental data well at very high concentration of filler because the suspensions become non-Newtonian in behavior, and the coefficient of viscosity is not constant.<sup>30</sup>

Compared to theories for the increase in modulus, the theory explaining the decrease in elongation at break due to the addition of rigid fillers is more complex and semiquantitative. Assuming there is a perfect adhesion between the phases, the following simple model developed by Nielsen predicts the elongation at break of filled system in a qualitative or semiquantitative manner. (Equation 1-8)<sup>28, 30</sup>

$$\frac{\epsilon}{\epsilon_0} = 1 - \phi^{1/3} \quad 1-8$$

Tavman investigated the mechanical properties such as tensile strength, elongation at break, and elastic modulus of aluminum powder-filled, high-density polyethylene composites

experimentally in the range of filler content 0-50% by volume.<sup>31</sup> With increasing filler content, the elongation at break of the filled polymer decreased (Figure 1-5); elastic modulus first increased but then decreased as filler content became higher than 30%, which may be attributed to the formation of cavities around filler particles during stretching in tensile tests (Figure 1-6).

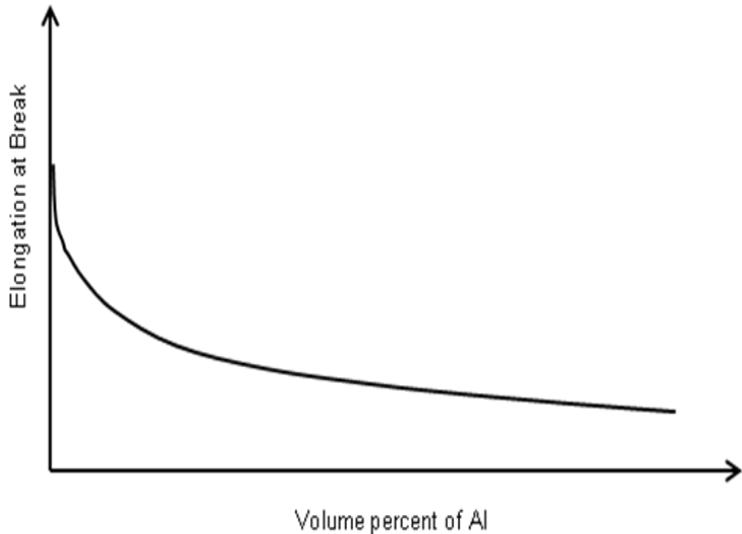


Figure 1-5. Variation trend of elongation at break of HDPE-A1 composite versus volume percent of Al (adapted from the data in reference 31)

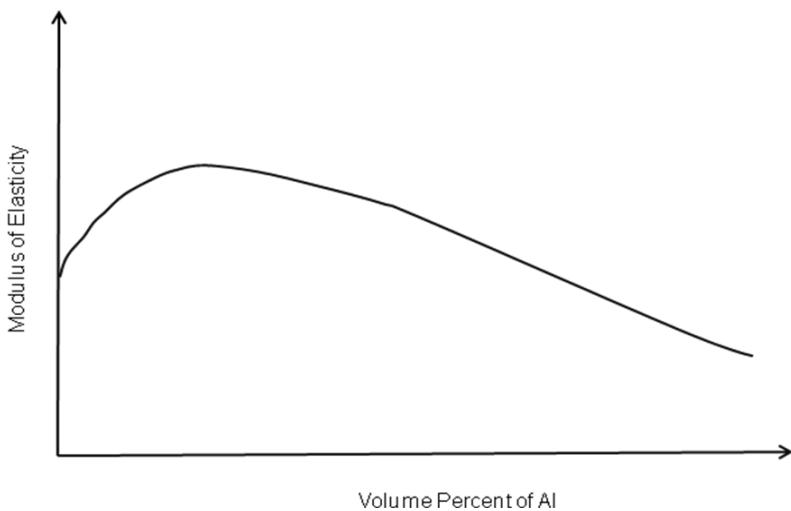


Figure 1-6. The variation trend of modulus of elasticity of HDPE-A1 composite versus volume percent of Al (adapted from the data in reference 31)

## Effect of crosslinking of binder

The binder polymer is critical for rocket propellant operation. The mechanical properties of binder polymer are significantly influenced by their molecular structures such as chain length between the triazole.<sup>21</sup> Crosslinking is another structural feature that can drastically affect polymer's behaviors. Uncrosslinked polymers are randomly packed and entangled linear chains.<sup>10</sup> Adjacent polymer chains can be connected to form a vast molecular network by forming chemical bonds between them. These connections are called crosslinks. (Figure 1-7) The number of crosslinks per unit volume or length is called crosslink density. Crosslinkers are crosslinking reagents that link the linear polymer chains together to form network structure, which limits the mobility of the individual polymer chain. Accordingly, the mechanical properties of polymers, such as tensile strength, modulus and elasticity, are changed by crosslinking. The effect of crosslink density on the mechanical properties of rubbery polymers has been studied extensively and well understood.<sup>32</sup> Increasing crosslinker density, usually, increases a polymer's strength and modulus but decreases elongation to failure.<sup>32</sup> Besides natural rubber, the relationship between crosslinker density and mechanical properties has been studied on various polymers such as polyurethanes,<sup>32,33</sup> hydrogels,<sup>34,35</sup> and acrylate networks.<sup>35-37</sup>

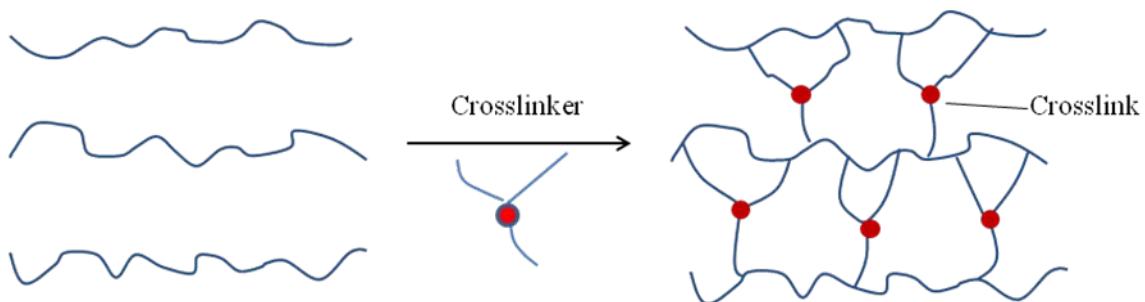


Figure 1-7. Formation of crosslinking

S. Özkar's group developed a polyurethane elastomer using hydroxyl-terminated polybutadiene (HTPB) as the prepolymer and Isophorone Diisocyanate (IPDI) as the curing

agent for liner applications in solid rocket propellants. Triethanolamine was used as the crosslinker of the polyurethane composition matrix. The crosslinker density was increased by varying the triol/diol ratio from 0 to 0.5 and the mechanical properties of resulting polymers were investigated. As the crosslink density in the elastomeric polyurethane matrix increases, the modulus of the matrix decreases initially and starts to increase due to an initial decrease in the average molecular weight with inclusion of crosslinking into system (Figure 1-8); The elongation at break increases first with the increasing concentration of triol, and after reaching a maximum at the triol/diol ratio of 0.031, it starts to decrease. (Figure 1-9)<sup>38</sup>

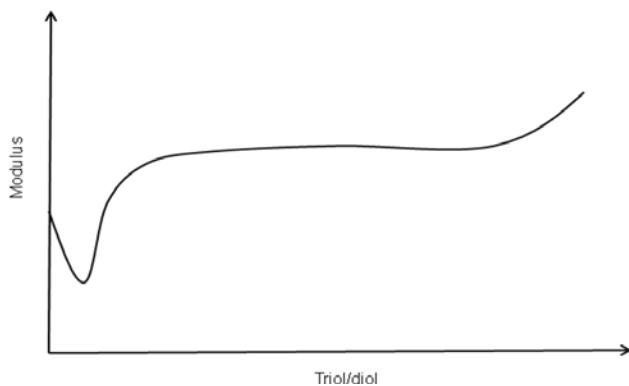


Figure 1-8. Variation trend of modulus of the HTPB-based polyurethane elastomer with increasing triol concentration (adapted from the data in reference 38)

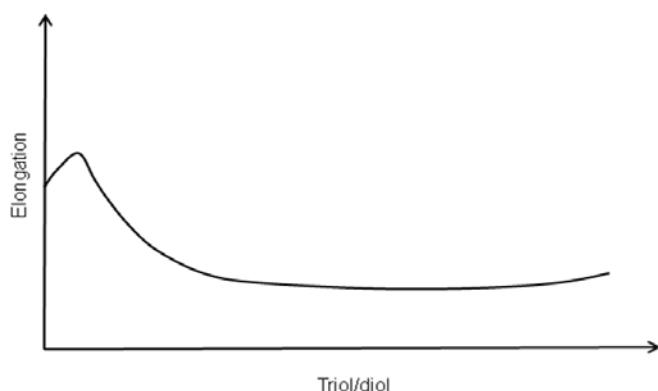


Figure 1-9. Variation trend of elongation at break of the HTPB-based polyurethane elastomer with increasing triol concentration (adapted from the data in reference 38)

The crosslinker functionality  $f$  also plays an important role in polymer network structure. However, compared to the studies on crosslinker density, much less effort has been given to investigating the relationship between crosslinker functionality and physical properties of crosslinked polymers.

James E. Mark's group did a series of studies on effect of crosslink functionality on the elastomeric properties of crosslinked polymers decades ago.<sup>39-41</sup> Unlike previous method of preparing polymer network, by which the crosslinks are usually introduced in a highly random, uncontrolled manner, they prepared "model" networks by linking the polydimethylsiloxane (PDMS) chains exclusively through functional groups placed at their two ends with crosslinkers having different functionality. An example of the formation of a hexafunctional network is given by Figure 1-10. Since the chain length of PDMS chains between crosslinks is the same as before their incorporation into the network structure, the molecular weight  $Mc$  between crosslinks is then simply known. Crosslinkers with different functionality ranging from 3 to 37 were used to investigate the relationship between crosslinker functionality and elastomeric properties of resulting polymers. The semiempirical equation of Mooney and Rivlin described the relationship between modulus and elongation. (Equation 1-9) In Equation 1-9,  $f^*$  is defined as "reduced stress" or modulus.  $\alpha$  is values of elongation.  $2C_1$  and  $2C_2$  are constants independent of  $\alpha$ . According to new Florey theory of rubber-like elasticity,  $2C_1$  should be proportional to the factor  $(1-2/f)$ , where  $f$  is the functionality of the crosslinker. The other constant  $2C_2$ , which is a measure of decrease in modulus as the elongation  $\alpha$  increases, decreases with increasing crosslinker functionality  $f$ . Thus in a network having higher junction functionality, its modulus should decrease less with increasing elongation. Mark's experimental results are in satisfactory agreement with Flory's theory.<sup>39</sup>

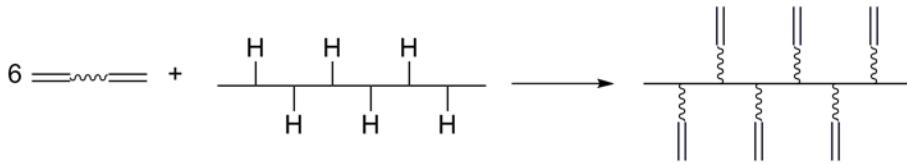


Figure 1-10. Scheme of a hexafunctional network formation (adapted from reference 39)

$$[f^*] = 2C_1 + 2C_2 \alpha^{-1}$$

1-9

Mesfin Tsige and Mark J. Stevens studied the effect of crosslinker functionality and interfacial bond density on the fracture behavior of highly crosslinked polymer networks bonded to a solid surface. Three different crosslinker functionalities ( $f=3, 4$ , or  $6$ ) were studied. They used molecular dynamics (MD) simulations of highly crosslinked polymer networks bonded to a rigid surface to directly determine the local structure of the adhesive as a function of deformation and simultaneously calculate the stress-strain curves based on the bead-spring model. The simulations showed that the plateau regime in the stress-strain curve was found to depend on  $f$ . (Figure 1-11) The strain range of the plateau regime is found to decrease with an increase in  $f$ . As  $f$  increased, failure stress increased while failure strain decreased. Experiments results showed that the simulation values of failure strain are larger due to the flexibility of the model (i.e., there is no stiffness in the bead-spring strands). However, this bead-spring model can still give us a systematic understanding of the role of crosslinker functionality in a crosslinked polymer network.<sup>42</sup>

The studies on the effects of filler and crosslinker on the mechanical properties of triazole polymers have not been systematically performed. The reactions to form triazole polymers are good models to investigate the relationship between crosslinking and polymer mechanical properties since acetylene and azide groups should react with each other at 1:1 molar ratio, no small molecules are produced, the reaction should not be influenced by residual moisture, and side reactions should not occur. Understanding the relationship between crosslinking and

mechanical properties of triazole polymers, the synthesis then can be optimized to result in polymers with desired mechanical properties.

