



Azide-bearing polymer-based solid composite propellant prepared by a dual curing system consisting of a urethane-forming reaction and a dipolar addition reaction



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HIGHLIGHTS

- Azide-bearing polymer-based solid propellants were prepared by using the urethane, the triazole, or dual curing systems.
- The dual curing system offered the best mechanical properties as well as high burn rate and low pressure exponent.
- The dual curing system also produced excellent adhesion between the GAP-based solid propellant and the HTPB liner.

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ABSTRACT

Solid composite propellants based on a polymer bearing azide pendent groups, glycidyl azide polymer (GAP), were prepared by urethane- or triazole-forming reactions and their combination. Dipolarophiles featuring diacetylenic groups, such as bispropargyl succinate (BPS) and 1,4-bis(1-hydroxypropargyl) benzene (BHPB), were used as the curatives in the triazole curing system. Among the three types of curing systems used for the preparation of GAP-based solid composite propellants, dual curing systems provided the best mechanical properties, regardless of the oxidizer type included in the solid composite propellant. The dual curing system produced GAP-based solid composite propellants that exhibited a higher burn rate and a lower pressure exponent compared to propellants obtained from a single triazole curing system. Finally, good adhesion to the hydroxyl-terminated polybutadiene (HTPB)-based liner was observed in the GAP-based solid propellants prepared from the dual curing system.

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1. Introduction

Glycidyl azide polymer (GAP) is a highly energetic polymer that can be used as a solid rocket propellant. Since the synthetic reports in 1980s, GAP has been widely studied as a prepolymer for the preparation of nitrate ester polyether (or polyester) (NEPE) propellants due to its high positive formation energy [1–5]. GAP-based solid composite propellants exhibit a lower flame temperature without significant decreasing of the specific impulse compared to other NEPE propellants, such as polyethylene glycol (PEG), polyglycidyl adipate (PGA), and hydroxyl-terminated polyether (HTPE)-based solid propellants [5]. So, the reliability of the components in a propulsion system, such as the nozzle, pintle, and composite case, can be further assured during the combustion of GAP-based solid propellants. Recently, the remarkable thermal characteristics of

GAP have been recognized as useful in a fuel-rich solid propellant for ducted rocket or solid ramjet propulsion systems [6].

Despite its unique thermal properties, GAP-based propellants exhibit weak mechanical properties due to the poor polymer backbone flexibility of GAP, which includes rigid conjugated azide side groups [7–9]. Therefore, much work has been done to improve the mechanical properties of the GAP-based composite propellants good enough to endure the pressure generated in rocket motor. Our team has addressed the poor mechanical properties of GAP in several previous studies that suggest a feasible solution to the problems in the field [7,8]. The advantage of the energetic azide-bearing GAP permits the introduction of a new curing system that can replace conventional urethane curing systems long favored by solid propellant formulators. A demand for an alternative to the urethane curing system in solid propellants formulation has been raised in the field due to the high sensitivity of isocyanate groups to moisture and hazardous manufacturing process of isocyanate using toxic phosgen [10–13].

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The triazole curing system has been investigated as a next-generation eco-friendly curing system for solid propellants. In this system, azide-bearing polymer chains may be readily crosslinked via a triazole linkage formed by a 1,3-dipolar cycloaddition reaction between the azides pendent groups of GAP and the diacetylenic compound. We previously examined the polymeric binder networks prepared with a triazole curing system including azide end-capped polyethers and polycaprolactone with two diacetylenic compounds [14,15]. Our earlier studies on GAP employed bis-propargyl succinate (BPS) and 1,4-bis(1-hydroxypropargyl)benzene (BHPB) as a dipolarophile compound. BPS has ester groups attached to each terminal triple bond, and BHPB has a hydroxyl group adjacent to the triple bond, as shown in Scheme 1.

Compared to the polymeric networks prepared under the urethane curing system, the GAP-based triazole cured networks could be readily prepared at 50 °C without a curing catalyst within only a few days. Unlike the urethane curing system, in which each hydroxyl group at the ends of a polymer chain will react with an isocyanate in the polyfunctional isocyanate curative, the GAP-based triazole side-linked networks could be obtained if 10% of the azides had reacted with a dipolarophile; however, the GAP-based triazole-cured networks did not display good mechanical properties due to the presence of the triazole side-linkages formed between the GAP chains, rather than the chain end linkages (Scheme 2) [14].

