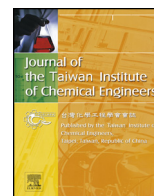




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## Characterization of 1,2,3-triazole crosslinked polymers based on azide chain-ends prepolymers and a dipolarophile curing agent as propellant binders: The effect of a plasticizer

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### ABSTRACT

The 1,2,3-triazole crosslinked polymers with potential use as a binder system in solid rocket propellants were prepared by mixing of an azide chain-ends diazide prepolymer, a dipolarophile curing agent, which act as a crosslinker, and a plasticizer at C≡C/N<sub>3</sub> ratio of 1.1. A wide range of the plasticizer ratios were investigated: 0–300 wt% for the polycaprolactone (PCP) and polycaprolactone ether (PCE) prepolymer based binders, and 0–500 wt% for the polyethylene glycol (PEG) prepolymer based binder. Even at high amounts of plasticizer, sufficient initial reactivity and good conversion were obtained, however the increase of viscosity was considerably delayed. Crystalline domains of in the 1,2,3-triazole crosslinked polymers were effectively eliminated by the plasticizer. The tensile strength and modulus (100% and 300%, respectively) decreased with increasing of the amount of plasticizer whereas the elongation at the break was only modestly affected. PCP showed excellent elongation at the break compared to PEG at the same levels of plasticizer as well as good tensile strength. In contrast, the binder network prepared from the PCE prepolymer collapsed due to its low degree of crosslinking.

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## 1. Introduction

The compositions of state-of-the-art solid rocket propellants include low vulnerability binders, including prepolymers/plasticizers, oxidizers, metal fuels, and other minor additives, which contain energetic groups [1,2]. All solid ingredients are distributed uniformly in a matrix provided by the polymeric binder [3]. The use of energetic additives, mainly as binders and plasticizers, is considered to be one of the practical ways to improve the energy level and other technical performances of solid rocket propellants [4]. To that end, the prepolymers and curing agents are frequently dissolved and cured in a plasticizer in order to impart flexibility, good processability, and low-temperature mechanical properties

to the compounds [5]. Since the 1950s, polyurethane networks have been widely used as binders for solid rocket propellants due to their excellent mechanical properties, being shrink-free, low temperature-controlled cure and acceptable compatibility with metal powders and oxidizers [6]. However, the moisture sensitivity of polyurethane networks requires elimination of moisture from both the propellant ingredients and the manufacturing environment. Furthermore, when ammonium dinitramide (ADN) is used as a chlorine-free and smokeless oxidizer, the hydrolysis of the polyurethane network become a severe problem because of ADN's high hygroscopicity [4]. For this reason, 1,2,3-triazole curing systems, being insensitive to moisture and free of side reactions during their synthesis, have attracted growing interests [6–9]. 1,2,3-Triazole crosslinked polymers are readily formed by 1,3-dipolar cycloaddition between azide and ethynyl groups. Huisgen [10], Katrizky et al. [11], and Wang et al. [12] have studied this reaction in depth with respect to reactant scope, curing temperature, and rate acceleration by catalysts. 1,2,3-Triazole crosslinked polymers can be used as high energy binders for explosives or rocket propellants, destructive adhesives, or other high energy and

**Abbreviations:** PCP, polycaprolactone; PCE, polycaprolactone ether; PEG, polyethylene glycol; ADN, ammonium dinitramide; GAP, glycidyl azide polymer; DSC, differential scanning calorimeter; RDA, rheometric dynamic analyzer; UTM, universal testing machine; MsCl, methanesulfonyl chloride; NE, nitrate ester.

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destructible products [13]. Since the late 1980s, solid rocket propellant binder composed of 1,2,3-triazole crosslinked polymer, have been patented [6,13,14], and extensively studied [5,9,11,12].

Recently, Min et al. [2] evaluated the mechanical properties of 1,2,3-triazole sidelinked polyurethane networks, using glycidyl azide polymer (GAP) prepared 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. However, GAP, which has azide groups grafted on the polymer backbone instead of located at the chain-ends can participate in intramolecular reactions between adjacent azide groups as well as intermolecular reactions between polymer chains. As a result, wasted loops, which do not play a role in the networks, may be formed resulting in inferior mechanical properties.

Our group previously reported a 1,2,3-triazole curing system using azide chain-ends polycaprolactone (PCP) prepolymer, crosslinker, and dipolarophile curing agents, exhibiting excellent mechanical properties at curing temperature of 52 °C [15,16]. In the present study, the effect of a plasticizer on a single 1,2,3-triazole curing system using azide chain-ends prepolymers and a dipolarophile curing agent was evaluated. The 1,2,3-triazole crosslinked polymers containing different amounts of plasticizer were cured at 52 °C for 7 days. The curing reactivities of plasticized 1,2,3-triazole crosslinked polymers were determined from the change of the FTIR absorption peak of azide and terminal ethynyl functional groups in the polymers. Thermal/rheological/mechanical properties of these binders were investigated by using a differential scanning calorimeter (DSC), a rheometric dynamic analyzer (RDA), and a universal testing machine (UTM).