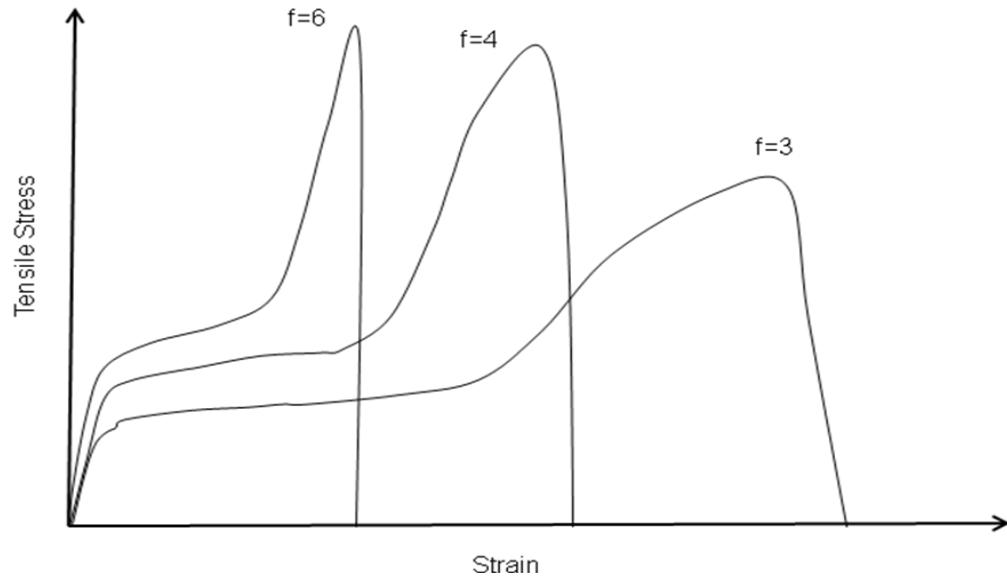


Figure 1-11. Tensile stress-strain curves for the three different functionalities. (adapted from the data in reference 42)

### Thesis overview

This thesis has five chapters. Chapter 1 is the introduction to the research. Chapter 2 illustrates the experimental method and explains how a reaction of polymerization was selected as a model for future studies. The third and fourth chapters discuss the effects of crosslinker and filler on the mechanical properties of triazole polymers, respectively. The conclusions of this research and future work are summarized in the last chapter.

## CHAPTER 2 EXPERIMENTAL AND OPTIMIZATION OF POLYMERIZATION<sup>a</sup>

### Experimental

#### General

Commercially obtained reagents were used without further purification. All monomers except **14** were prepared following reported procedures<sup>21,26,43</sup>. Solvents were distilled by standard methods. <sup>13</sup>C and <sup>1</sup>H NMR spectra were recorded at 75 and 300 MHz, using tetramethylsilane (TMS) as an internal standard. In view of the stringent stoichiometry requirements for step polymerization, the monomers were systematically dried by azotropic distillation and lyophilization. The uniaxial test specimen was a standard microtensile dogbone, with dimensions 0.88"×0.19"×0.13,"<sup>44</sup>(Figure 2-1) Strain (% elongation at break) and elastic modulus (Young's modulus) in Figure were measured by Instron Universal Tensile Testing Machine (Upgrade package, Model no. 1122). Each data point in the figures is an average of at least two measurements. The error bars in Figure 3-3, 4 and 4-7, 8 indicate mean standard deviation for each data set. Figure 3-7 to 3-10 don't show error bars for readability. The mean standard deviation for the measurements in Figure 3-7 and 3-8 are 0.13 Mpa and 70%, respectively.

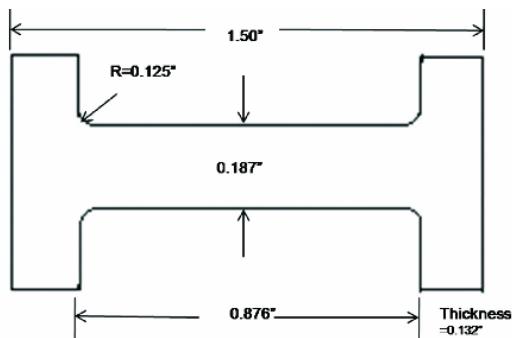


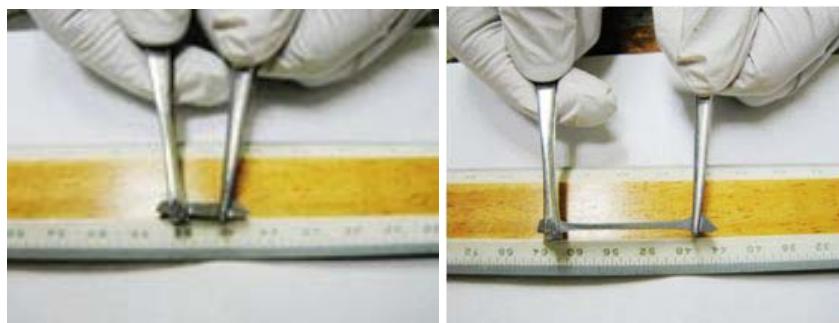
Figure 2-1. Dimension of dogbone mold

<sup>a</sup> The article related to the work in Chapter 2, 3 and 4 has been submitted to the journal as following:  
“Preparation and Mechanical Properties of Crosslinked 1,2,3-Triazole-Polymers as Potential Propellant Binders”,  
submitted to “Journal of Applied Polymer Science” 2009

The mechanical properties of triazole polymers were compared with two gumstocks obtained from U.S. NAVY. Gumstock 1 used Desmodur N-100, a polyfunctional aliphatic isocyanate as crosslinking agent, and Gumstock 2 used hexamethylene diisocyanate (HDI), a difunctional curative. The isocyanate-to-hydroxyl (NCO:OH) ratio was in both instances 1.1. The mechanical properties of the gumstocks were tested by Instron Universal Tensile Testing Machine with a strain rate of 50mm/min.

### **Method of manual testing strain and modulus**

The strain of the polymers was estimated by subjecting much smaller thin film samples to external deformation and measuring the original and increased length of the samples by a fine scale. (Figure 2-2) This allowed for the testing of many more compositions on the tens of milligram scale and the concomitant gains in safety, sample waste, and efficiency. The process of tests of modulus on the mini samples is illustrated in Figure 2-3.



A) Original sample      B) Sample under extension

Figure 2-2. Method of manual testing strain. The sample was stretched by two tweezers. The original length ( $L_0$ ) and increased length ( $\Delta L$ ) of the sample were measured by a fine scale. The strain at failure was calculated by the equation 2-1.

$$\text{Strain} = \frac{L - L_0}{L_0} \times 100\% = \frac{\Delta L}{L_0} \times 100\% \quad 2-1$$

### **General procedures for preparation of unfilled linear triazole polymer mini samples**

The monomers were mixed in an aluminum pan at a small scale (<300mg) until a homogenous mixture was obtained. The pan was cured in a vacuum oven under the conditions

described in Figure 2-5. The reactions were monitored by NMR. The strain and modulus of the polymers were estimated manually as described in Figure 2-2 and 2-3.

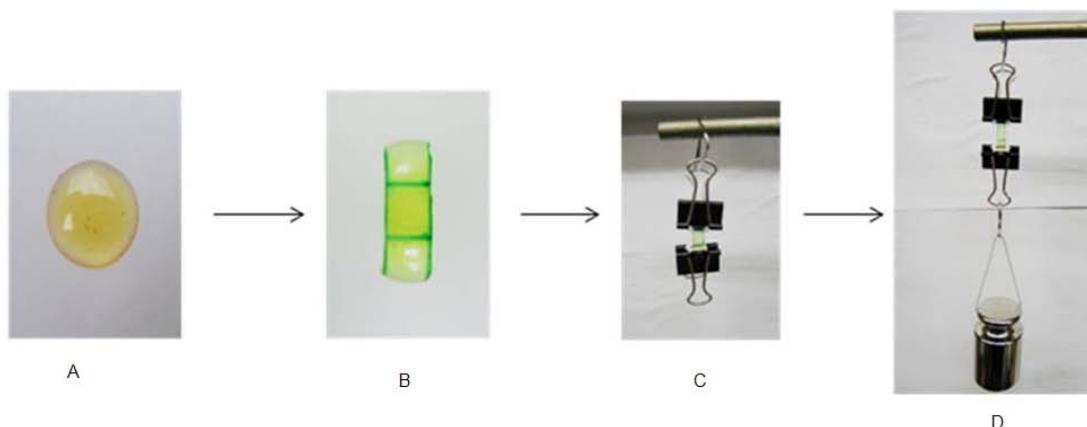


Figure 2-3. Method of manual testing modulus. A) A typical mini sample film was obtained from the polymerization at a scale of hundreds of milligrams. B) The film was cut into a 5mm wide rectangular strip. The strip was marked by two green lines. The length between the green lines was the original length ( $L_0$ ). C) The sample was then loaded with a certain weight. The force ( $F$ ) loaded on the sample should be the weight attached to the sample. D) The original length, the original width, the thickness of cross section and the increased length under the tensile load were measured by a fine scale. The value of modulus is then calculated by equation 2-2.

$$\text{Young's modulus} = \frac{\text{Stress}}{\text{Strain}} \quad \text{stress} = \frac{F}{A_0} \quad 2-2$$

(F: force loaded on the sample,  $A_0$ : original area of sample cross section)

### General procedures for preparation of crosslinked triazole polymer mini samples

In an aluminum pan, diacetylene (**1**) was weighed and different concentrations of crosslinker (Figure 2-4) were added and stirred until it dissolved completely. This was followed by the addition of diazide (**2**), which on stirring gave a homogeneous mixture. For an unfilled system, this pan was degassed under vacuum at room temperature for 3 hours and the curing was done in a vacuum oven at 55 °C for 72 hours. For the filled systems, aluminum powder was added to the homogeneous mixture of diacetylene (**1**), diazide (**2**) and crosslinker, then mixed uniformly and degassed followed by curing in a vacuum oven at 55 °C for 1hour. After that, the mixture was stirred again and cured at 55 °C for an additional 71 hours.

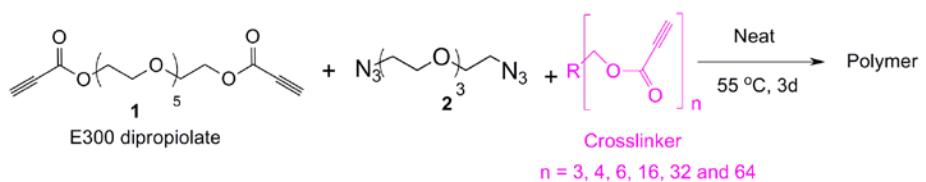


Figure 2-4. Formation of crosslinked triazole polymers with different crosslinkers

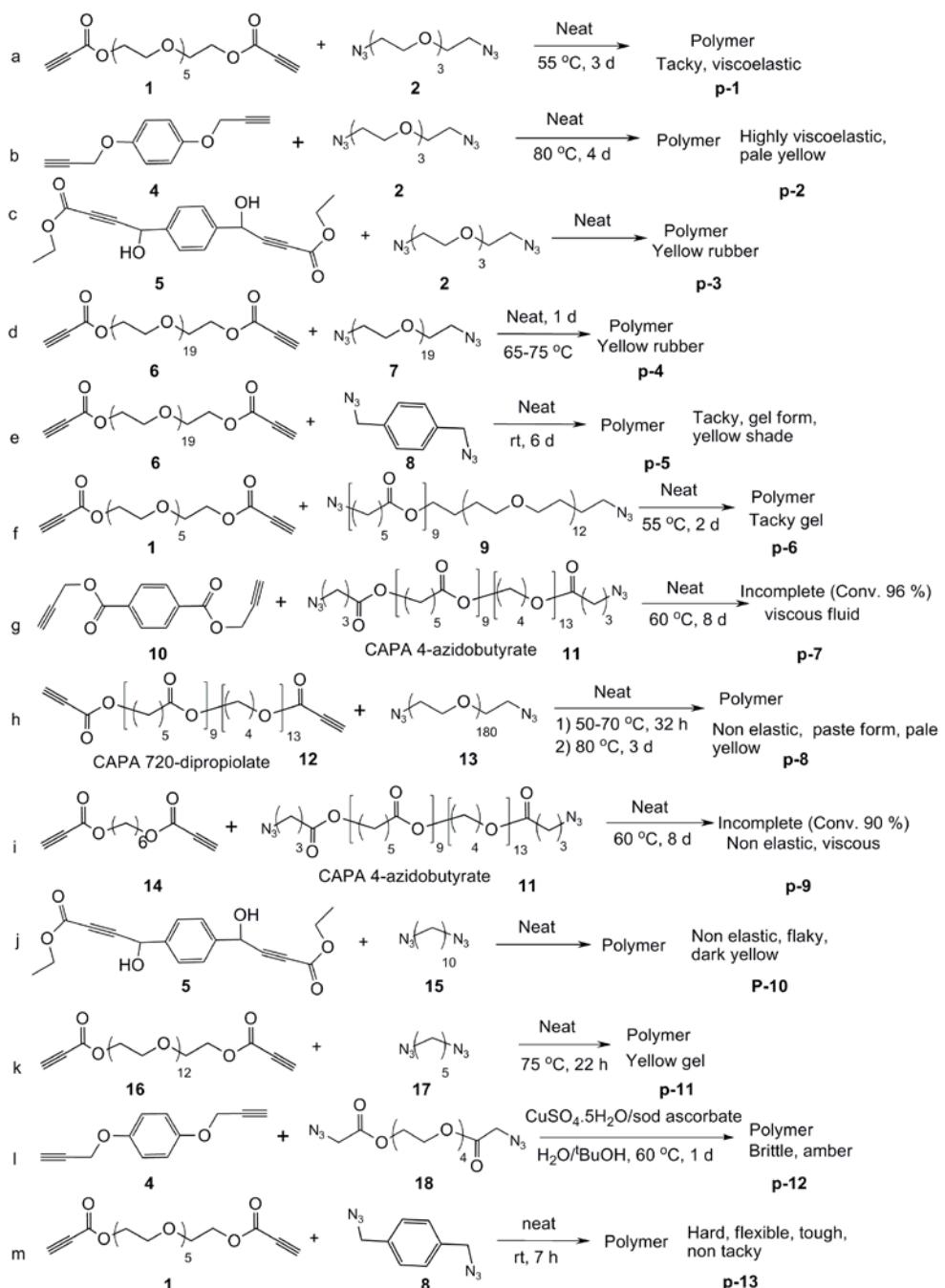


Figure 2-5. Formation of different triazole polymers and their properties

## **General procedures for preparation of dogbone samples**

For preparing dogbone samples, the above mentioned procedure was used with larger amounts (approx. 2g). The mixture was casted into a dogbone mold (Figure 2-6) and cured as described above. The dogbone samples were carefully removed from the mold. After they cooled, they were tested using Instron tensile testing machine. Results for the trends from mini and dogbone samples were compared to assure reproducibility.

