

## 1,2,3-Triazole Crosslinked Polymers as Binders for Solid Rocket Propellants

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**ABSTRACT:** In this study, 1,2,3-triazole crosslinked polymers were synthesized as a new binder for solid rocket propellant systems by reacting the azide groups of the polymer with the ethynyl groups of a dipolarophile curing agent. All the mixtures were cured in an oven at 52°C for 7 days, and the curing reactivity of the products was analyzed using a Fourier transform-infrared spectrometer. The carbonyl group adjacent to the triple bond, which acts as an electron-withdrawing group, considerably accelerated the 1,3-dipolar cycloaddition reaction between the azide and ethynyl functional groups, affording rubbery materials. The modulus of the polymers increased whereas the elongation at the break decreased with increasing ratio of the crosslinker to the prepolymer, resulting in highly crosslinked polymers. The molecular weights between the crosslinking points and interaction parameters of the 1,2,3-triazole crosslinked polymers were determined from the swelling data, Flory–Rehner equation, and Mooney–Rivlin equation. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40594.

**KEYWORDS:** crosslinking; elastomers; mechanical properties; swelling

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### INTRODUCTION

The need for developing high-energy rocket propellants with high ballistic performance and excellent mechanical properties is steadily increasing because of their application in the aerospace industry and long-range missiles. In particular, the development of composite solid propellants has been investigated because of their favorable storage characteristics and suitability for a high thrust within short periods of time, which can be appropriate for high-speed acceleration of an object. A composite solid propellant includes an oxidizer that supplies the necessary oxygen for combustion, a metal fuel powder, and a polymeric binder that combines these materials physically and chemically. The polymeric binder can provide sufficient mechanical strength to the propellant grains exposed to a wide range of operating temperatures and also acts as a combustible material.<sup>1</sup>

Since the 1950s, a polyurethane network system has been widely used as a binder for solid rocket propellants; this system is prepared by the polyaddition reaction of hydroxyl-terminated polymers with isocyanate curing agents. The polyurethane network

system shows excellent mechanical properties, processabilities, and aging properties compared to the conventional network system, which uses epoxy-cured carboxylated binders.<sup>2</sup> However, the polyurethane network system, which is moisture sensitive, requires the elimination of moisture from both propellant ingredients and manufacturing environments. Furthermore, when ammonium dinitramide (ADN), the well-known substitute for ammonium perchlorate, is used as the chlorine-free smokeless oxidizer, the polyurethane network system may suffer from the hydrolysis problem because of ADN's highly hygroscopic properties.<sup>1</sup> Consequently, a new curing system for solid propellants to replace the urethane curing systems is being increasingly demanded.

Recently, a binder prepared using a 1,2,3-triazole network system has been developed as an eco-friendly binder. In this system, hygroscopic ADN can be applied as an oxidizer because the 1,2,3-triazole networks are not sensitive to moisture and are free of side reaction during the synthesis process.<sup>3–6</sup> 1,2,3-Triazole crosslinked polymers are readily formed by the 1,3-dipolar cycloaddition reaction between azide and ethynyl functional groups, and have been studied widely by Huisgen,<sup>7</sup> Katritzky

et al.,<sup>8</sup> and Wang et al.<sup>9</sup> for various reactants, curing temperature, and catalysts. Since the late 1980s, the solid rocket propellant binder, which is composed of 1,2,3-triazole crosslinked polymer, has been the subject of many applications and distinguished patents.<sup>2,10,11</sup> Many new studies<sup>5,6,8,9</sup> on the use of 1,2,3-triazole crosslinked binder as propellants have also been published in recent years.

Sukumaran et al.<sup>12</sup> synthesized in-chain modified acrylic copolymers using azide and ethynyl groups. They then introduced “click reaction” at 60°C/20 h by using Cu(I) catalyst and acetonitrile solvent, and calculated the average molecular weight between the crosslinking points by measuring the swelling ratio and storage modulus using dynamic mechanical analyzer. Min et al.<sup>13</sup> evaluated the mechanical properties of 1,2,3-triazole side-linked polyurethane networks using glycidyl azide polymer (GAP) diol and GAP polyol, which is an in-chain modified by the azide group, that is, pendant azides are present. Under dual curing systems based on both isocyanate and dipolarophile curing agents as well as those of polyurethane networks prepared under a single curing system based on a mixture of isocyanate curing agents. Min et al.<sup>14</sup> also evaluated the mechanical properties of 1,2,3-triazole crosslinked polymer binders using three types of diazide prepolymers, which are chain-end modified using the azide group, one triazide chain-end crosslinker, and two types of ethynyl curing agents: *bis*-propargyl succinate (BPS) and 1,4-*bis*(1-hydroxypropargyl)benzene. However, the recommended curing conditions (below 60°C, 7 days) for the solid propellant cannot be applied to these binders because of low activity of the curing agents; therefore, the binders were cured at 80°C for 7 days, followed by curing at 60°C for 2 weeks.

In this study, we studied an appropriate 1,2,3-triazole network system that can form 1,3-dipolar cycloaddition sufficiently well between azide and ethynyl functional groups at a low curing temperature of 52°C for 7 days by controlling the chemical structure of dipolarophile curing agents. The reactivities of ethynyl curing agents were investigated by measuring the change in the FTIR absorption peak of azide and ethynyl functional groups in the 1,2,3-triazole crosslinked polymers. The mechanical properties of these binders were also investigated by the tensile and swelling tests.