## 2. Materials and methods

### 2.1. Preparation of PCP diazide prepolymer

Methanesulfonyl chloride (MsCl) (10.3 mL, 0.133 mol) was added dropwise to a solution of polycaprolactone 0260 (PCP) (3000 g/mol, 100 g, 0.033 mol) and pyridine (10.8 mL, 0.133 mol) in methylene chloride (1 L). The resulting solution was stirred for 3 days at room temperature. After distilled water (150 mL) was added, the solution was stirred for 1 day. The reaction mixture was subsequently washed with saturated aqueous sodium bicarbonate solution (200 mL), 1N hydrochloric acid (200 mL), and distilled water (200 mL). The organic layer was dried with sodium sulfate and concentrated in a vacuum to give a dimesylate intermediate. The dimesylate (77.6 g, 0.025 mol) was dissolved in dimethyl formamide (1 L) and sodium azide (16.0 g, 0.246 mol) was added. The resulting solution was heated to 100 °C for 2 days and then concentrated in a vacuum. The residue was extracted with methylene chloride (200 mL × 3) and distilled water. The organic layer was separated, dried with sodium sulfate, and concentrated in a vacuum to acquire 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 showed an azide peak at 2095 cm<sup>-1</sup> and no hydroxyl peak.

### 2.2. Preparation of PCE diazide prepolymer

Hydroxy-terminated polycaprolactone ether (PCE) (2000 g/mol, 101.5 g, 0.051 mol) was subjected to the above reaction conditions to give the desired diazide prepolymer in 40% yield: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 4.04 (t, 6H), 3.39 (brs, 18H), 3.25 (t, H), 2.28 (t, 6H), 1.67–1.60 (m, 33H), 1.40–1.32 (m, 6H). The FTIR spectra showed an azide peak at 2099 cm<sup>-1</sup> and no hydroxyl peak.

### 2.3. Preparation of PEG diazide prepolymer

Polyethylene glycol 4500 (PEG) (4500 g/mol, 100 g, 0.022 mol) was subjected to the above reaction conditions to give the desired diazide prepolymer in 87% yield: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.46 (brs, 420H), 2.74 (t, 4H). The FTIR spectra showed an azide peak at 2107 cm<sup>-1</sup> and no hydroxyl peak.

### 2.4. Preparation of 1,1,1-tris[(propioyloxy)methyl] propane (the dipolarophile curing agent)

*p*-Toluenesulfonic acid (*p*-TsOH) (3.21 g, 0.016 mol) was added to a solution of 1,1,1-tris(hydroxymethyl)propane (20.0 g, 0.149 mol) and propionic acid (37.0 mL, 0.597 mol) in benzene (800 mL). The resulting solution was heated to 100 °C for 2 days using a Dean-Stark trap to remove water. The reaction mixture was concentrated in a vacuum and the residue was subjected to column chromatography (eluent: ethyl acetate: hexane = 1/1). The curing agent was obtained in a 35% yield: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 4.16 (s, 6H), 2.91 (s, 3H), 1.54 (q, 2H), 0.90 (t, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 152.1, 75.6, 74.0, 65.1, 40.6, 22.7, 7.2. The FTIR spectra showed an ethynyl peak at 2122 cm<sup>-1</sup> and no hydroxyl peak (Fig. 1).

### 2.5. Selection of a plasticizer

Nitrate ester (NE)-type plasticizer can enhance the energetic performance of the propellant due their NE moieties, so many NEs have been used for the military applications [17,18]. Most of the energetic NEs are explosives that possess low critical diameters, high volatility, and high sensitivity [19]. Among binders in common use in high energy formulations are those formulated from hydroxy-terminated PCP, PEG, and PCP/PEG mixtures under the urethane network system. These binders are commonly plasticized with NEs which enhance elastomeric properties of the binders without chemical reaction each other and contribute substantially to the high energy of the binders as a whole during combustion [20]. Recently, the effect of NE plasticizer on the GAP/PCP and GAP/PEG block copolymer urethane binders was investigated by Min [21]. According to the results, the GAP/PCP and NE plasticizer system showed better mechanical and thermal properties than the GAP/PEG and azide-terminated GAP oligomer plasticizer system because the crystalline domain could be readily eliminated by the NE plasticizer. NE plasticizer was also selected for our 1,2,3-triazole curing system using azide-terminated prepolymer which has the same backbone structure of traditional hydroxy-terminated prepolymers (PCP, PEG).

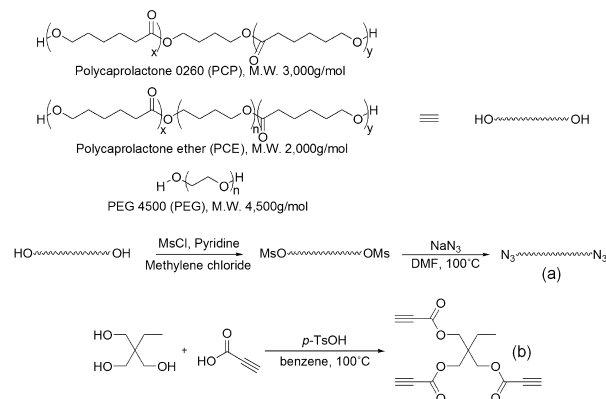


Fig. 1. Synthesis of (a) azide chain-ends prepolymers and (b) a dipolarophile curing agent.

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