



DFAMO/BAMO copolymer as a potential energetic binder: Thermal decomposition study

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ABSTRACT

A novel energetic binder was prepared through the copolymerization between 3-difluoroaminomethyl-3-methyloxetane (DFAMO) and 3,3'-bis(azidomethyl)oxetane (BAMO). With the help of thermogravimetric analysis (TG) and differential scanning calorimetry (DSC), the thermal decomposition study of poly(DFAMO/BAMO) was conducted to understand its decomposition behavior and kinetics, and the possible mechanism, which are crucial parameters as an energetic binder. The results showed that the difluoroamino and azido groups mainly contributed to the weight loss during the thermolysis of the polymer. The activation energy of the first and second pyrolysis shoulder are $115 \pm 5 \text{ kJ mol}^{-1}$ and $165 \pm 5 \text{ kJ mol}^{-1}$, respectively. Additionally, fourier transform infrared (FTIR) of pyrolysis residues suggested that the complete pyrolysis of the azido groups occurred after the pyrolysis of difluoroamino. And the main degradation products of the polymer were CH_3^+ , NH_3 , H_2O , HF, HCN, N_2 , NO, H_2CO and CF_4 by TG-FTIR-MS.

1. Introduction

Oxetane-based polymer with energetic groups is of great potential as energetic binders, especially for the binding of solid propellant and polymer bonder explosive (PBX), because such energetic binder has desirable low glass transition temperature ($T_g < -40^\circ\text{C}$), low polydispersity, thermal stability, as well as polyfunctionality, and the understanding of the thermal decomposition parameters of such energetic binders is crucial prior to their application [1–9]. Specifically, it has been demonstrated that the performance of the oxidizer in solid propellant or PBX formulations could be influenced by the thermal decomposition behavior of the added energetic binder [10–14]. As promising candidates, poly(3-difluoroaminomethyl-3-methyloxetane) (poly(DFAMO)) and poly(3,3'-bis(azidomethyl)oxetane) (poly(BAMO)) exhibit great potential in improving the performance of solid propellant or PBX formulations due to the difluoroamino groups and the azido groups grafted. To date, most studies focused on the pyrolysis characteristics of DFAMO, BAMO and their copolymers with other monomers, to understand the thermal decomposition behavior, kinetics, and mechanism, thus facilitate their application as energetic binders [6,15,16]. Lee et al. [16] studied the effect of titanium dioxide (TiO_2)

on the thermal decomposition of BAMO/AMMO copolymer. It was observed that the addition of TiO_2 could solely induce an increase in the release of ammonia (NH_3). Additionally, Ang et al. [17] investigated the thermal decomposition behavior of glycidyl azide polymer (GAP), poly(BAMO), and its copolymer poly(GAP/BAMO). The results indicated that the activation energy of the decomposition of the azido groups could be adjusted through the copolymerization of the two polymers. Moreover, Li et al. [18] investigated the thermal decomposition and the associated kinetics of poly(BDFAO/tetrahydrofuran (THF)), poly(DFAMO/THF), and poly(BDFAO/DFAMO/THF). All three polymers exhibited a two-step mass-loss process, and the first stage was dominated via the elimination of HF, while the second stage was contributed by the pyrolysis of the monofluoroimino and cyano groups in the main chain of the polymers.

In our study, a novel energetic binder was prepared through the copolymerization between DFAMO and BAMO, and the thermal decomposition of poly(DFAMO/BAMO) was investigated by DSC, TG, FTIR, and TG-FTIR-MS methods. Besides, the associated non-isothermal decomposition kinetic parameters were calculated by referring to three different model-free methods of Flynn-Wall-Ozawa (FWO) [19,20], Kissinger-Akahira-Sunose (KAS) [21,22] and Vyazovkin and Dollimore

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[23]. Our study on the thermal decomposition of difluoroamino-substituted energetic binders would be of great importance for oxetane-based polymers.

2. Experimental

2.1. Synthesis

The copolymerization between DFAMO and BAMO was synthesized with trimethylolpropane (TMP) as the evocator, whereas boron trifluoride etherate (TFBE) is used as the catalyzer,

The copolymerization between DFAMO and BAMO was synthesized, where the mole ratio of DFAMO and BAMO is 1. Trimethylolpropane (TMP) is used as an evocator and boron trifluoride etherate (TFBE) is used as the catalyzer, where the mole ratio of TFBE and TMP is 3. In addition, TMP is recrystallized in acetone/ether and TFBE is purged under vacuum before use. Moreover, the reaction was terminated with saturated sodium carbonate, neutralized, and dried. And poly(DFAMO/BAMO) was dried in a vacuum drying oven for 24 h at 50 °C before use [18,24]. FTIR: $\nu(-OH) = 3322 \text{ cm}^{-1}$, $\nu(C-N_3) = 2093 \text{ cm}^{-1}$, $\nu(-NF_2) = 1740 \text{ cm}^{-1}$, $\nu(C-O-C) = 1110 \text{ cm}^{-1}$. $^1\text{H NMR}(\text{CDCl}_3)$: $\delta = 1.08 \text{ ppm}$ (3H, $-\text{CH}_3$), $\delta = 3.29 \text{ ppm}$ (4H, $-\text{OCH}_2-$), $\delta = 3.32 \text{ ppm}$ (4H, $-\text{CH}_2\text{N}_3$), $\delta = 3.37 \text{ ppm}$ (4H, $-\text{OCH}_2-$), $\delta = 3.55 \text{ ppm}$ (2H, $-\text{CH}_2\text{NF}_2$). $^{19}\text{F NMR}(\text{CDCl}_3)$: $\delta = 64.41 \text{ ppm}$ ($-\text{NF}_2$).