## EXPERIMENTAL

### Materials

**Preparation of PCP 0260 Diazide Prepolymer.** Methanesulfonyl chloride (15.3 g, 0.133 mol) was added dropwise to a solution of polycaprolactone 0260 (PCP 0260, 100 g, 0.033 mol) and pyridine (10.6 g, 0.133 mol) in CH<sub>2</sub>Cl<sub>2</sub> (1 L). The resulting solution was stirred for 3 days at room temperature. After H<sub>2</sub>O (150 mL) was added, the solution was stirred for 1 day. The reaction mixture was subsequently washed with saturated aqueous NaHCO<sub>3</sub> solution (200 mL), 1N HCl (200 mL), and H<sub>2</sub>O (200 mL). The organic layer was dried with Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuum to afford dimesylate intermediate (77.6 g, 0.025 mol), which was dissolved in DMF (1 L). NaN<sub>3</sub> (16.0 g, 0.246 mol) was then added to the solution. The resulting solution was heated to 100°C for 2 days and then concentrated in

vacuum. The residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> (200 mL × 3) and H<sub>2</sub>O. The organic layer was separated, dried with Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuum to obtain the desired diazide prepolymer in 58% yield.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 1.32–1.40 (m, 30H), 1.53–1.66 (m, 60H), 2.26–2.35 (m, 28H), 3.25 (t, 2H), 3.67 (t, 2H), 4.02–4.05 (m, 28H), 4.21 (t, 2H). The FTIR spectra did not show a hydroxyl peak, but showed an azide peak at 2095 cm<sup>-1</sup>.

**Preparation of PCP 0310 Triazide Crosslinker.** Polycaprolactone 0310 (PCP 0310, 109 g, 0.121 mol) was subjected to the same reaction conditions as those used for the preparation of diazide prepolymer from PCP 0260 to obtain the desired triazide crosslinker in 67% yield.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 1.32–1.42 (m, 18H), 1.60–1.66 (m, 33H), 2.26–2.33 (m, 15H), 3.23–3.32 (m, 6H), 3.91–4.05 (m, 14H). The FTIR spectra did not show a hydroxyl peak, but showed an azide peak at 2101 cm<sup>-1</sup> (Figures 1 and 2).

**Preparation of Diprop-2-ynyl Succinate (Curing Agent A).** *p*-Toluenesulfonic acid (3.21 g, 0.016 mol) was added to a solution of succinic acid (20.0 g, 0.169 mol) and propargyl alcohol (23.8 g, 0.424 mol) in benzene (500 mL). The resulting solution was heated to 100°C for 2 days using a Dean-Stark trap to remove H<sub>2</sub>O. The reaction mixture was concentrated in vacuum and the residue was subjected to column chromatography using ethyl acetate (EtOAc)–hexane (1/3) solution as the eluent to obtain the desired curing agent A in 52% yield.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 2.46 (t, *J* = 2.4 Hz, 2H), 2.68 (s, 4H), 4.68 (d, *J* = 2.4 Hz, 4H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 28.7, 52.2, 75.0, 77.3, 171.2. The FTIR spectra did not show a hydroxyl peak, but showed an ethynyl peak at 2122 cm<sup>-1</sup>.

**Preparation of 1,2-Di(propioloyloxy)ethane (Curing Agent B).** Ethylene diol (10.0 g, 0.161 mol) and propiolic acid (45.1 g, 0.644 mol) were subjected to the same reaction conditions as those for the preparation of curing agent A. The reaction mixture was subjected to column chromatography using the EtOAc–hexane (1/3) solution as the eluent to obtain the desired curing agent B in 56% yield.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 2.92 (s, 2H), 4.41 (s, 4H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 63.0, 74.0, 75.7, 152.2. The FTIR spectra did not show a hydroxyl peak, but showed an ethynyl peak at 2122 cm<sup>-1</sup>.

**Preparation of Propargyl Ether of Polycaprolactonediol (Curing Agent C).** Propargyl bromide (13.5 g, 0.113 mol) was added to a solution of PCP (530 g mol<sup>-1</sup>, 20.0 g, 0.037 mol) and KOH (6.35 g, 0.113 mol) in DMF (200 mL). The resulting solution was stirred at room temperature for 2 days and then concentrated in vacuum. The residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> (200 mL × 3) and H<sub>2</sub>O. The organic layer was separated, dried with Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuum. The residue was subjected to column chromatography using the EtOAc–hexane (2/1) solution as the eluent to obtain the desired curing agent C in 52% yield.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 1.34–1.41 (m, 21H), 1.54–1.66 (m, 49H), 2.26–2.35 (m, 20H), 2.42 (s, 2H), 2.45 (m, 1H),