The mechanical properties of the triazole side-linked networks were even worse than those obtained from the urethane chain-end linked networks. To overcome the poor mechanical properties displayed by the GAP-based propellant prepared under a single

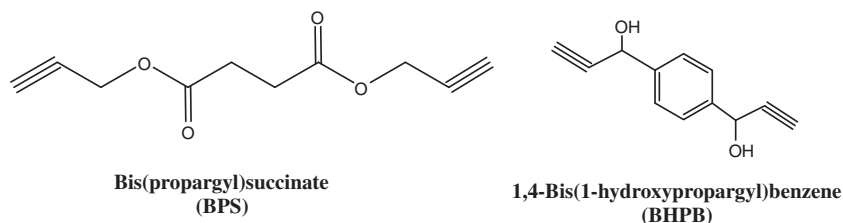
curing system, such as a urethane or a triazole system, we attempted to combine the conventional urethane curing system with an azide-bearing polymer, GAP, as an amphiphilic polymer to both the isocyanate group and the dipolarophile group such as an acetylenic group. Surprisingly, the mechanical properties of the GAP-based polymeric networks obtained from this dual curing system were excellent and even comparable to the properties of hydroxyl-terminated polybutadiene (HTPB)-based networks.

The mechanical properties of solid composite propellants prepared using the novel dual curing system were characterized. The burning characteristics of the GAP-based solid composite propellants were examined as a function of the curing system. Finally, we investigated the adhesion properties between the GAP-based propellants obtained with the different curing systems and the HTPB-based polymer crosslinked liner.

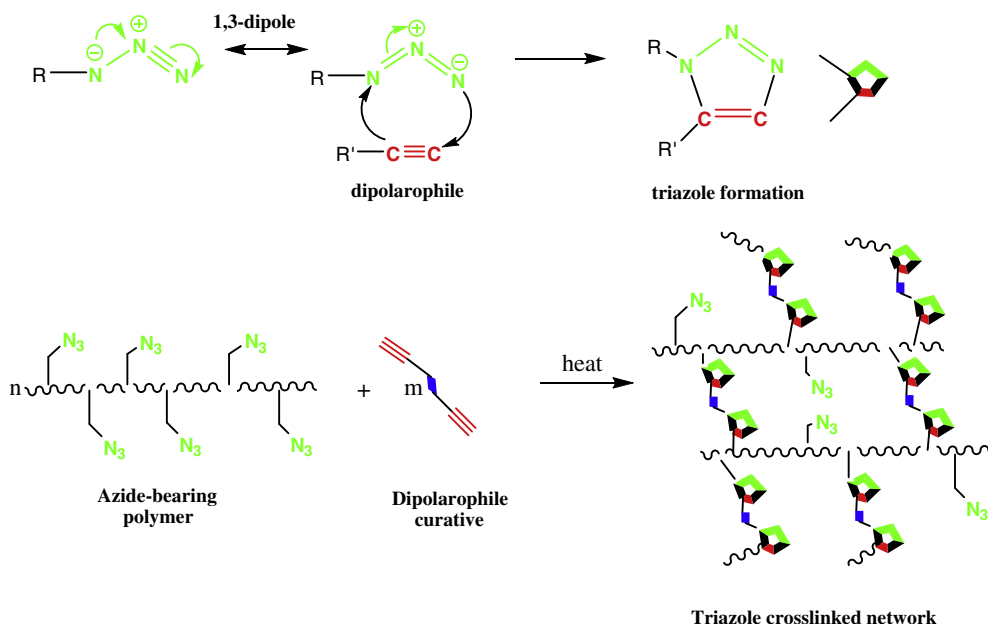
2. Materials and methods

2.1. Materials

The azide-bearing polymer used in this study was hydroxyl-bifunctionalized GAP, with molecular weights and a hydroxyl index of 2400 g mol⁻¹ and 0.74 eq kg⁻¹, respectively. GAP was purchased from 3 M under the trade name GAP diol (L9961). Along with GAP diol, we used GAP polyol (5500 g mol⁻¹, -OH index = 0.49 eq kg⁻¹), which features a hydroxy(-OH) functionality exceeding 2.0. The isocyanate-terminated GAP (IT-GAP) was obtained from the reaction of GAP with toluene diisocyanate



Scheme 1. The chemical structures of the dipolarophile compounds.



Scheme 2. The azide-bearing polymer side-crosslinked with triazole moieties.

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