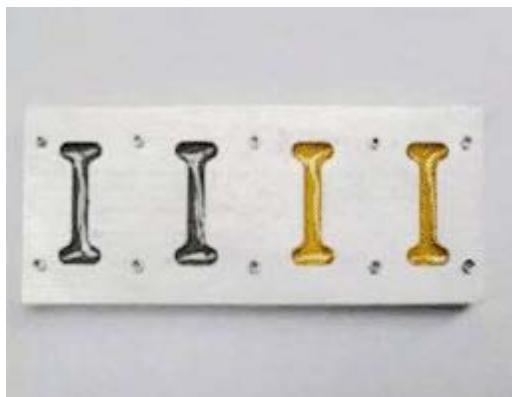


Figure 2-6. Dogbone mold with unfilled and filled samples

## **Optimization of polymerization**

### **Selection of monomers**

Figure 2-5 lists thirteen reactions of the polymerization of different diazides and diacetylenes. These reactions were screened by the following criteria: As per the specification of rocket propellant binders, the monomers should be reactive at low temperatures (room temperature to 60 °C) with no or little side reactions; The polymerization process should proceed in the absence of any solvent or heavy metal catalysts; In addition, the polymerization should be easily scaled up.

As shown in Figure 2-5, diacetylenes with acetylene groups connected to electron withdrawing groups showed better activities than propargyl esters or ethers (Figure 2-5, Reaction b, g, l) that needed higher temperature and/or catalyst to react with azides. Benzyl azides (Figure

2-5, Reaction e, m) can react with propiolates easily at room temperature. However, the reactions are more vigorous and sometimes too violent. Reactions c and j (Figure 2-5, Reaction c, j) were also ruled out because of difficulties in scaling up the preparation of starting material (7). Moreover, the reactions of monomers with longer spacers between end groups (Figure 2-5, Reaction d, f, h, i, k) need higher temperature or longer reaction time.

Based on the above discussion, Reaction a was finally selected as a model system to study the relationship between crosslinker concentration and mechanical properties of triazole polymers.

### **Stoichiometry effect on the mechanical properties of triazole polymers**

The effect of diacetylene to diazide stoichiometry on the mechanical properties of triazole polymers was studied. The ratio of diacetylene to diazide was varied from 0.98:1 to 1.12:1. (Figure 2-7) Since many of the resulting polymers were too soft and tacky to cast into dogbone molds, the strain and modulus of the polymers were estimated by the manual method described earlier. The results are listed in Table 2-1.

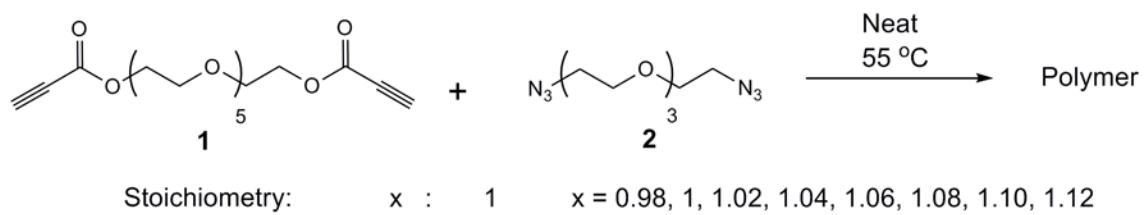


Figure 2-7. Triazole polymer formation at different stoichiometry

As shown in Table 2-1, the polymers with azide stoichiometry in excess are not elastic (Entry 1). With slight excess of diacetylene, the polymer becomes viscoelastic (Entry 3). If the excess acetylene is further increased, the elasticity decreases and the modulus increased and reaching the maximum value at the ratio of 1.10:1 (Entry 7), then finally decreases. These results were unexpected because in a step polymerization involving two difunctional monomers, the

polymer should give the best mechanical properties at 1:1 stoichiometry of the monomers since any imbalance in stoichiometry should significantly lower the degree of polymerization.<sup>45,46</sup> However, these results showed that the ratio of 1.10:1 gave the highest value of modulus and a systematic shift towards excess acetylene was observed in spite of the purification noted in the experimental section. Side reactions may account for this shift. For instance, it has been reported that the reaction of propiolate coupling to form enyne could be catalyzed by Lewis bases such as aromatic and aliphatic amines due to the lone pairs on the nitrogens.<sup>47</sup> In this case such excess unreacted diacetylenes might then undergo self condensation or oxidative coupling in the presence of triazole acting as a catalyst to result in internal crosslinking, increase in molecular weight, and ultimately shifting the stoichiometry from the expected 1:1 toward excess acetylene. To study this systematic shift towards excess acetylene, two reactions were performed. The first is the self reaction of pure diacetylene (**1**) (Figure 2-8); the second is the reaction of diacetylene (**1**) with diazide (**2**) at 1:1 molar ratio. (Figure 2-9) After three days of reaction, the first reaction seemed incomplete while the second reaction gave tacky and soft gel. The first reaction resulted in a non tacky brittle solid on the eighth day while the triazole polymer from the second reaction stayed the same. NMR results suggested that no side reaction occurred for the second reaction. Unfortunately, the solid from the first reaction was insoluble in any organic solvent thus unanalyzable. However, the reaction of pure acetylene clearly indicates that side reactions may occur in the case of excess acetylene, which could result in unstable triazole polymers. Therefore, the ratio of acetylene to azide groups was kept at 1:1 to avoid any potential side reactions in the following experiments.

### Summary

A method of manual testing strain and modulus on mini samples was developed for safety, cost, and sample waste. The results from mini samples will be compared with dogbone samples

to assure reproducibility. The reaction of E300 dipropiolate (**1**) with diazide from tetraethylene glycol (**2**) was selected to study the effects of crosslinker and filler on the mechanical properties of resulting triazole polymers. In the following studies, the ratio of acetylene to azide groups was kept at 1:1 to avoid any potential side reactions.

Table 2-1. Effect of stoichiometry on the mechanical properties of triazole polymers (data from mini samples)

Entry	Diacetylene : diazide	Modulus(psi)	Strain (%)	Sample description
1	0.98:1	N/A	N/A	Non elastic
2	1:1	N/A	N/A	Non elastic
3	1.02:1	N/A	N/A	Viscoelastic, very tacky
4	1.04:1	<1	1470	Elastic, very tacky and soft
5	1.06:1	1	3180	Elastic, tacky
6	1.08:1	4	2980	Elastic, tacky
7	1.10:1	7	2800	Elastic, tacky
8	1.12:1	<1	1580	Elastic, very tacky and soft

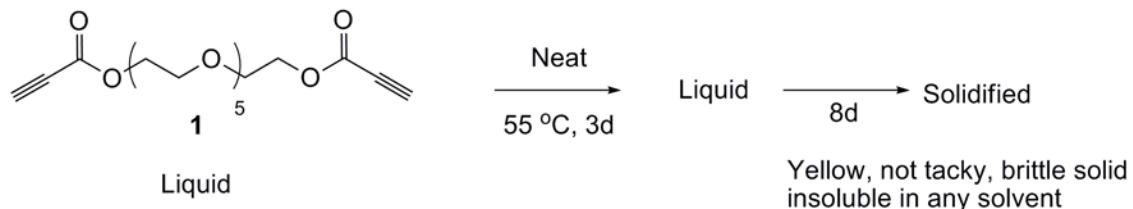


Figure 2-8. Reaction of pure acetylene

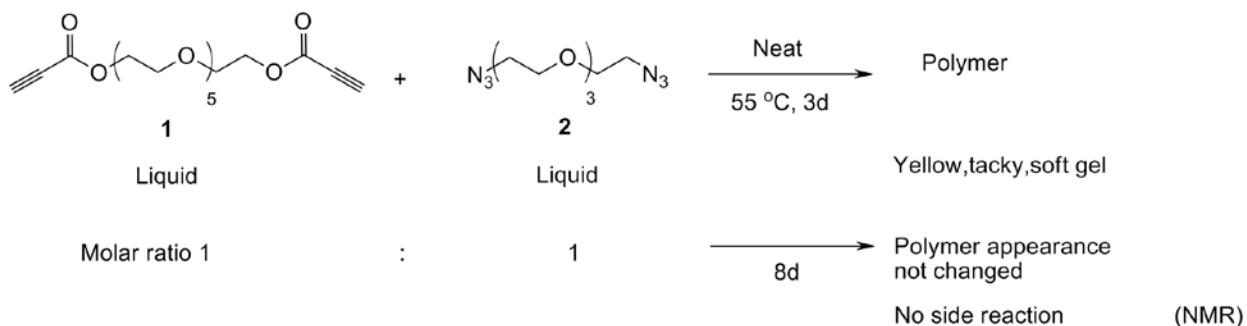


Figure 2-9. Reaction of diacetylene and diazide at 1:1 ratio

## CHAPTER 3

### EFFECT OF CROSSLINKER ON THE MECHANICAL PROPERTIES OF UNFILLED TRIAZOLE POLYMERS

### **Effect of crosslinker concentration**

The effect of increasing concentration of crosslinker (**3**) on the strain and modulus of the resulting polymers was studied in unfilled system having end groups in the ratio of 1:1 ((diacetylene + tetrapropiolate):diazide, Figure 3-1). Thermal gravimetric analysis (TGA) shows the decomposition temperature of unfilled triazole polymers is around 300°C. (Figure 3-2)

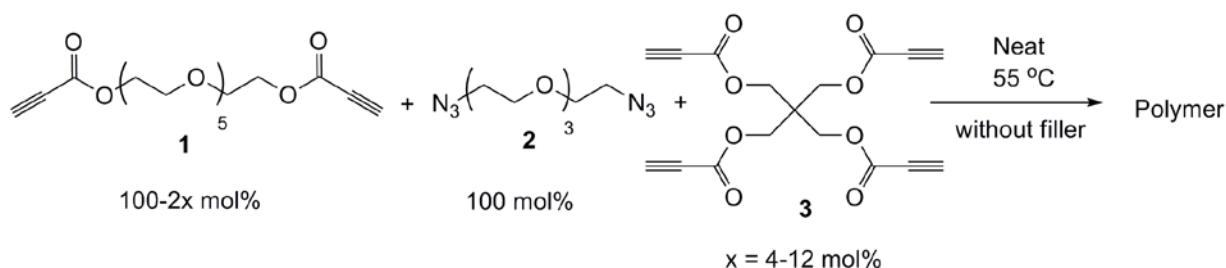


Figure 3-1. Formation of triazole polymers with varied crosslinker concentration

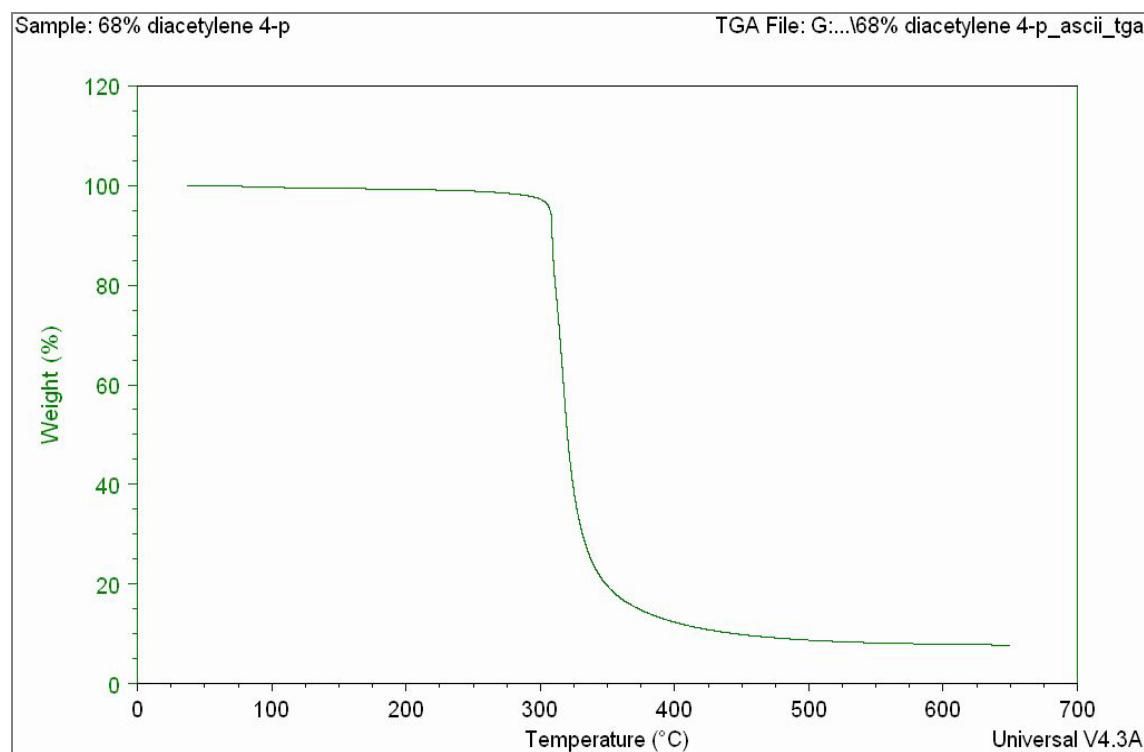


Figure 3-2. TGA curve of unfilled crosslinked triazole polymer (with 16mol% tetra-propoalate)

The variation trends of strain and modulus values with increasing crosslinker concentration for unfilled triazole polymers is shown in Figure 3-3 and 3-4. The data in Figure 3-3 are from manual tests on mini samples while the data in Figure 3-4 are from tests on dogbone samples by Instron tensile tester with 20mm/min strain rate and listed in Table 3-1. The results from mini samples and dogbone samples show the same variation trends of the strain and modulus. The difference in strain and modulus values between Figures 3-3 and 3-4 is likely due to lack of controlled strain rate in the manual measurement, though errors associated with the different sample size of mini samples (<100 mg) and dogbone samples (~2g), and measuring errors during manual testing may also contribute.