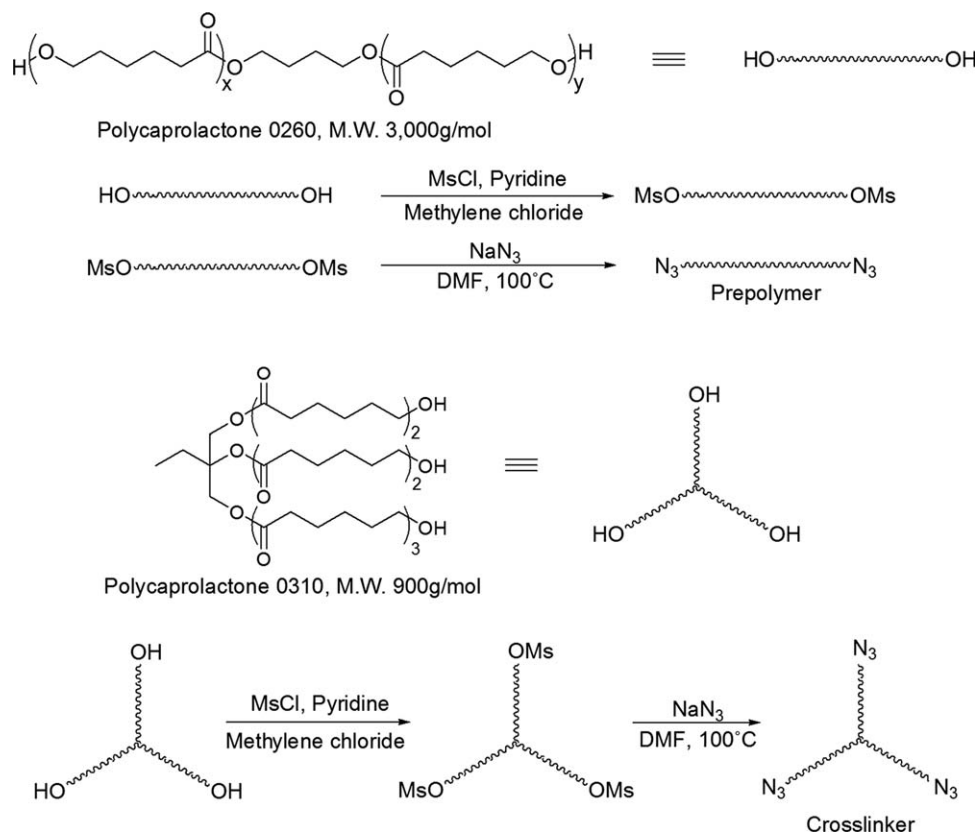


Figure 1. Azidation of prepolymer and crosslinker.

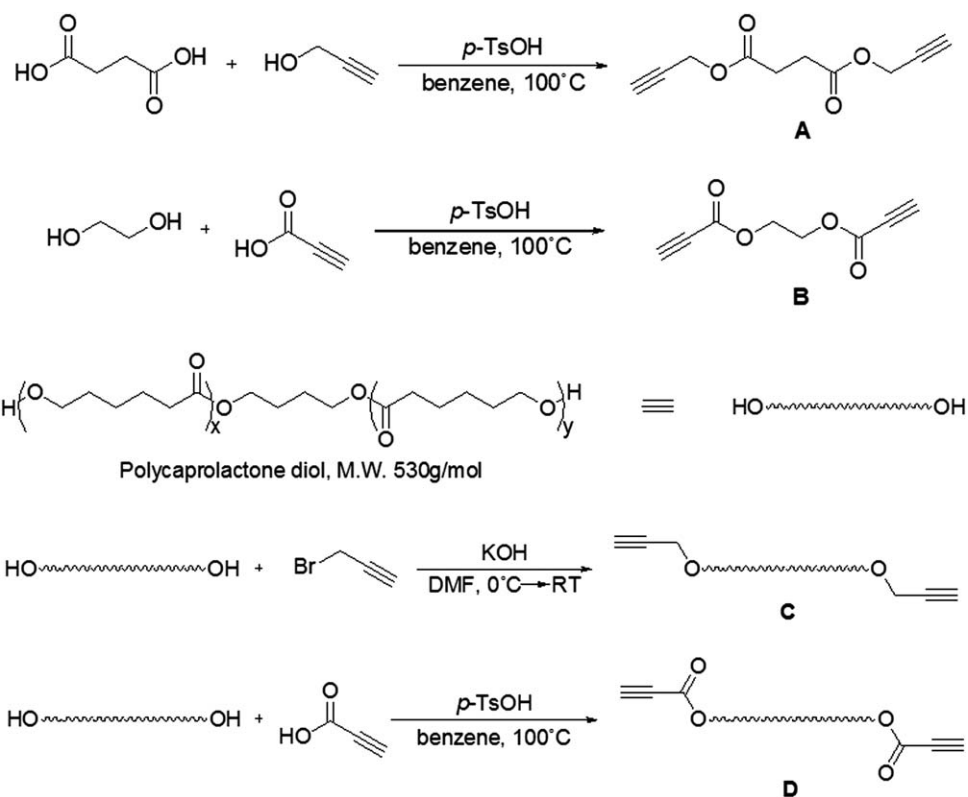


Figure 2. Four types of dipolarophile curing agent.

**Table I.** Properties of Raw Materials

Materials	Prepolymer PCP 0260	Crosslinker PCP 0310	Curing agent A	Curing agent B	Curing agent C	Curing agent D
Molecular weight (g mol <sup>-1</sup> )	3050.026	975.038	194.190	166.133	606.098	634.065
Index of the functional group (equiv kg <sup>-1</sup> )	0.656	3.077	10.299	12.039	3.300	3.154

3.61–3.69 (m, 17H), 4.02–4.05 (m, 15H), 4.11 (s, 1H), 4.11–4.22 (m, 8H). The FTIR spectra did not show a hydroxyl peak, but showed an ethynyl peak at 2115 cm<sup>-1</sup>.

**Preparation of Propiolic Ester of Polycaprolactonediol (Curing Agent D).** Propargyl bromide (13.5 g, 0.113 mol) was added to a solution of PCP (530 g mol<sup>-1</sup>, 20.0 g, 0.037 mol) and KOH (6.35 g, 0.113 mol) in DMF (200 mL). The resulting solution was stirred at room temperature for 2 days and then concentrated in vacuum. The residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> (200 mL × 3) and H<sub>2</sub>O. The organic layer was separated, dried with Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuum. The residue was subjected to column chromatography using the EtOAc-hexane (2/1) solution as the eluent to obtain the desired curing agent C in 52% yield.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 1.34–1.41 (m, 21H), 1.54–1.66 (m, 49H), 2.26–2.35 (m, 20H), 2.42 (s, 2H), 2.45 (m, 1H), 3.61–3.69 (m, 17H), 4.02–4.05 (m, 15H), 4.11 (s, 1H), 4.11–4.22 (m, 8H). The FTIR spectra did not show a hydroxyl peak, but showed an ethynyl peak at 2115 cm<sup>-1</sup>.

**Instrumental Analysis.** <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded by using a JNM-AL400 spectrometer (JEOL, Japan), operating at 400 and 100 MHz, respectively. CDCl<sub>3</sub> was used as the solvent. The FTIR spectra were measured on a Nicolet 6700 spectrometer (Thermo Scientific) by using an ATR method with diamond crystal in the range 650–4000 cm<sup>-1</sup> with a resolution of 8 cm<sup>-1</sup>.