2.2. Methods and instrumentation

The copolymer was characterized by gel permeation chromatograph (GPC) from the United States Waters company. $^1\text{H NMR}$ and $^{19}\text{F NMR}$ spectra were obtained in a Varian 500 MHz instrument using CDCl_3 solvent. FTIR spectra were obtained from a Nicolet iS10 and the wavelength range was 4000–500 cm^{-1} .

The thermal behavior study was performed on DSC823e from Swiss-Mettler-toledo company, under the nitrogen atmosphere at a flow rate of 30 mL min^{-1} . The constant samples mass of $(0.5 \pm 0.02) \text{ mg}$ in alumina crucible were heated from 50 to 500 °C at various rates of 5, 10, 15 and 20 °C min^{-1} .

TG was used to study the thermal decomposition characteristics of the polymer, and the instrument model used here is TG/SDTA851e from Swiss tole-Mettler-do company. The constant samples $(0.5 \pm 0.02) \text{ mg}$ were used for each run. Here the samples were heated from 50 to 500 °C at rates of 5, 10, 15 and 20 °C min^{-1} in a nitrogen atmosphere, and the flow rate of the nitrogen was stabilized at 30 mL min^{-1} .

TG-FTIR-MS technique was used to detect the gaseous products during the thermal decomposition process. STA6000-Frontier-SQ8T from the United States PE company was employed. The sample (15 mg) in the alumina crucible was heated from 50 to 400 °C at rates of 20 °C min^{-1} under the helium atmosphere at a flow rate of 30 mL min^{-1} .

3. Results and discussion

3.1. Polymer preparation

The detailed methods for the copolymer preparation was described in the experimental section. The prepared poly(DFAMO/BAMO) was characterized by GPC, M_n , M_w , and polydispersity index (PDI) were found to be 10257, 14983, and 1.46, respectively. The FTIR and NMR experiments were employed to demonstrate the successful preparation of the polymer. The peaks observed in the FTIR spectra (Fig. 1), $^1\text{H NMR}$ spectra (Fig. 2a) and $^{19}\text{F NMR}$ spectra (Fig. 2b) could be well assigned to the characteristic peaks of poly(DFAMO/BAMO) (values in the experimental section).

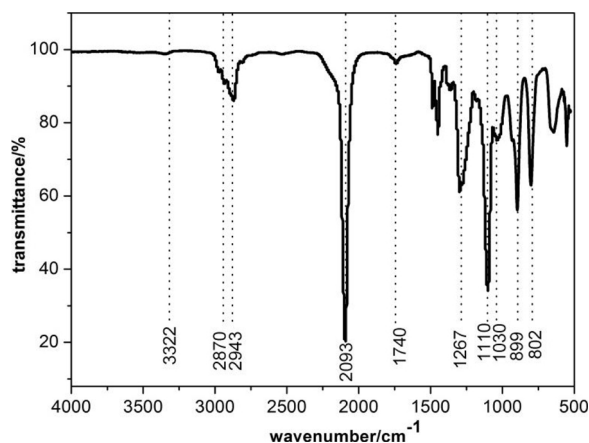


Fig. 1. FTIR spectra of poly(DFAMO/BAMO).

3.2. Thermal decomposition characteristics

It is of great value to study the thermal decomposition characteristics of the energetic adhesive, since the overall performance of the propellant could be influenced by the added energetic binder, and the understanding of the thermal decomposition of energetic binder could provide valuable information regarding the production, safety profile, compatibility, and shelf life of the binder for the future application of the propellants.

Fig. 3 displayed the obtained TG and DSC curves at a heating rate of 10 °C min^{-1} for poly(DFAMO/BAMO). The TG curve shows that the thermal weight loss is a continuous process. The weight loss could be attributed to the thermal decomposition of the difluoroamino groups and the azido groups in the polymer. DSC curve showed that there were two exothermic peaks at 222.4 °C and 256.4 °C, respectively. The mass loss continues along with the increased temperature, with a complete weight loss observed at 500 °C. All the related DSC and TG data of poly(DFAMO/BAMO) were listed in Table 1.

3.3. Kinetics

Other than explosion heat, Chapman-Jouguet pressure and explosion velocity, the activation energy of thermolysis is another important parameter to evaluate the performance of energetic materials [25]. In this section, different model-free methods were employed to analyze the non-isothermal kinetic data from the TG and DSC curves.

As described in Fig. 4a, model-free KAS and FWO methods were used to process the thermal decomposition dynamic data obtained by DSC with different heating rates β . In the Kissinger equation (1), the peak temperature in DSC (T_p) was used to obtain the values of activation energies (E_a) and $\ln A_k$ by the linear regression analysis of $\ln(\beta/T_p^2)$ to $1/T_p$, and according to the Ozawa Eq. (2) to carry on the $\lg\beta$ to $1/T_p$ linear regression analysis. The values of activation energies E_a :

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln \frac{AR}{E_a} - \frac{E_a}{RT_p} \quad (1)$$

$$\lg\beta = \lg\left(\frac{AE_a}{Rg(\alpha)}\right) - 2.3153 - 0.4567 \frac{E_a}{RT_p} \quad (2)$$

Where α is the reaction depth, and $g(\alpha)$ is the integral form of the mechanism function. The activation Energies (E_a) and pre-exponential factor (A) were obtained by fitting out a suitable function of slope and intercept in Kissinger and Ozawa methods. These kinetic parameters were shown in Table 2, and the values of activation energies calculated by the Kissinger equation was slightly lower than that by the Ozawa equation.

On the other hand, another model-free method of Vyazovkin was

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