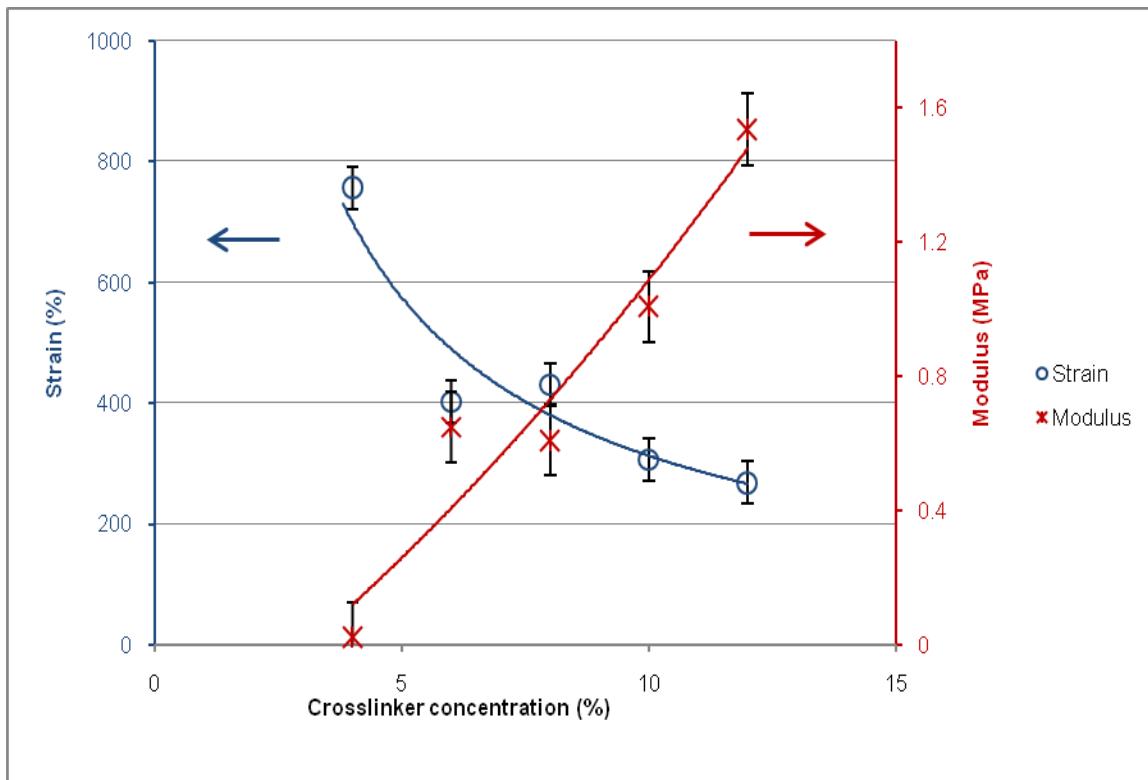


Figure 3-3. Effect of crosslinker concentration on the mechanical properties of unfilled triazole polymers (data from mini samples)

As shown in Figure 3-4 and Table 3-1, as crosslinker concentration was increased from 4 to 12 mol%, the modulus increased from 0.18 to 1.0 MPa while the strain decreased from 400 to

70%. This trend is due to increasing crosslink density. As the amount of crosslinker was increased, crosslink density was also increased, which means more crosslinks to restrict the individual chain mobility. This five-fold modulus increase and correlated stiffness increase occurs over a convenient range of crosslinker concentration and gives a facile method to control mechanical properties in these systems.

Table 3-1. Strain and modulus of unfilled triazole polymers (data from dogbone samples)

Entry	Crosslinker concentration (mol %)	Strain (%)	Modulus (Mpa)
1	4	400	0.18
2	6	200	0.38
3	8	120	0.62
4	10	88	0.93
5	12	70	1.0

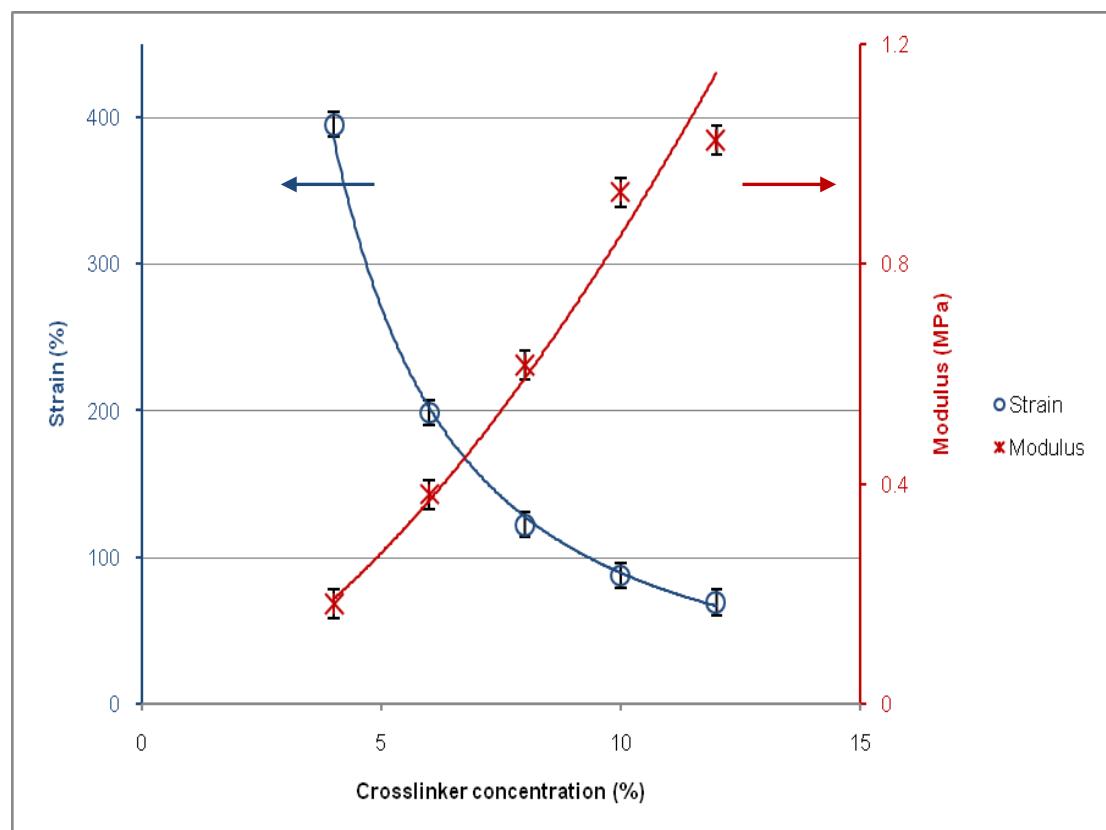


Figure 3-4. Effect of crosslinker concentration on the mechanical properties of unfilled triazole polymers (data from dogbone samples)

## Effect of crosslinker functionality<sup>b</sup>

To study the effect of crosslinker functionality on the mechanical properties of triazole polymers, crosslinkers having different functionality  $f$  ( $f=3, 4, 6, 16, 32, 64$ ) (Figure 3-5) were used with varied concentrations. Mini samples and dogbone samples were prepared (Figure 3-6), and their mechanical properties were tested manually (for mini samples) and by Instron tensile tester with a strain rate of 50mm/min (for dogbone samples).

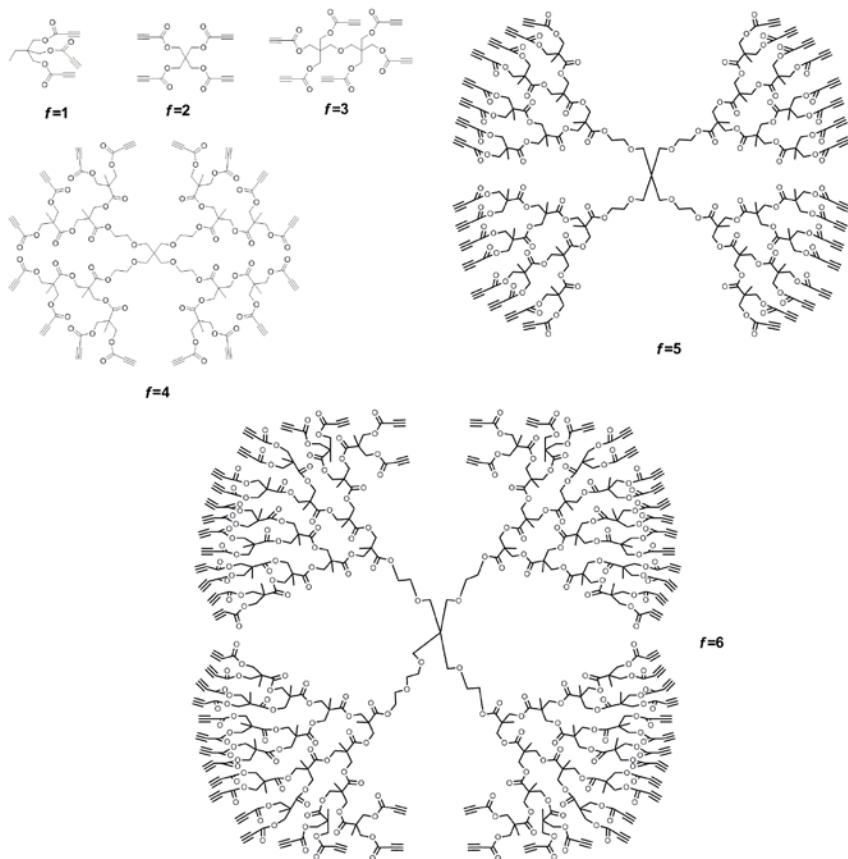


Figure 3-5. Crosslinkers with different functionality  $f$  ( $f=3, 4, 6, 16, 32, 64$ )

<sup>b</sup> The article related to the work in this section has been submitted to the journal as following:

“Effect of Crosslink Functionality on the Mechanical Properties of Crosslinked 1,2,3-Triazole-Polymers as Potential Binders for Rocket Propellants”, submitted to “Polymer” 2009

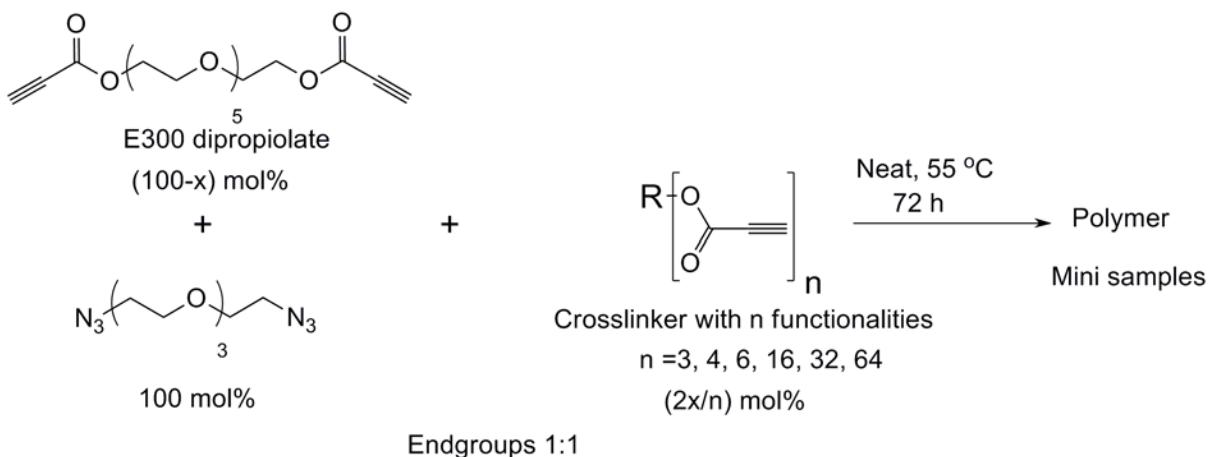


Figure 3-6. Formation of unfilled triazole polymers with different crosslinkers. X = (The number of acetylene groups provided by crosslinker) / (Total number of acetylene groups provided by crosslinker and diacetylene).

The variation trends of strain and modulus with increasing concentration of crosslinkers having different functionalities are illustrated in Figure 3-7, 3-8 (data from mini samples) and 3-9, 3-10 (data from dogbone samples). Figure 3-11 compares the stress-strain curves of the polymer having different crosslinker functionality. For figure 3-7 to 3-11, the amount of diacetylene was kept at 80 mol%, thus x (x in Figure 3-6) equals to 20 mol %. Table 3-2 lists the strain and modulus values corresponding to figure 3-9 and 3-10. As expected, for each crosslinker, with increasing crosslinker concentration, the strain decreases while modulus increases, which is consistent with previous results. (Chapter 3.1) Comparing the trends of different crosslinkers, at the same concentration of acetylene groups ( $x = 20$  mol% in Figure 6) provided by the crosslinker, the polymers having higher crosslink or junction functionality give lower strain and higher modulus than those having lower crosslink functionality. For example, at 68 mol % diacetylene, as crosslinker functionality increased from 3 to 6, the corresponding modulus of the resulting triazole polymers also increased from 0.87 to 2.73 Mpa , while the failure strain decreased from 113 to 72%, respectively. Junctions of higher functionality will be more firmly embedded within the polymer network.<sup>39</sup> With higher crosslinker functionality,

more polymer chains extend from each crosslink, which should also introduce more entanglements and steric hindrance.<sup>39</sup> Therefore such networks should be stiffer and less flexible thus have higher modulus and lower strain. However, for crosslinkers having higher average functionalities of 16, 32 and 64 end groups, such trends are not obvious. In fact, the modulus vs functionality appears to level off. This behavior may be explained by the following reasons. First, Peppas 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 of on the junction functionality  $f$ . As  $f$  increased from 2 to 20,  $M_c$  undergoes the greatest variation near  $f=4$ . It is also observed that  $M_c$  levels off if  $f$  is further increased.<sup>48</sup> It should also be noted that the crosslinkers ( $f=16, 32, 64$ ) are derived from commercial available Boltorn polyols that are, of course, mixtures of highly-branched polymers and the functionality is an average value. In addition, the highest crosslink functionality can introduce possible steric difficulties in terms of many chains terminating within a relatively small volume, which may cause incomplete end-link reaction during the polymerization.