#### Preparation of 1,2,3-Triazole Crosslinked Polymers

For the preparation of 1,2,3-triazole crosslinked polymers, dipolarophile curing agents, a prepolymer, and a crosslinker were

**Table II.** Codes of 1,2,3-Triazole Crosslinked Polymers

Codes	Curing agent	Equivalent ratio (-C≡CH/-N <sub>3</sub> )	Crosslinker contents
P-20A	A	1.1	20 wt % to prepolymer
P-30A	A	1.1	30 wt % to prepolymer
P-40A	A	1.1	40 wt % to prepolymer
P-20B	B	1.1	20 wt % to prepolymer
P-30B	B	1.1	30 wt % to prepolymer
P-40B	B	1.1	40 wt % to prepolymer
P-20C	C	1.1	20 wt % to prepolymer
P-30C	C	1.1	30 wt % to prepolymer
P-40C	C	1.1	40 wt % to prepolymer
P-20D	D	1.1	20 wt % to prepolymer
P-30D	D	1.1	30 wt % to prepolymer
P-40D	D	1.1	40 wt % to prepolymer

mixed under an equivalent ratio (-C≡CH/-N<sub>3</sub>) of 1.1 in a rotary evaporator, followed by degassing at 55°C for 30 min. Tables I and II show the properties of raw materials and formulation information. The reaction catalyst was not used for the preparation of 1,2,3-triazole crosslinked polymers because of its solubility and dispersion problems in the reaction mixture.<sup>5</sup>

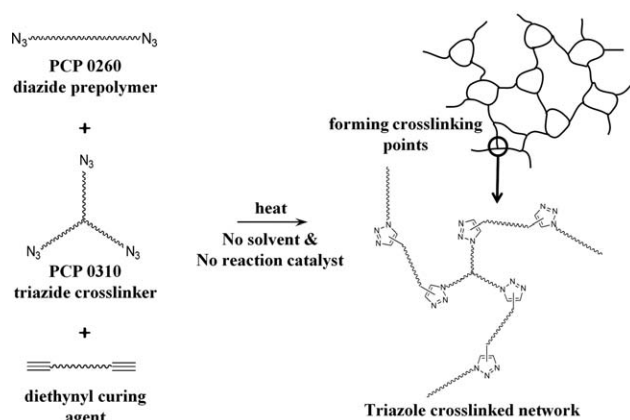
The mixture was poured into a Teflon-coated steel mold and cured at 52°C for 7 days. Schematic diagram for the formation of 1,2,3-triazole crosslinked network is shown in Figure 3. All 1,2,3-triazole crosslinked polymers were cut into a dumbbell-shaped specimens (35 × 6 × 1 mm, ISO 37 type 4) to measure the mechanical properties using a universal testing machine (KSU-05M-C, KS-tester, Korea) at a crosshead speed of 50 mm min<sup>-1</sup> at 52°C.

#### Swelling of 1,2,3-Triazole Crosslinked Polymers

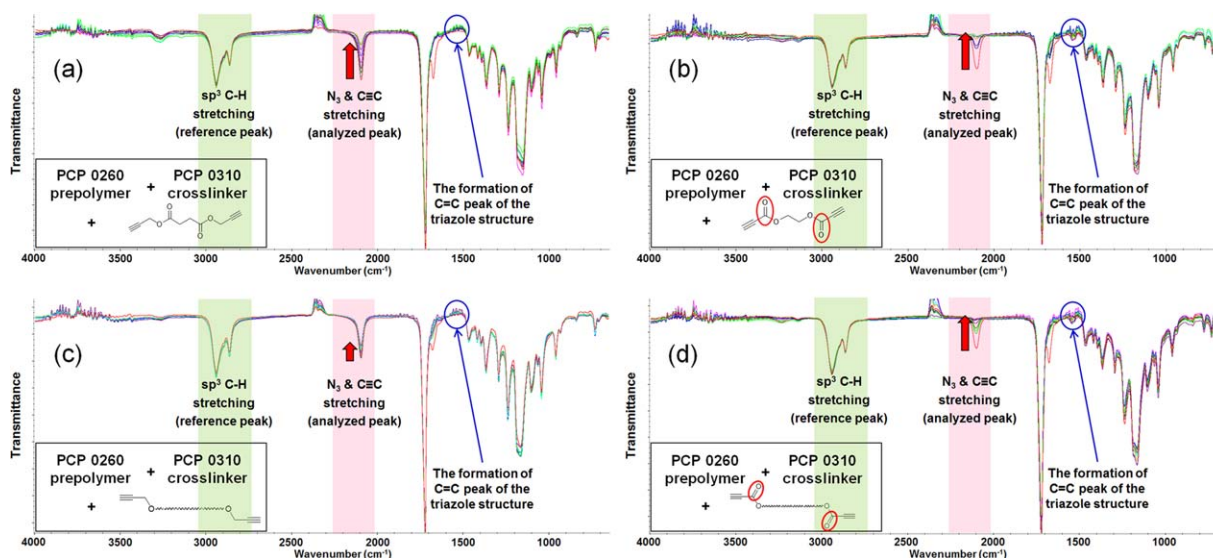
To calculate the degree of crosslinking of synthesized 1,2,3-triazole crosslinked polymers, various organic solvents with solubility parameters in the range 14.9–29.7 MPa<sup>1/2</sup> (*n*-hexane, 14.9; cyclohexane, 16.8; toluene, 18.3; chloroform, 18.7; methylene chloride, 20.2; pyridine, 21.7; dimethylformamide, 24.7; ethyl alcohol, 26.2; methyl alcohol, 29.7 MPa<sup>1/2</sup>) were used in the swelling experiment. The specimens were cut into similar sizes (20 × 2 × 1 mm, 50 mg) and immersed in solvents for 1 day at room temperature. Subsequently, the specimens were swollen and weighed to obtain the swelling ratio (*Q*) from the following eq. (1):

$$Q (\%) = \left\{ 1 + \left( \frac{\omega_2}{\omega_1} - 1 \right) \frac{\rho_2}{\rho_1} \right\} \times 100 \quad (1)$$

where  $\omega_1$  and  $\omega_2$  are the weights of the unswollen and swollen specimens and  $\rho_1$  and  $\rho_2$  are the densities of the solvent and polymer, respectively.

