

# Rheological Studies on Energetic Thermoplastic Elastomers

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**ABSTRACT:** Energetic thermoplastic elastomers containing energetic groups, such as azido, nitrate, nitro, and so forth, are emerging as attractive binder systems for advanced solid rocket propellants. Poly[3,3-bis(Azidomethyl) oxetane (BAMO)-co-3-azidomethyl-3-methyl oxetane (AMMO)] comprising hard crystalline BAMO segment and the soft/amorphous AMMO segment in various molar ratios (80 : 20, 50 : 50 and 20 : 80) were synthesized during the present work. The homo polymers namely Poly-BAMO and Poly-AMMO were also synthesized. All

the polymers and copolymers were characterized by spectral and thermal methods. They were found to be thermally stable. The most promising 80 : 20 copolymer softened at 56°C with  $T_g$  of -36°C. Rheological studies were also carried out to determine their suitability as a binder in explosive and propellant formulations. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 2365–2368, 2010

**Key words:** ETPE; binder;  $G'$  (loss/viscous modulus);  $G''$  (elastic/storage modulus); dilatant; linear viscoelastic region

## INTRODUCTION

Thermoplastic elastomers (TPEs) are being envisaged as excellent candidates for use in reusable/recyclable green propellants and are being developed as an alternative approach to irreversible isocyanate cured binder-based systems.<sup>1</sup> Major impact of this reversibility is that the propellant scrap is dramatically reduced and demilitarization rendered hazard free to a great extent. Extensive work on the optimization of TPE-based formulations that could find application across a wide range of munitions is in progress.<sup>2</sup> Estane, hytrel, and ethylene vinyl acetate are reported as TPE binders for advanced propellants/explosive systems for specific applications.<sup>3</sup> Emergence of azido, nitro, and nitrate polymers has led to the intensive research in the area of energetic TPEs. Bis(azidomethyl) oxetane (BAMO)-based copolymers have evinced interest as energetic TPEs, as BAMO forms the thermoplastic segment in these copolymers. BAMO-AMMO (Azido methyl methyl oxetane) and BAMO-NIMMO (Nitrate methyl methyl oxetane) copolymers yield ETPEs, which are of great interest in extruded propellants and plastic-bonded explosives.

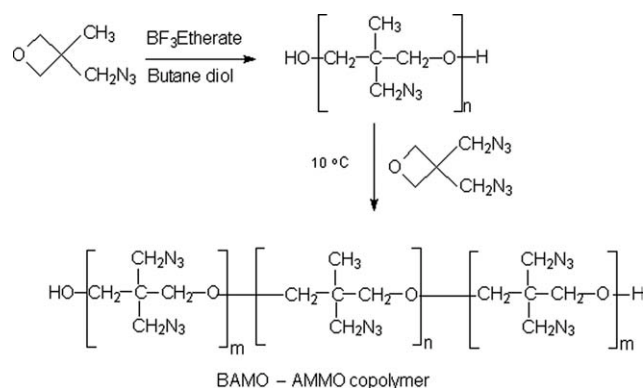
The synthesis and characterization of BAMO has already been reported by authors.<sup>4</sup> Poly-BAMO is a solid, whereas Poly-AMMO is a viscous liquid. Depending on the application point of view of these

copolymers, one can adjust the BAMO content in copolymer so as to get the desired TPE.

The present work was undertaken to synthesize BAMO-AMMO copolymer in various molar ratios to obtain a desired ETPE binder for explosive and propellant formulations. Rheological studies on various BAMO-AMMO copolymers were also carried out to select the suitable copolymer, from the processing point of view.

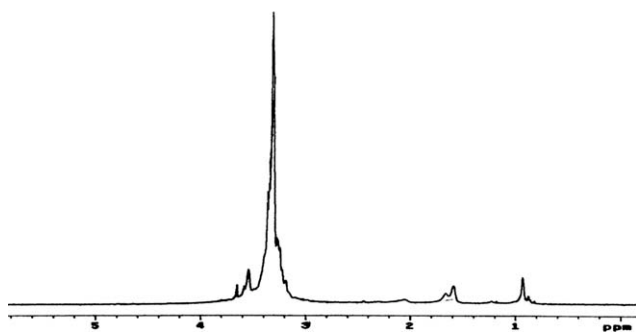
## EXPERIMENTAL

BAMO, AMMO, their homo polymers, and copolymers in various molar ratios (Scheme 1) were synthesized, according to the procedure reported by the authors.<sup>5</sup> A typical copolymerization method for synthesis of BAMO-AMMO copolymer (80 : 20) is as follows. AMMO (0.2M) was added to the mixture of  $\text{BF}_3$  etherate (0.01M) and 1,4-butane diol (0.005M) in dichloromethane and stirred for 2 h at 10°C.