### Conclusion

The reaction of E300 dipropiolate (**1**) with diazide from tetraethylene glycol (**2**) was selected from thirteen reactions of various organic diazides and diacetylenes as a model reaction to study the effects of crosslinker on the mechanical properties of triazole polymers. The variation trends obtained by manual testing and mechanical testing agreed with each other. The modulus of unfilled polymers increased while the strain decreased with increasing percentage of crosslinker. At the same amount of acetylene groups provided by different crosslinkers (x in Figure 3-6), higher junction functionality polymers show lower strain and higher modulus, although the mechanical properties change much less at functionalities higher than 6. Thus, the

triazole polymers with desired mechanical properties as potential rocket propellant can be obtained by selecting appropriate crosslinker and adjusting the crosslinker concentration during the polymerization. Some of the resulting triazole polymers can obtain comparable mechanical properties to those of polyurethanes.

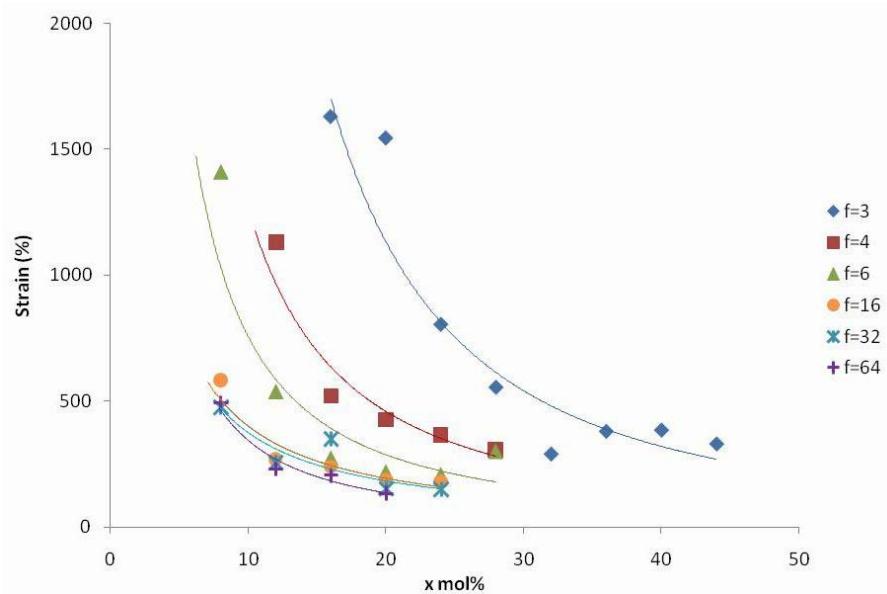


Figure 3-7. Effect of crosslinker functionality on the strain of triazole polymers (data from mini samples)

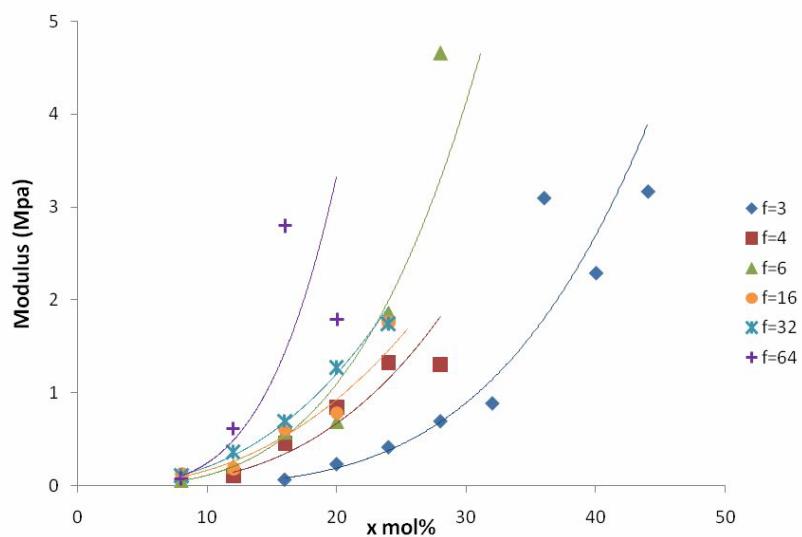


Figure 3-8. Effect of crosslinker functionality on the modulus of triazole polymers (data from mini samples)

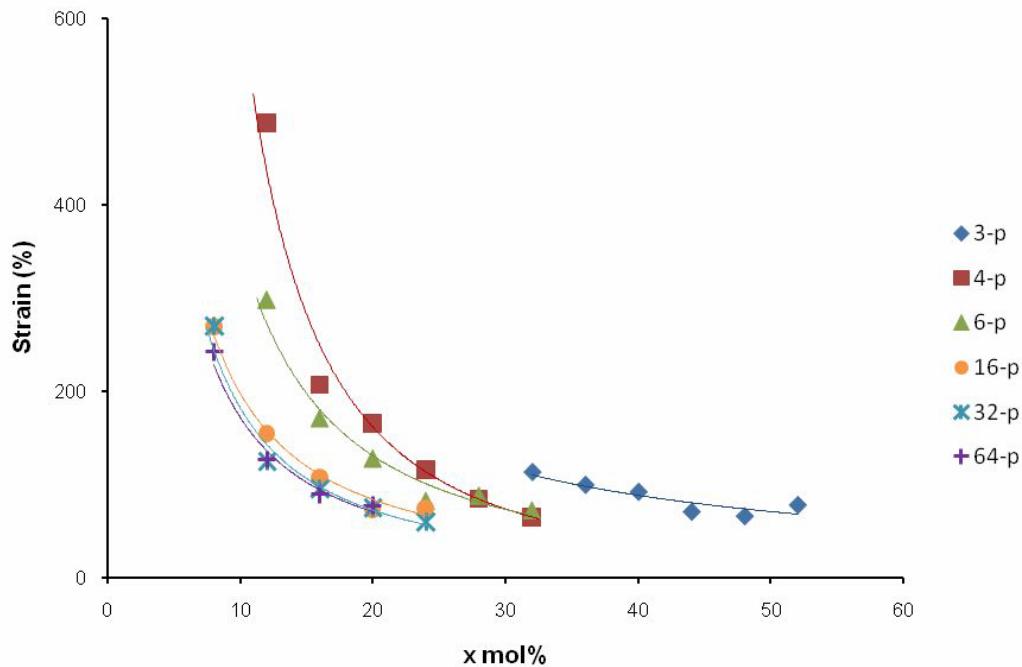


Figure 3-9. Effect of crosslinker functionality on the strain of triazole polymers (data from dogbone samples)

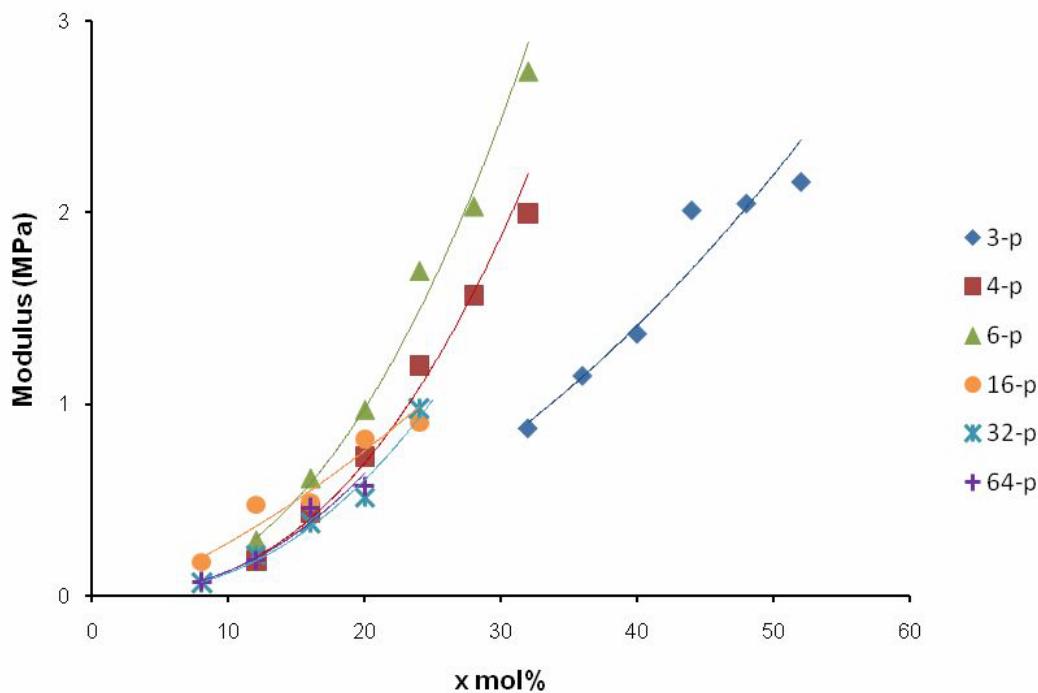


Figure 3-10. Effect of crosslinker functionality on the modulus of triazole polymers (data from dogbone samples)

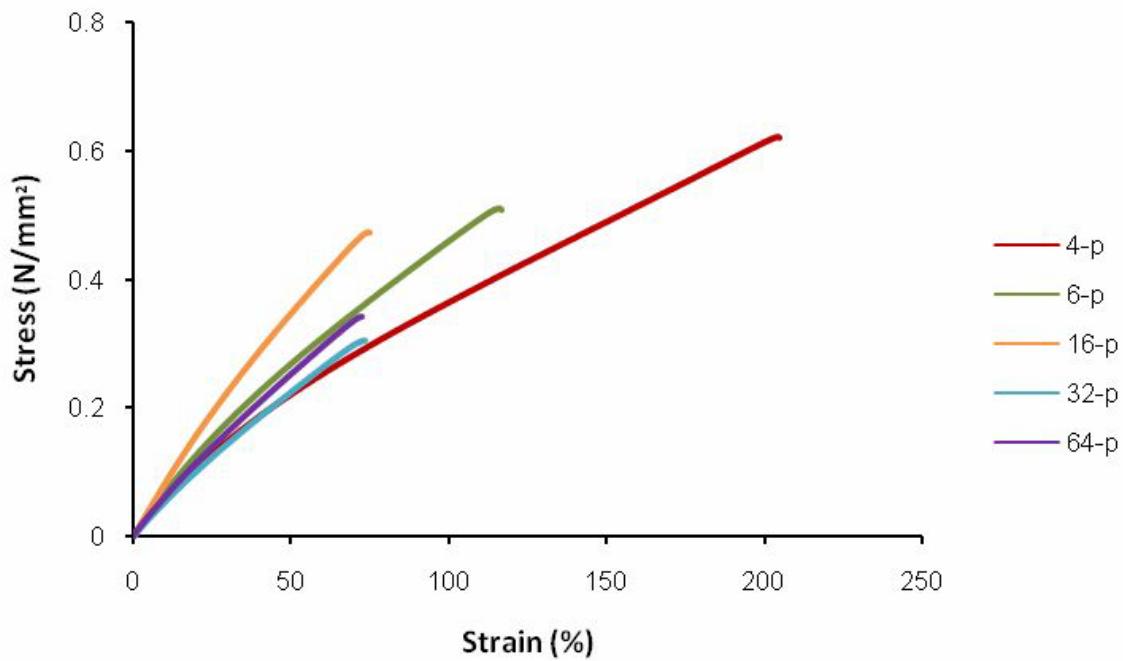


Figure 3-11. Stress-strain curves of the polymers having different crosslink functionality (data from dogbone samples)

Table 3-2. Strain and modulus values of crosslinked triazole polymers having different crosslink functionality (data from dogbone samples)

Entry	Crosslinker functionality ( $f$ )	Diacetylene 7 (mol %)	X (mol %)	Modulus (Mpa)	Strain (%)
1	3	68	32	0.87	113
2	3	64	36	1.14	99
3	3	60	40	1.36	92
4	3	56	44	2.01	71
5	3	52	48	2.04	66
6	3	48	52	2.16	78
7	4	88	12	0.18	488
8	4	84	16	0.43	207
9	4	80	20	0.72	166
10	4	76	24	1.20	116
11	4	72	28	1.57	85
12	4	68	32	1.99	65
13	6	88	12	0.29	298
14	6	84	16	0.61	171
15	6	80	20	0.97	128
16	6	76	24	1.69	82
17	6	72	28	2.03	88
18	6	68	32	2.73	72

Table 3-2. Continued

Entry	Crosslinker functionality ( $f$ )	Diacetylene 7 (mol %)	X (mol %)	Modulus (Mpa)	Strain (%)
19	16	92	8	0.17	270
20	16	88	12	0.47	155
21	16	84	16	0.48	108
22	16	80	20	0.82	73
23	16	76	24	0.90	74
24	32	92	8	0.064	269
25	32	88	12	0.21	124
26	32	84	16	0.38	95
27	32	80	20	0.51	75
28	32	76	24	0.98	59
29	64	92	8	0.074	242
30	64	88	12	0.18	126
31	64	84	16	0.46	89
32	64	80	20	0.57	77

CHAPTER 4  
EFFECT OF FILLER ON THE MECHANICAL PROPERTIES OF TRIAZOLE POLYMERS

**Effect of filler type**

To study the effect of different fillers on the mechanical properties of resulting filled triazole polymers, several fillers including inorganic salts and metals were added during the polymerization. (Figure 4-1) The concentration of filler was calculated by Equation 4-1. Samples with different fillers are compared in Table 4-1.