**Figure 3.** Formation of 1,2,3-triazole crosslinked network.





**Figure 4.** Curing characteristics (FTIR spectra, 7 days elapsed) of dipolarophile curing agents according to the type of curing agent and the position of a carbonyl group: (a) curing agent A, (b) curing agent B, (c) curing agent C, and (d) curing agent D. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

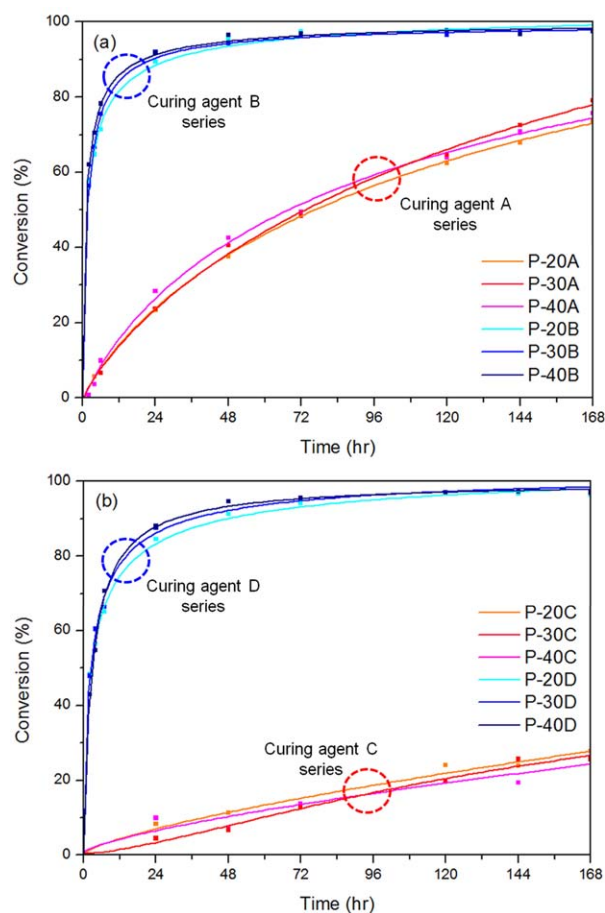
## RESULTS AND DISCUSSION

### Characterization of Curing Behavior

The FTIR spectra were measured to confirm the formation of 1,2,3-triazole crosslinked polymers. Generally, it has been known that the rate of 1,3-dipolar cycloaddition reaction depends on the chemical structure of the moiety adjacent to the azide and ethynyl functional groups. Reportedly, electron-withdrawing groups close to triple bonds and electron-donating groups close to azides accelerate the 1,3-dipolar cycloaddition reaction.<sup>5</sup> In this study, the curing kinetics corresponding to the presence or absence of the carbonyl group close to the triple bonds were compared by using dipolarophile curing agents possessing a similar structure; this kinetics has not been investigated in previous studies.

The formation of the 1,2,3-triazole crosslinked polymers was investigated using an FTIR spectrometer every day for 7 days. Conversion was carried out from the ethynyl and azide absorption peak area (at 2030–2260  $\text{cm}^{-1}$ ), which is reduced in accordance with the generated 1,2,3-triazole network, compared to the  $\text{sp}^3$  C-H absorption peak area (at 2710–3045  $\text{cm}^{-1}$ ), which does not change during the reaction, as shown in Figure 4. As reported,<sup>15</sup> the C=C absorption peak of the triazole structure (at 1508–1558  $\text{cm}^{-1}$ ) was also confirmed in our works, but this peak was very weak. For this reason, the triazole absorption peak was not used for the analysis of the conversion. When the carbonyl group was adjacent to the triple bonds, as shown in Figure 4(b,d), the triazole peak was detected quite clearly, and the azide and the ethynyl peak areas decreased rapidly than the cases of Figure 4(a,c).

Conversion was completed after 7 days by using the curing agents B and D in which the carbonyl group was adjacent to the triple bonds, as shown in Figure 5 and Tables III and IV. The initial curing reactivity was slightly accelerated by



**Figure 5.** Conversion of azide functional group in the reaction of PCP 0260 prepolymer, PCP 0310 crosslinker, and (a) curing agent A, B, or (b) curing agent C, D. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Table III.** Final Conversion of 1,2,3-Triazole Crosslinked Polymers According to Monomer-Type Curing Agent A and B

Codes	P-20A	P-30A	P-40A	P-20B	P-30B	P-40B
Final conversion (%)	73.13	74.45	78.06	99.06	97.78	98.25

**Table IV.** Final Conversion of 1,2,3-Triazole Crosslinked Polymers According to the Oligomer-Type Curing Agent C and D

Codes	P-20C	P-30C	P-40C	P-20D	P-30D	P-40D
Final conversion (%)	27.79	24.31	26.60	97.97	98.49	97.87

increasing the crosslinker contents. As a result, these products showed rubbery characteristics under the curing condition of 52°C for approximately 3 days. On the other hand, when curing agents A and C were used, the carbonyl group was not adjacent to the triple bonds, full conversion was not obtained, and the cured polymer was still brittle and weak even after curing for 7 days. Moreover, the formation of the polymers decreased when the oligomer-type dipolarophile curing agent C was used.