$$\text{Filler wt\%} = \frac{m_{\text{filler}}}{m_{\text{filler}} + m_{\text{binder}}} \times 100\% \quad 4-1$$

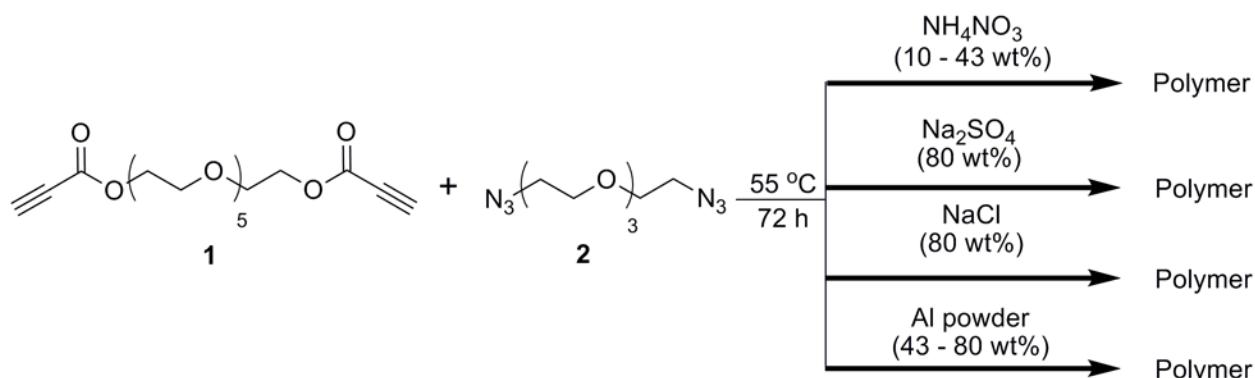


Figure 4-1. Formation of triazole polymers with different fillers

Table 4-1. Triazole polymers with different fillers (mini samples)

Entry	Filler	Sample description
1	$\text{NH}_4\text{NO}_3$	Not uniform, bubbles, elastic, easy to break from the interface between binder and crystals
2	$\text{NaSO}_4$	easy to break from the interface between binder and crystals
3	$\text{NaCl}$	easy to break from the interface between binder and crystals
4	Al	Much more uniform compared to above binders, elastic

Ammonium nitrate is commonly used as oxidizer in rocket propellant.<sup>49</sup> To investigate its effect on the mechanical properties of resulting triazole polymers, different concentrations of ammonium nitrate were added to the polymer. The resulting mini samples with ammonium nitrate filler were not uniform and had poor elasticity. The filled samples were easy to break

from the interface between ammonium nitrate crystals and triazole polymer when they were stretched. The poor mechanical properties of triazole polymers filled with ammonium nitrate crystals resulted from their large size. Large particles have smaller specific surface area compared to small ones. The tensile strength and elongation of filled polymers decrease with decreasing specific surface area of oxidizer, or increasing filler particle size.<sup>50</sup> In addition, the air bubbles in the samples also degraded their mechanical properties. Degassing the samples in a pre vacuum for several hours prior curing could greatly reduce the bubbles. (Figure 4-2)



Figure 4-2. Mini samples of triazole polymers filled with  $\text{NH}_4\text{NO}_3$  with and without degassing

Since ammonium nitrate itself or in combination with other compounds such as aluminum powder is high explosive, sodium sulfate and sodium chloride were used to replace ammonium nitrate to study the effect of inorganic oxidizer on triazole polymer's mechanical properties. To imitate real rocket propellant system, which is highly filled with 75-85wt% solids,<sup>51</sup> Attempts were made to maximize the amount of sodium sulfate or sodium chloride included in the triazole polymer. The content of sodium sulfate or sodium chloride can be maximized to 80 wt%. However, the resulting filled polymers presented the same problem as the polymers filled with ammonium nitrate: samples are not uniform and lack of good interfacial adhesion between the

binder and filler. Continuing research attempts to solve these problems by optimizing filler's size and adding wetting/coupling agents in the future work.<sup>28, 30</sup>

Compared to the polymers filled with inorganic salts, triazole polymers filled with aluminum powder were much more uniform due to smaller filler particle size, and better adhesion between filler particles and polymer binder was observed. (Figure 3-3)



Figure 4-3. Triazole polymers filled with different content of aluminum powder

### Effect of aluminum filler content

To study the effect of filler content on the mechanical properties of triazole polymers, the content of aluminum powder was varied from 0 to 74wt%. (Figure 4-4) The modulus and strain of resulting triazole polymers are listed in table 4-2. Figure 4-5 compares their stress and strain curves.

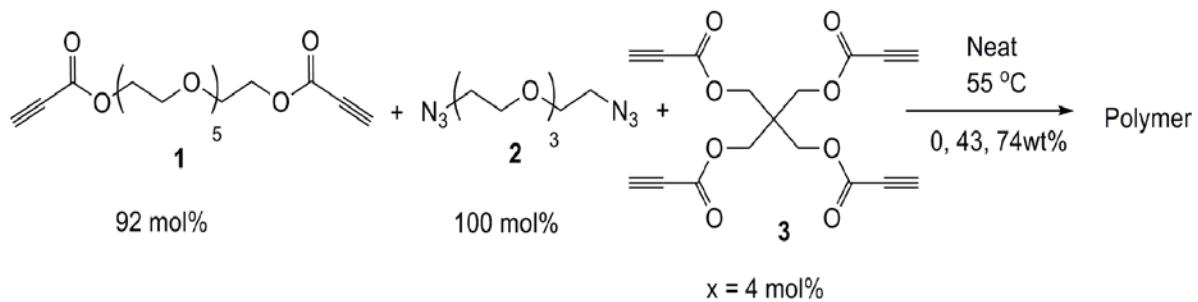


Figure 4-4. Formation of triazole polymers with different aluminum content

Table 4-2. Effect of Al filler content on the mechanical properties of triazole polymers (Strain and modulus data from dogbone samples)

Al content by weight %	Al content by volume %	Strain (%)	Modulus (Mpa)
0	0	396	0.18
43	27	308	0.50
74	58	53	5.5

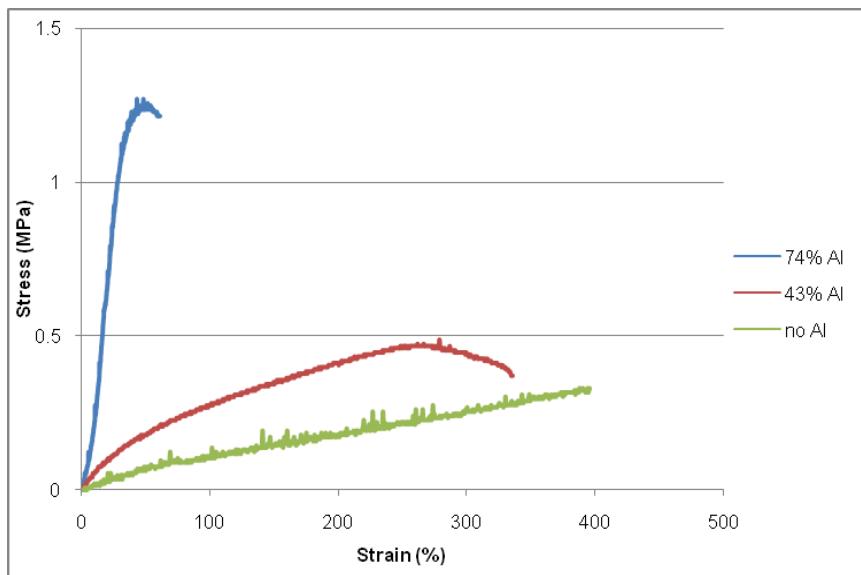


Figure 4-5. Stress-strain curves of triazole polymers with different aluminum content

As shown in Table 4-2 and Figure 4-5, with increasing aluminum content, the modulus of the polymers increased due to the addition of much stiffer aluminum powder to the polymer matrix while the strain decreased, and this is in accordance with literature which states that the filler restricts the mobility of polymer chains leading to decrease of strain.<sup>52</sup>

For unfilled triazole polymers, the modulus increases while strain decreases with increasing crosslinker concentration. (Chapter 1.3) The strain and modulus of filled triazole polymers should give the same variation trends. To verify this, 43wt% of aluminum powder was added to the crosslinked binder as a filler. (Figure 4-6) With 43wt% aluminum filler, the polymer had good processability, which facilitated the study of the crosslinker effect on the mechanical properties of filled triazole polymers. Manually tested and mechanical tested data (strain rate:

20mm/min) are plotted in Figures 4-7 and 4-8. Table 4-3 gives the specific values of strain and modulus corresponding to the data points in Figure 4-8. Compared to unfilled polymers, more measuring errors occurred for filled triazole polymer mini samples during manual testing of strain and modulus. Therefore, more mini samples were tested (with crosslinker concentration from 3 to 15%) so that a more reliable variation trend of strain and modulus of filled triazole polymers was achieved. (Figure 4-7) For unfilled and filled triazole polymers, crosslinker has the same effect on their strain and modulus: with increasing crosslinker concentration, the modulus increases while the strain decreases. As shown in Table 4-3 and Figure 4-8, for triazole polymers with 43% aluminum filler, with increasing crosslinker from 4 to 12mol%, the modulus increased from 0.5 to 3.9Mpa, an 8-fold change, while the strain decreased from 310% to 50%. (Table 4-2) Since the strain and modulus for potential propellant binders should be at least 50% and 1.4Mpa respectively, the ideal range of crosslinker concentration to achieve the goal is around 9 - 12mol%. For more highly filled triazole-based systems, the modulus can be expected to show further increases. Compared to a typical polyurethane elastomer matrix for rocket propellants (with 83wt% filler) having modulus around 2.8 Mpa, the modulus of these filled triazole polymers is comparable. It should be noted that dogbone samples with 43% aluminum filler were somewhat hard to keep uniform because heavier aluminum powder tended to settle during polymerization. This may be why larger error bars were observed in Figure 4-8 compared to Figure 3-4.

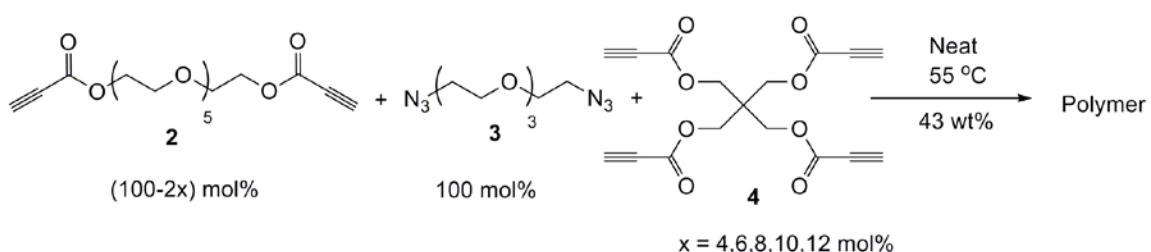


Figure 4-6. Formation of filled triazole polymers with different crosslinker concentration

Table 4-3. Strain and modulus of filled triazole polymers (43wt% Al, data from dogbone samples)

Entry	Crosslinker concentration (mol%)	Strain (%)	Modulus (Mpa)
1	4	310	0.5
2	6	180	1.1
3	8	120	1.2
4	10	95	2.2
5	12	50	3.9

Figure 4-9 compares the stress-strain curves of filled triazole polymers with different crosslinker concentration measured on the dogbone samples at controlled strain rate. The change of mechanical properties of the polymers with different crosslinker concentrations can be clearly seen from these stress-strain curves. With lower crosslinker concentration, the polymer is softer and more elastic. Likewise the samples become stiffer and more prone to elongational failure as the crosslinker concentration was increased.

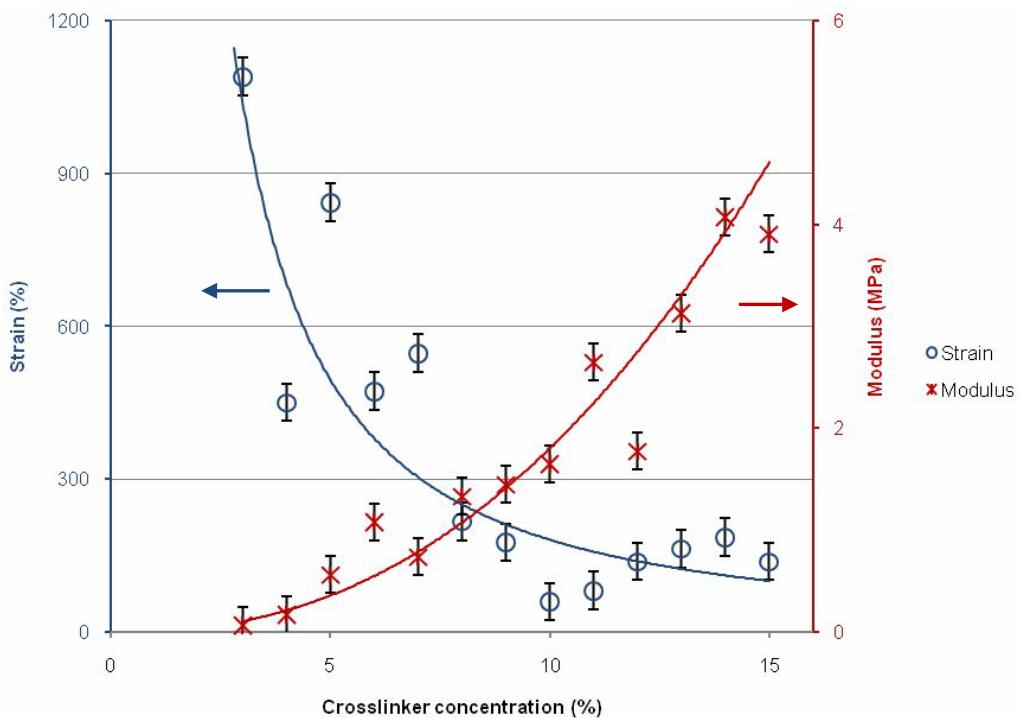


Figure 4-7. Effect of crosslinker concentration on the mechanical properties of filled triazole polymers (43wt% Al, data from mini samples)

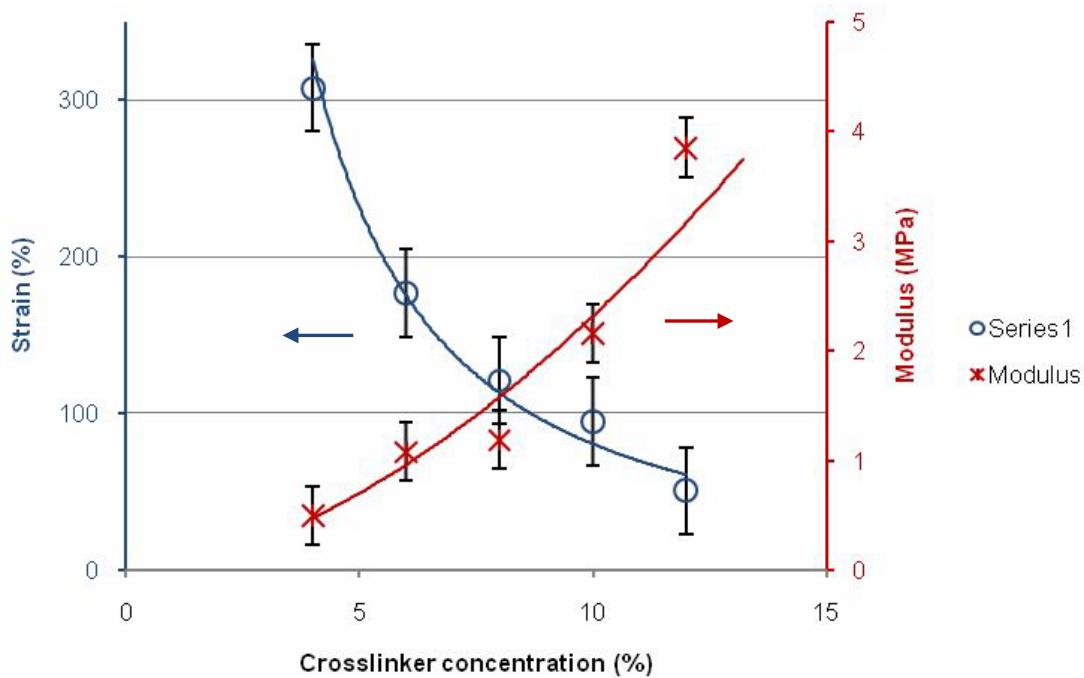


Figure 4-8. Effect of crosslinker concentration on the mechanical properties of filled triazole polymers (43wt% Al, data from dogbone samples)

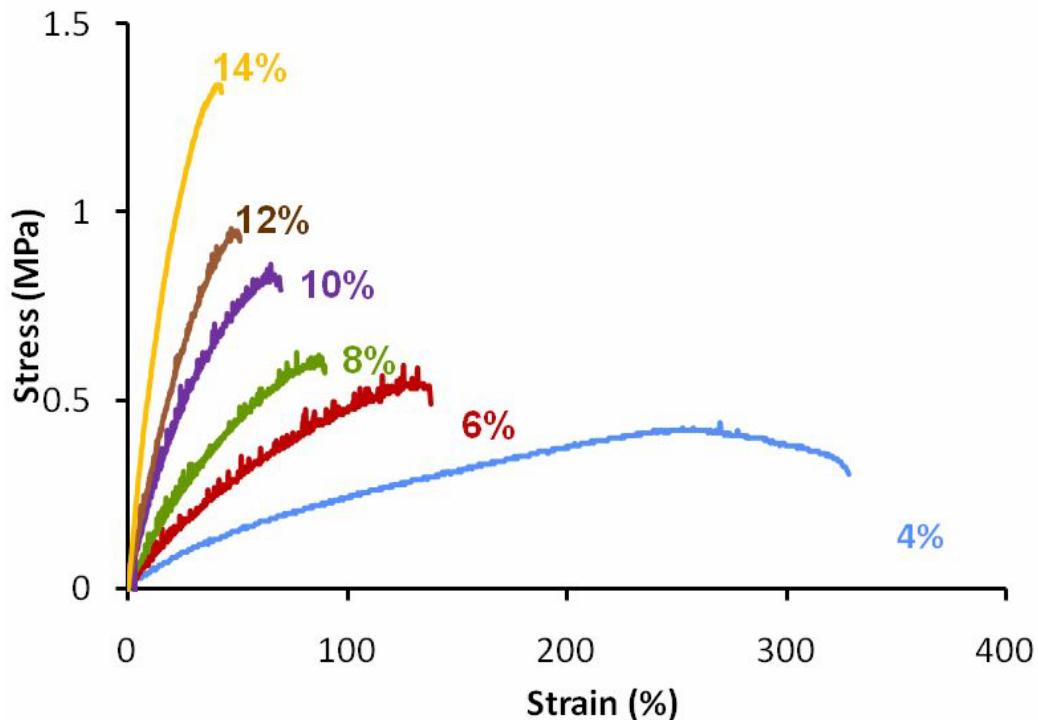


Figure 4-9. Stress-strain curves of filled triazole polymers with increasing crosslinker concentration (4mol%-14mol%)

The mechanical properties of unfilled and filled triazole polymers are compared in Figure 4-10. The modulus of filled polymers is at least two times that of the unfilled polymers due to the addition of much stiffer aluminum powder to the polymer matrix. Generally, the decrease in strain of the polymers with 43wt% Al filler is not drastic compared to the unfilled polymers, and this may be due to the good tack of these materials noted above and adhesion of binder to the filler.

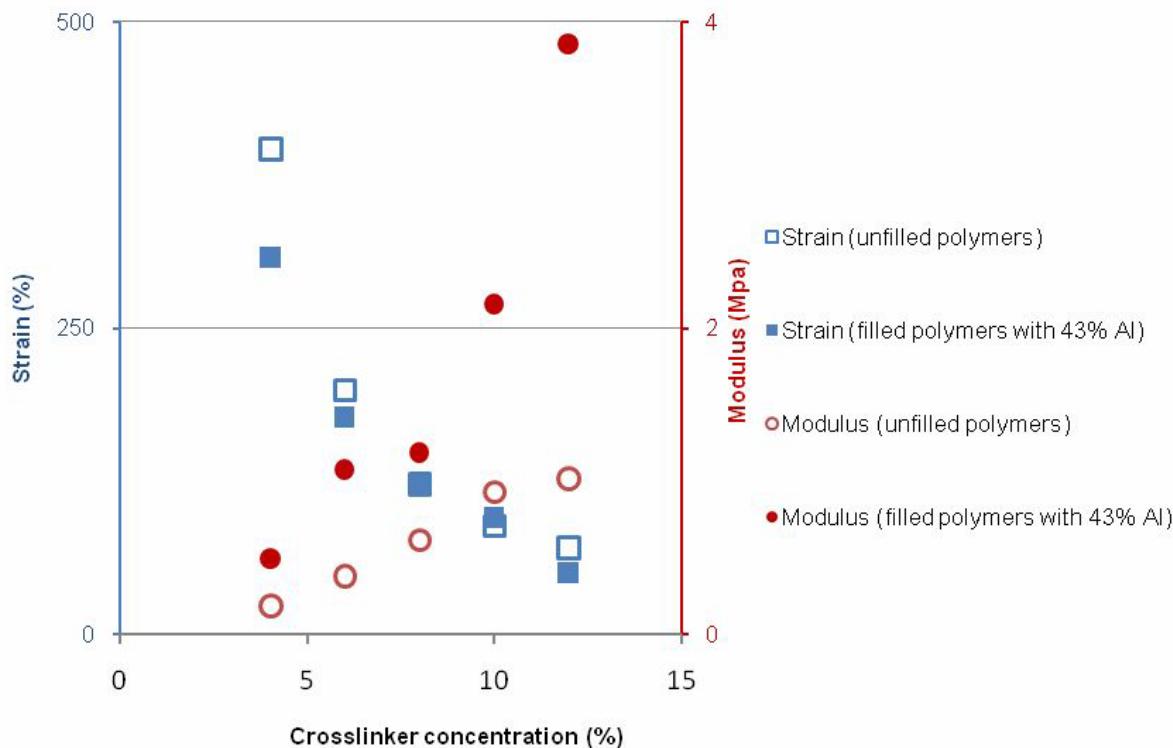


Figure 4-10. Comparison of mechanical properties of unfilled and filled (with 43% Al) triazole polymers (data from dogbone samples)

As mentioned in the introduction (Chapter 1.3), various mathematical equations have been developed to predict the increase in the modulus of an elastomer resulting from the addition of filler. Three simple equations, Guth-Smallwood equation (1-3), Eilers-Van Dijick equation (1-4) and modified Roscoe equation (1-6), were used to predict the modulus of triazole polymers with 43wt% (27vol%) aluminum filler. The data predicted by the three equations and the data

obtained experimentally were compared in Table 4-4 and Figure 4-11. As shown in Table 4-4 and Figure 4-11, the data from all three equations fit the experimental data reasonably and Guth-Smallwood equation appears to be the best. However, it is hard to say that the Guth-Smallwood equation is the best theory because the experimental data usually show great variability on filled systems.<sup>30</sup> In addition, the theoretical  $\Phi_m$  0.74 used in the equations is not the true value because the filler particles are not perfectly spherical or of exactly the same size.<sup>29</sup> Agglomeration of particles also impacts the value of  $\Phi_m$ .<sup>30</sup> The difference between theoretical and true values of  $\Phi_m$  may cause larger discrepancies between the experimental data and the data predicted by Eilers-Van Dijick equation and modified Roscoe equation.

Table 4-4. Experimental and predicted values of the modulus of filled triazole polymers (27 vol% Al)

Crosslinker concentration (mol%)	Modulus <sup>a</sup> (MPa)	Modulus <sup>b</sup> (MPa)	Modulus <sup>c</sup> (MPa)	Modulus <sup>d</sup> (MPa)
4	0.5	0.48	0.41	0.55
6	1.08	1.01	0.88	1.16
8	1.19	1.65	1.43	1.88
10	2.16	2.48	2.14	2.83
12	3.86	2.72	2.35	3.10

<sup>a</sup> data obtained from dogbone samples; Modulus<sup>b</sup> data predicted by Guth-Smallwood equation;  
<sup>c</sup> data predicted by Eilers-Van Dijick equation; <sup>d</sup> data predicted by modified Roscoe equation.

## Conclusion

The content of filler can modify the mechanical properties of resulting filled polymers. Among the fillers of ammonium nitrate, sodium sulfate, sodium chloride and aluminum, aluminum powder gave triazole polymers the best mechanical properties due to much smaller size (14um). Generally, increasing filler content increases the modulus of triazole polymers but decreases their strain. Therefore, the mechanical properties of triazole polymers can be modified by adjusting filler content. The triazole polymers with 74 wt% aluminum filler and 4mol% tetra-

propiolate crosslinker can reach 5.5Mpa modulus and 53% strain, which fulfills the requirements for rocker propellant. The effect of crosslinker concentration on filled triazole polymers is the same as that of unfilled triazole polymers. The modulus values of triazole polymers filled with 43wt% (27vol%) aluminum powder predicted by Guth-Smallwood equation approach to the experimental data.

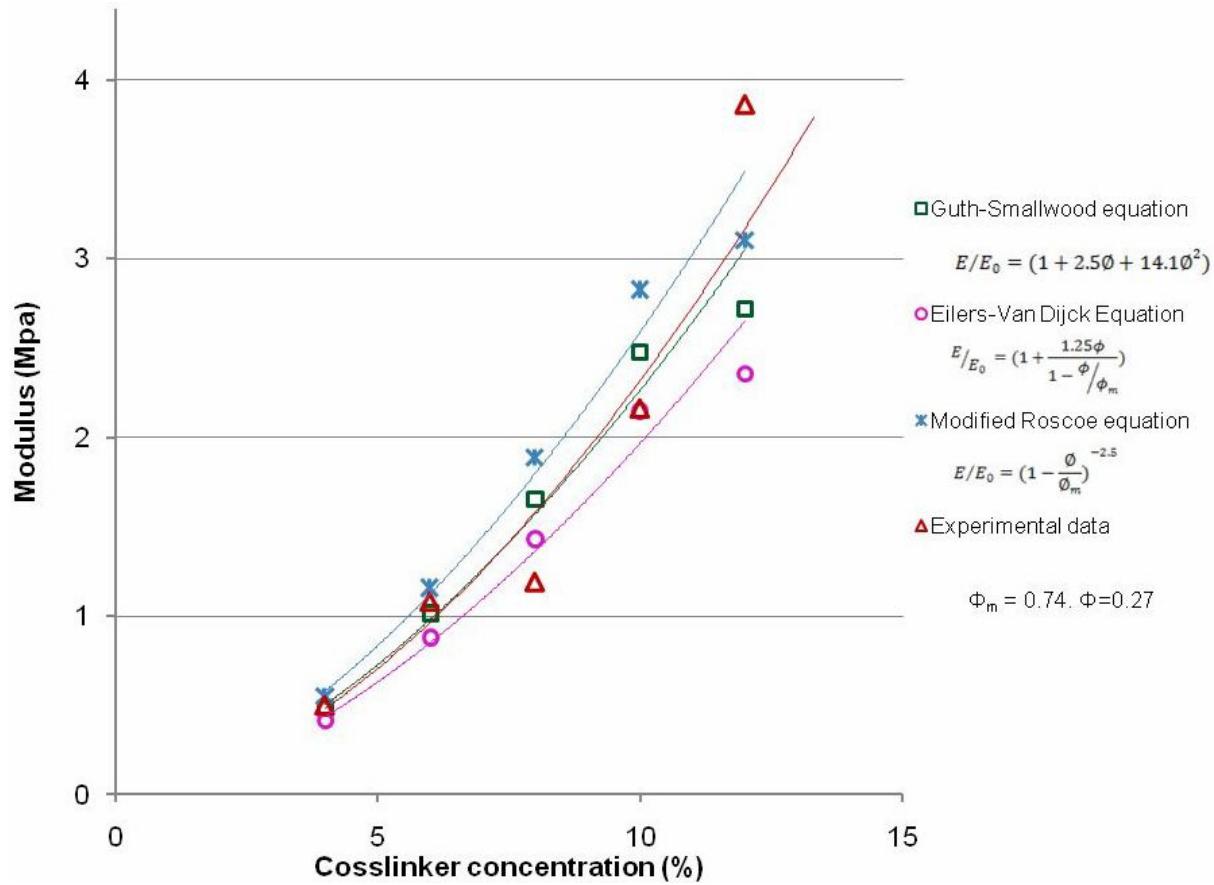


Figure 4-11. Comparison of predicted modulus and experimental modulus.