### Mechanical Properties

Under the given curing condition (52°C for 7 days), 1,2,3-triazole crosslinked polymers prepared using curing agents B and D were able to form a network that showed rubbery properties. The mechanical properties of the cured polymers are shown in Figure 6 and Table V. Curing agents A and C could not introduce a polymer binder into the rubbery matrix; therefore, we could not measure the mechanical properties of the binder network. According to a recent study,<sup>14</sup> 1,2,3-triazole crosslinked polymers consisting of PCP 0260 diazide prepolymer, PCP 0310 triazide crosslinker, and BPS, which is indicated as curing agent A in our work, resulted in poor tensile strength and elongation at the break (0.620 MPa, 734% of P-20A; 0.820 MPa, 204% of P-30A, respectively), even after using curing conditions such as 80°C for 7 days, followed by curing at 60°C for 2 weeks, which is not commonly used for the manufacturing of solid propellants. Actually, in the family of solid propellants, keeping incompletely cured energetic binders at 80°C for long durations is not recommended owing to the possibility of the decomposition of energetic materials.<sup>14</sup> We could confirm the importance of the carbonyl group adjacent to the triple bond by the direct comparison of the mechanical properties of the binder network using curing agents A and B, which shows that the chemical structures of dipolarophile curing agents were similar, except for the position of carbonyl group. P-20B and P-30B, similar crosslinking systems of P-20A and P-30A mentioned above, showed excellent tensile strength and elongation at the break (1.351 MPa, 605.9% of P-20B; 1.094 MPa, 355.3% of P-30B, respectively) under milder curing conditions of 52°C for 7 days, whereas P-20A and P-30A did not convert to a rubbery state. The formation of the highly crosslinked polymer led to an increase in the 100% modulus of the cured binder, whereas the tensile strength (0.914 MPa of P-40B) was decreased due to the reduction of the elongation at the break (192.8% of P-40B). Similarly, this tendency of the mechanical properties was also shown in the binder network using curing agent D. However, the product that used curing agent B showed higher tensile

strength, higher modulus, and lower elongation at the break than the product that used curing agent D at the same contents of the crosslinker (P-20B vs. P-20D, P-30B vs. P-30D, and P-40B vs. P-40D, respectively). It is concluded that the mechanical properties of polymers are also dependent on the index of the functional group in accordance with the molecular weight of the curing agent.

### Swelling Test

The measured swelling ratios of the 1,2,3-triazole crosslinked polymers in various organic solvents are shown in Figure 7. The relationship of the swelling ratio as a function of the solubility parameter of solvents shows Gaussian distributions, as in the usual cases of crosslinked network polymers. When the amounts of crosslinkers were increased, a highly crosslinked network polymer was obtained, as a result, the swelling ratio was decreased.

For the crosslinked network polymers, the crosslinking density and average molecular weight between the crosslinking points ( $M_c$ ) can be calculated from the swelling data and the solubility parameter of the polymer. This parameter should be determined for the study of crosslinked polymer networks.

From the swelling data, the crosslinking density of the network polymer can be calculated from the Flory–Rehner equation, which can be used for filled network polymers, as shown in eq. (2):<sup>16–18</sup>

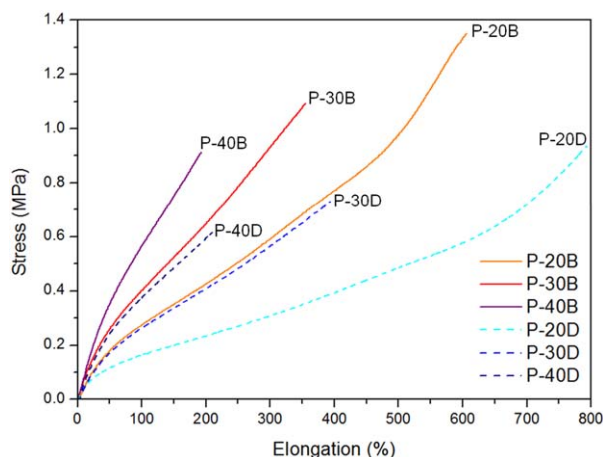
$$v = \frac{1}{2M_c} = - \frac{\ln(1-V_1) + V_1 + \chi V_1^2}{2\rho V_0 (V_1^{1/3} - V_1/2)} \quad (2)$$

Here,  $v$  is the crosslinking density ( $\text{mol g}^{-1}$ ),  $M_c$  is the average molecular weights between crosslinking points ( $\text{g mol}^{-1}$ ),  $\rho$  is the density ( $\text{g cm}^{-3}$ ) of the specimen,  $V_1$  is the volume fraction of rubber in the swollen gel at equilibrium,  $V_0$  is the molar volume of the solvent ( $\text{cm}^3 \text{mol}^{-1}$ ), and  $\chi$  is the polymer–solvent interaction parameter.

To determine the crosslinking density from the Flory–Rehner equation, the polymer–solvent interaction parameter  $\chi$  should be determined, which is sensitively dependent on factors such as the type of polymer, molecular weight, the type of solvent, temperature, and crosslinking structure.

$$\chi = \beta_1 + \frac{V_0}{RT} (\delta_p - \delta_s)^2 \quad (3)$$

The above eq. (3) is widely used to determine  $\chi$  based on the Hilderbrand solubility parameters, where  $\delta_p$  and  $\delta_s$  are the solubility parameters for polymer and solvent, respectively;  $R$  is the gas constant; and  $T$  is the absolute temperature.<sup>19</sup> The lattice



**Figure 6.** Stress–strain curves of 1,2,3-triazole crosslinked polymers. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