## CHAPTER 5 SUMMARY AND FUTURE WORK

### Summary

The reactions of azides with terminal alkynes to form triazole polymers following “Click” chemistry are good models to investigate the relationship between crosslinking and polymer mechanical properties since acetylene and azide groups should react with each other at 1:1 molar ratio, no small molecules are produced, the reaction should not be influenced by residual moisture, and side reactions should not occur. The reaction of E300 dipropiolate (**1**) with diazide obtained from tetraethylene glycol (**2**) was selected from thirteen reactions of various organic diazides and diacetylenes as a model reaction to study the effects of crosslinker and filler on the mechanical properties of triazole polymers.

The modulus of triazole polymers increased while the elongation at break decreased with increasing crosslinker concentration or functionality, although this trend is not obvious at crosslinker functionality higher than 6. Thus, the triazole polymers with desired mechanical properties as potential rocket propellant can be obtained by choosing a crosslinker with appropriate functionality and adjusting the crosslinker concentration during the polymerization. Some of resulting unfilled triazole polymers have comparable mechanical properties compared to commonly used polyurethane binders. For example, with the crosslinker of hexapropiolate, one of the crosslinked triazole polymers can reach 2.73 MPa modulus and still have 72% strain.

The type, size and content of fillers also affect mechanical properties of triazole polymers. Fillers of inorganic salts such as ammonium nitrate, sodium sulfate and sodium chloride don't have good adhesion with triazole polymers due to their large filler particle size, which degrades the mechanical properties of triazole polymers. Polymers filled with aluminum powders are uniform and thus was selected to study the effects of filler and crosslinker on the filled the

triazole polymers. Generally, the addition of filler improved the modulus of triazole polymers but decreased strain. The increase in the modulus due to the addition of aluminum powder predicted by the equation of Guth and Smallwood approach the experimental data. The modulus of polymers with 74wt% aluminum filler and 4mol% tetra-propionate (**3**) can reach nearly 5.5 MPa modulus while the strain is still acceptable (53%). Compared to a typical polyurethane elastomeric liner matrix with 83wt% solids for rocket propellants having modulus of 2.8 MPa, these unoptimized triazole polymers have comparable modulus.

### **Future work**

#### **Optimization of filler's size and composition**

As mentioned in chapter 4, the large size of fillers degrades filled polymer's mechanical properties. Filler particles such as sodium sulfate or sodium chloride will be ground to defined smaller sizes.<sup>53</sup> The portion of each filler size will be optimized to give the polymers best mechanical properties. Since metallic additive and oxidizer are essential ingredients in rocket propellant, aluminum powder and inorganic salts such as sodium chloride will be mixed and the fraction of each ingredient will also be optimized.

#### **Optimization of plasticizers**

Plasticizers are usually used to improve the processability of binder matrices. The mechanical properties of polymers can be affected by the type and content of plasticizers. Different plasticizers will be tried and screened. The type of the plasticizer and its concentration will be selected according to the mechanical properties of resulting triazole polymers.

#### **Preparation and characterization of high filled triazole polymers**

To imitate real rocket propellant that is highly filled, triazole polymers having 75%-85wt% fillers will be prepared and fully characterized. Tensile tests, thermal analysis such as DSC (Differential Scanning Calorimetry) and TGA (Thermo Gravimetric Analysis), and

dynamic mechanical analysis will be performed to study the properties of highly filled triazole polymers.

## LIST OF REFERENCES

1. Rastogi, R. P.; Kishore, K. Journal of Scientific&Industrial Research 1973, 32, 279.
2. Avallone, E. A.; Baumeister, T.; Sadegh, A. In Marks' Standard Handbook for Mechanical Engineers, Avallone, E. A.; Baumeister, T.; Sadegh, A., Eds.; McGraw-Hill Professional Publishing: New York, 2006, Chapter 11, p11-98.
3. Reed, R, Jr. U.S. Patent 6,103,029, August 15, 2000.
4. Ciaramitora, D.U.S. Patent 6,872,266, March 29, 2005.
5. Lutz, J. F. Angew Chem Int Ed 2007, 46, 8.
6. Wolfgang, H; Binder, R. S. Macromol. Rapid Commun. 2007, 28, 40.
7. Manzara, A. P.; Minn, L. E. US 5,681,904, Oct, 1997.
8. Takizawa, K. N., H.; Thibault, R. J.; Lowenhielm, P.; Yoshinaga, K.; Wooley, K.; Hawker, C. J. J Polym Sci Part A: Polym Chem 2008, 46, 2897-2912.
9. Nagal, A. K., Y.; Wang, X.; Omura, M.; Sudo, A.; Nishida, H.; Kawamoto, E.; Endo, T. J Polym Sci Part A: Polym Chem 2008, 46, 2316-2325.
10. Evans, R. A. Aust J Chem 2007, 60, 384-395.
11. Wu, P. F., A. K.; Nugent, A. K.; Hawker, C. J.; Scheel, A.; Voit, B.; Pyun, J.; Frechet, J. M. J.; Sharpless K. B.; Fokin, V. V. Angew Chem Int Ed 2004, 43, 3928-3932.
12. Helms, B. M., Mynar, J. L.; Hawker C. J.; Frechet, J. M. J. J Am Chem Soc 2004, 126, 15020- 15021.
13. Dirks, A. J. Van Berkel, S. S.; Hatzakis, N. S.; Opsteen, J. A.; Van Delft, F. L.; Cornelissen, J. J. L.M.; Rowan, A. E.; Van Hest, J. C. M.; Rutjes, F. P. J. T.; Nolte, R. J. M. Chem Commun 2005, 4172-4174.
14. Parent, M.; Mongin, O.; Kamada, K.; Katan, C.; Blanchard-Desce, M. Chem Commun 2005, 2029-2031.
15. Dirks, A. J. V. B., S. S.; Hatzakis, N. S.; Opsteen, J. A.; Van Delft, F. L.; Cornelissen, J. J. L.M.; Rowan, A. E.; Van Hest, J. C. M.; Rutjes, F. P. J. T.; Nolte, R. J. M. Chem Commun 2005, 4172-4174.
16. Quemener, D. D., T. P.; Barner-Kowollik, C.;Stenzel, M. H. Chem Commun 2006, 5051-5053.
17. Zhou, Y. J., K.; Chen, Y.; Liu, S. J Polym Sci Part A: Polym Chem 2008, 46, 6518-6531.

18. Joosten, J. A. F. Tholen, N. T. H.; Ei Maate, F. A.; Brouwer, A. J.; Van Esse, G. W.; Rijkers, D. T. S.; Liskamp, R. M. J.; Pieters, R. J. *Eur J Org Chem* 2005, 3182-3185.
19. Laurent, B. A.; Grayson, S. M. *J Am Chem Soc* 2006, 128, 4238-4239.
20. Diaz, D. D. Punna, S.; Holzer, P.; McPherson, A. K.; Sharpless, K. B.; Fokin, V. V.; Finn, M. G. *J Polym Sci Part A: Polym Chem* 2004, 42, 4392-4403.
21. Katritzky, A. R. Meher, N. K.; Hanci, S.; Gyanda, R.; Tala, S. R.; Mathai, S.; Duran, R. S.; Bernard, S.; Sabri, F.; Singh, S. K.; Doskocz, J.; Ciaramitato, D. A. *J Polym Sci Part A: Polym Chem* 2008, 46, 238-256.
22. Thompson, C. M. Hergenrother, P. M. *High Perform Polym* 2001, 13, 313-322.
23. Tian, J. W., L.; Huang, J.; Hu, Y.; Huang, F.; Du, L. *Polym Adv Technol* 2007, 18, 556-561.
24. Wan, L. L., Y.; Xue, L.; Tian, J.; Hu, Y.; Qi, H.; Shen, X.; Huang, F.; Du, L.; Chen, X. *J Appl Polym Sci* 2007, 104, 1038-1042.
25. Wan, L. T., J.; Huang, J.; Hu, Y.; Huang, F.; Du, L. *J Macromol Sci Part A: Pure Appl Chem* 2007, 44, 175-181.
26. Katritzky, A. R. Singh, S. K.; Meher, N. K.; Doskocz, J.; Suzuki, K.; Jiang, R.; Sommen, G. L.; Ciaramitato, D. A.; Steel, P. J. *Arkivoc* 2006, 5, 43-62.
27. Daniel, M. A. Polyurethane Binder Systems for Polymer Bonded Explosives, Report DSTO-GD-0492, Dec 2006, <http://hdl.handle.net/1947/4736>
28. Nielsen, L. E. *J. Composite Materials* 1967, 1, 100-119.
29. Nicholas, T.; *Rheologica Acta* 1968, 7, (2) 174-179.
30. Nielsen, L. E.; Landel, R. F. In Mechanical properties of polymers and composites, Faulkner, L. L., Ed.; Mechanical Engineering Series 90; Marcel Dekker, Inc: New York, 1994, Chapter 7, pp378-392.
31. Tavman, I. H. *J of Appl Polym Sci* 1996, 62, 2161-2167.
32. Fan, R.; Zhang, Y.; Huang, C.; Zhang, Y.; Fan, Y.; Sun, K. *J Appl Polym Sci* 2001, 81, 710-718.
33. Fan, Q.; Xiao, C. *Polymer Composites* 2008, 758-767.
34. Jeon, Q.; Song, S. J.; Lee, K.; Park, M. H.; Lee, S.; Hahn, S.K.; Kim, S.; Kim, B. *Carbohydrate Polymers* 2007 70, 251-257.

35. Issa Katime, E. D. a. d. A., E. Rodríguez. *J of Applied Polym Sci* 2006, 102, 4016-4022.
36. David, L; Safranski, K. G. *Polymer* 2008, 49, 4446-4455.
37. Jantas, R.; Szocik, H.; Stawski, D. *Polymer Bulletin* 2005, 53, 277-284.
38. Haska, S. B.; Bayramli, E.; Pekel, F.; Özkar, S. *Journal of Applied Polymer Science*, 64, 2347 - 2354.
39. Llorente, M. A.; Mark, J. E. *Macromol* 1980, 13, 681-685.
40. Llorente, M. A.; Mark, J. E. *J Am Chem Soc* 1980, 102, 632-636.
41. Tang, M. Y.; Mark, J. E. *Macromol* 1984, 17, 2616-2619.
42. Tsige, M.; Stevens, M. J. *Macromolecules* 2004, 37, 630-637.
43. Zhang, Y.; Hu, B.; Xia, C; Chen, Z; Yin, Q. *Hecheng Huaxue* 2002, 10, 335-337.
44. Riser, D.; Hunter, J.; Rast, R. In *AIAA/SAE/ASME/ASEE 28th Joint Propulsion Conference and Exhibit*, Nashville, TN, July 6-8, 1992, AIAA-1992-3723,
45. Cowie, J. M. G. In *Polymers: Chemistry and Physics of Modern Materials*; CRC Press: Boca Raton, 1991, Chapter 2, p31.
46. Rosato, D. V. In *Plastics Engineering Manufacturing & Data Handbook*; Rosato, D. V.; Schott, N. R.; Rosato, M. G., Eds.; Springer: Chicago, 2001; vol. 1, Chapter 2A, p 131.
47. Ramachandran, P. V.; Rudd, M. T.; Reddy, M. V. R. *Tetrahedron Letters* 2005, 46, 2547-2549.
48. Barr-Howell, B. D.; Peppas, N. A. *Polymer Bulletin* 1985, 13, 91-96
49. Engel, W.; Norbert, E.; W. E.; Annette, D.; Herrmann, M.; Lorenzo, M. J.; Kolarik, V. In *International Annual Conference of ICT*, 24th, (Energetic Materials: Insensitivity and Environmental Awareness), Fraunhoferinst, German, Mar 1-9, 1993
50. Suzuki, K. *Journal Of The Industrial Explosive Society* 1965, 26, 216-219.
51. Oberth, A. F.; Bruenner, R. S. U.S. Patent 3,919,011, Nov11, 1975.
52. Sutton, G. P.; Biblarz, O. In *Rocket Propulsion Elements*; Seifert, S. H., Ed.; Wiley: New York, 2001, Chapter 12, p499.
53. Bhattacharyya, S.; Basu, S.; DE, S. *J Material Sci* 1978, 13, 2109-2118.

## BIOGRAPHICAL SKETCH

Ling Wang was born in 1978 in Nantong, China. She graduated from Soochow University, China, in 2000 with a Bachelor of Science degree in chemistry. From the same university, she received her master's degree in education in 2003, under the supervision of Dr. Liming Shen. Then she taught chemistry in Nantong No.1 High School of Jiangsu Province, China during 2004.

Ling enrolled as a graduate student in chemistry at the University of Florida in the spring of 2006 under the direction of Dr. Randolph S. Duran. She graduated in May of 2009 with a Master of Science degree in analytical chemistry.