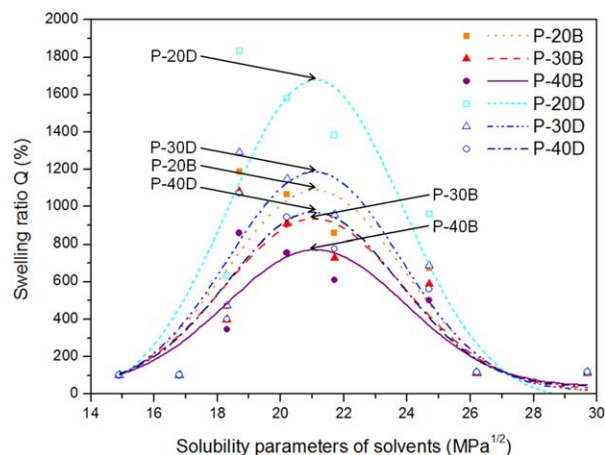
constant  $\beta_1$  of interaction parameter  $\chi$  is the experimental data obtained by rule of thumb. Usually, 0.34 is chosen for  $\beta_1$ ; however, sometimes 0.0 is chosen for other experiments.<sup>20</sup> In our experiments, 0.34 was chosen for  $\beta_1$ , and the solubility parameter of the 1,2,3-triazole crosslinked polymers was determined from the maximum swelling ratio observed in the trend line among the wide ranges of the solubility parameters of the solvent. Methylene chloride, which solubility is closest to that of 1,2,3-triazole crosslinked polymers, was selected as a solvent to calculate crosslinking density from the Flory–Rehner equation. The results of the calculation of the crosslinking density are shown in Figure 7 and Table VI. The trend of the low swelling ratios due to the high degree of crosslinking by using the low molecular weight curing agent B instead of the oligomer-type curing agent D and by using increased amounts of crosslinkers was consistent with the trend of the experimental results of the increased modulus in the stress–strain curves.

#### Analysis of Relationship between $\chi$ and Degree of Crosslinking

Many thermodynamic properties of polymer solutions such as solubility, swelling equilibria, and colligative properties can be expressed in terms of the polymer–solvent interaction parameter  $\chi$ . Some values of  $\chi$  for various polymer/solvent/temperature systems are tabulated,<sup>21</sup> however, to the best of the authors' knowledge, the value of  $\chi$  for 1,2,3-triazole crosslinked polymers has not yet been determined. Thus, in this study, to determine

**Table V.** Mechanical Properties of 1,2,3-Triazole Crosslinked Polymers

Codes	Elongation at the break (%)	Tensile strength (MPa)	100% Modulus (MPa)	300% Modulus (MPa)
P-20B	605.9	1.351	0.275	0.591
P-30B	355.3	1.094	0.400	0.930
P-40B	192.8	0.914	0.566	–
P-20D	793.5	0.936	0.163	0.308
P-30D	393.6	0.729	0.262	0.564
P-40D	209.7	0.615	0.375	–



**Figure 7.** Swelling ratios of 1,2,3-triazole crosslinked polymers according to the solubility parameters of various solvents. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

the values of  $\chi$ , average molecular weights between the crosslinking points ( $M_c$ ) of 1,2,3-triazole crosslinked polymers are determined for the first time from the Mooney–Rivlin equation in eq. (4):

$$\sigma = \frac{F}{A_0} = 2 \left( C_1 + \frac{C_2}{\lambda} \right) \left( \lambda - \frac{1}{\lambda^2} \right) \quad (4)$$

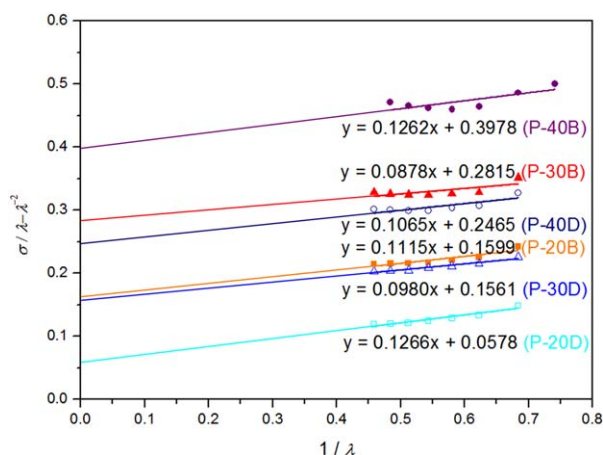
Subsequently, by using the determined values of the average molecular weights between the crosslinking points ( $M_c$ ), the values of  $\chi$  for 1,2,3-triazole crosslinked polymers were determined from the Flory–Rehner equation.<sup>18,22,23</sup> The Mooney–Rivlin equation can be applied for the unfilled crosslinked polymer networks, and the constants  $C_1$  and  $C_2$  can be determined from a tensile experiment using unswollen samples. Here,  $\sigma$  is the engineering stress ( $\sigma = F/A_0$ ),  $F$  is the force applied on the specimen,  $A_0$  is the original cross-sectional area of the specimen, and  $\lambda$  ( $= L/L_0$ ) is the extension ratio of the specimen. The Mooney–Rivlin constant  $2C_1$  can be expressed from the statistical model of molecular theory, as shown in eq. (5):

$$2C_1 = 2\rho RT\nu = \frac{\rho RT}{M_c} \quad (5)$$

where  $\rho$  is the density ( $\text{g cm}^{-3}$ ) of the specimen,  $R$  is the molar gas constant, and  $T$  is the absolute temperature. The average molecular weight between the crosslinking points ( $M_c$ ) and crosslinking density ( $\nu$ ) can be calculated from the determined

**Table VI.** Swelling Properties of 1,2,3-Triazole Crosslinked Polymers

Codes	Maximum swelling ratio (%)	Solubility parameter ( $\text{MPa}^{1/2}$ )	Crosslinking density ( $\times 10^{-4} \text{ mol g}^{-1}$ )	$M_c$ ( $\text{g mol}^{-1}$ )
P-20B	1088.0	21.20	0.27	18519
P-30B	935.9	21.20	0.39	12864
P-40B	771.9	21.20	0.54	9259
P-20D	1680.0	21.20	0.13	38462
P-30D	1187.9	21.20	0.23	21739
P-40D	970.1	21.06	0.35	14286

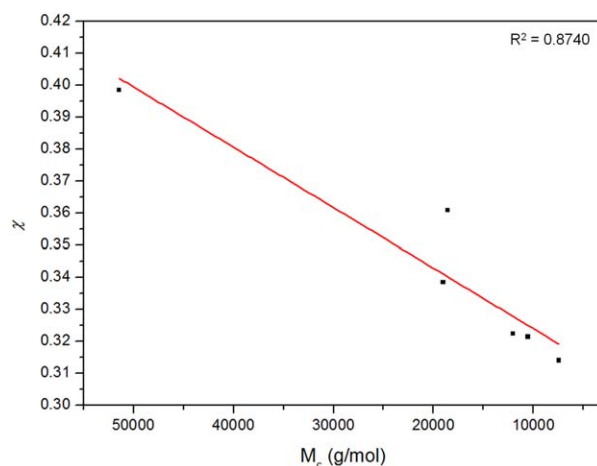


**Figure 8.** Determination of  $2C_1$  by plotting  $\sigma/(\lambda - \lambda^2)$  versus  $1/\lambda$  of 1,2,3-triazole crosslinked polymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

values of  $2C_1$ , which was at the intersection between the  $y$ -axis and the line of linear function in the relationship of  $\sigma/(\lambda - \lambda^2)$  versus  $1/\lambda$  from eq. (4), as shown in Figure 8.

According to eq. (5), if the value of  $2C_1$  is high, the value of  $M_c$  decreases; as a result, the degree of crosslinking of the network polymer increases. The 1,2,3-triazole crosslinked polymers (P-40B) that showed the highest modulus in the tensile experiment also showed the highest values of  $2C_1$  and vice versa for P-20D. Also, the specimen that showed lower values of the swelling ratio showed higher values of  $2C_1$ .

Generally, the average molecular weight between the crosslinking points ( $M_c$ ) in the Flory–Rehner and Mooney–Rivlin equations has the same definition; therefore, the values of  $\chi$  for the 1,2,3-triazole crosslinked polymers can be calculated from the Flory–Rehner equation if the value of  $M_c$  is known. Therefore,  $M_c$  was first determined from the Mooney–Rivlin equation from the tensile experiment data. Subsequently, the values of  $\chi$  were determined from the calculated  $M_c$  and swelling experiment data by using the Flory–Rehner equation. From the calculated values of  $\chi$ , the values of lattice constant  $\beta_1$  were determined from eq. (3). Also, by using the selected values of  $\beta_1$  (0.34 or 0.0) and the swelling experimental data,  $M_c$  of the 1,2,3-triazole crosslinked polymers was calculated from the Flory–Rehner equation; the results were then compared with those from the Mooney–Rivlin equation. The calculated results are shown in Table VII.



**Figure 9.** Dependence of  $\chi$  on average molecular weight between the crosslinking points for 1,2,3-triazole crosslinked polymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

From these results, it is determined that the values of  $\chi$  for 1,2,3-triazole crosslinked polymer, as shown in the fourth column of Table VII, ranged from 0.3141 to 0.3986 according to the degree of crosslinking. As shown in Figure 9, when the value of  $M_c$  increased, that is, degree of crosslinking decreased, the value of  $\chi$  also increased. Marzocca<sup>19</sup> also reported that the interaction parameter  $\chi$  is dependent on the degree of crosslinking. Also, these results are consistent with the theoretical studies by Freed and Pesci,<sup>24</sup> who showed the crosslink dependence of  $\chi$  in polymer networks.

From the determined values of  $\chi$ , it is found that the values of lattice constant  $\beta_1$  calculated from eq. (3), as shown in the fifth column of Table VII, ranged from 0.2932 to 0.3777. As shown in the sixth column of Table VII, the values of  $M_c$  calculated from the Flory–Rehner equation with  $\beta_1 = 0.34$  are fairly consistent with those calculated from the Mooney–Rivlin equation. This means that  $\beta_1 = 0.34$  is appropriate for the calculation of  $\chi$  in the 1,2,3-triazole crosslinked polymers.

## CONCLUSIONS

In this study, diazide prepolymer, triazide crosslinker, and four types of ethynyl terminated dipolarophile curing agents were synthesized to prepare a 1,2,3-triazole crosslinked polymer. In the chemical structure of dipolarophile curing agents, the

**Table VII.** Comparison of  $M_c$  by Using Flory–Rehner and Mooney–Rivlin Equations and Determination of  $\chi$  of 1,2,3-Triazole Crosslinked Polymers

Codes	Mooney–Rivlin equation		Flory–Rehner equation			
	$2C_1$ at $1/\lambda = 0$	$M_c$ (g mol <sup>-1</sup> )	$\chi$	$\beta_1$ from $\chi$	$M_c$ ( $\beta_1 = 0.34$ ) (g mol <sup>-1</sup> )	$M_c$ ( $\beta_1 = 0.0$ ) (g mol <sup>-1</sup> )
P-20B	0.1599	18,589	0.3610	0.3401	18,519	6250
P-30B	0.2815	10,559	0.3215	0.3006	12,864	4459
P-40B	0.3978	7472	0.3141	0.2932	9259	3333
P-20D	0.0578	51,426	0.3986	0.3777	38,462	12,821
P-30D	0.1561	19,042	0.3385	0.3176	21,739	7143
P-40D	0.2465	12,056	0.3225	0.3077	14,286	4950



carbonyl group adjacent to the triple bond, which acts as an electron-withdrawing group, considerably accelerated the 1,3-dipolar cycloaddition reaction between the azide and ethynyl functional groups. This result clearly demonstrates that 1,3-dipolar cycloaddition reaction strongly depends on the chemical structure of the moiety present adjacent to the azide and ethynyl functional groups. According to the results of the mechanical properties, the modulus of the polymers was increased, whereas the elongation at the break was decreased on increasing the ratio of the crosslinker to the prepolymer. The swelling ratios decreased when the concentration of the crosslinker was increased, resulting in highly crosslinked polymers. Moreover, the crosslinking densities of the 1,2,3-triazole crosslinked polymers were determined from the Flory–Rehner and Mooney–Rivlin equations. Depending on the degree of crosslinking, the values of interaction parameter  $\chi$  for the 1,2,3-triazole crosslinked polymers ranged from 0.3141 to 0.3986, and an inversely proportional relationship between  $\chi$  and the degree of crosslinking was obtained.

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