**Scheme 1** Synthesis of BAMO-AMMO copolymer.

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**Figure 1**  $^1\text{H-NMR}$  of BAMO-AMMO copolymer (80 : 20).

BAMO (0.8M) was then added to the reaction mixture over a period of 2 h at the same temperature, and the contents were stirred for 120 h at 25°C, under inert atmosphere. The polymerization was terminated using sodium chloride solution. The product was washed with 10% aqueous sodium bicarbonate solution followed by water. The contents were concentrated and precipitated in methanol. The copolymer was isolated and dried under vacuum for 24 h. Synthesis of BAMO-AMMO copolymers in molar ratio of 50 : 50 and 20 : 80 was also carried out on similar lines.

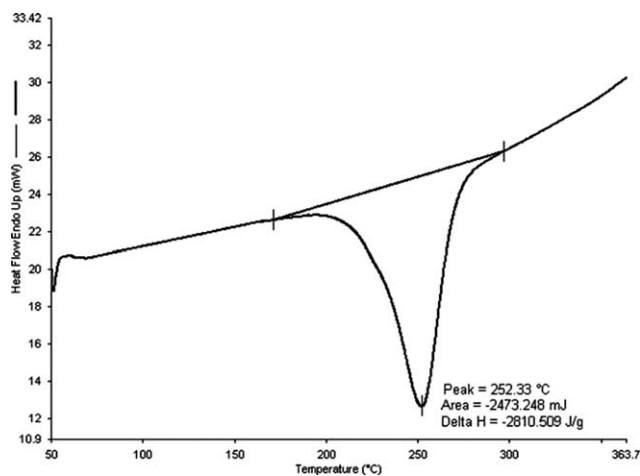
### Characterization

IR spectra were recorded on a PerkinElmer (USA) FTIR 1605 spectrophotometer. The  $^1\text{H-NMR}$  spectra were recorded on a Bruker-300 MHz instrument using tetra methyl silane as an internal reference and chloroform-d ( $\text{CDCl}_3$ ) as a solvent. Number average molecular weight ( $\bar{M}_n$ ), weight average molecular weight ( $\bar{M}_w$ ) along with polydispersity was obtained by gel permeation chromatography of Thermofinigan make (USA). The impact sensitivity was determined on a Julius Peter's apparatus of fall hammer-type by applying standard Bruceton staircase method using a 2-kg drop weight and height for 50% probability of explosion ( $h_{50}$ ) was determined statistically.<sup>6</sup> The friction sensitivity of the compound was determined on a Julius Peter's apparatus by incrementally increasing the load from 0.2 to 36 kg till there was no ignition/explosion in five consecutive test samples.

The DSC was recorded on a PerkinElmer Delta-Para series DSC-7 instrument (Waltham, MA) at the heating rate of 10°C/min under nitrogen atmosphere with a

**TABLE I**  
Azide Content of Various BAMO-AMMO Copolymers

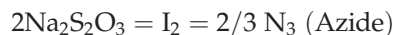
Copolymer ratio BAMO-AMMO	Azide content	
	Experimental	Theoretical
Poly-BAMO	49.7	50
80 : 20	46.2	47
50 : 50	41.4	42
20 : 80	34.5	36
Poly-AMMO	23.70	25



**Figure 2** DSC curve of BAMO-AMMO copolymer (80 : 20).

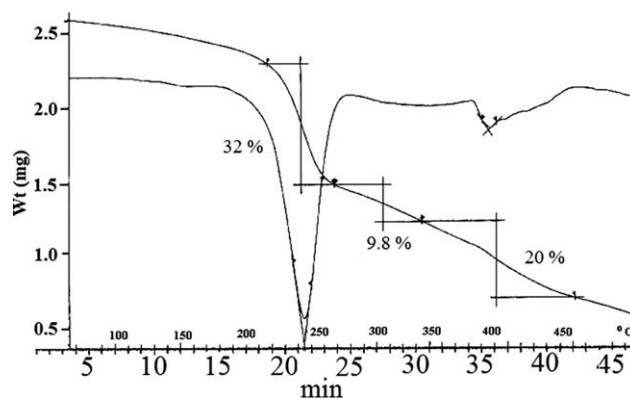
sample mass of 2 mg. The thermo gravimetric analysis was recorded on a Mettler-Toledo STAR instrument (Columbus, OH) model in nitrogen atmosphere with a sample mass of ~ 10 mg at heating rate of 10°C/min. Rheology of the copolymers was studied on a rheometer, model Stress Tech (Rheologica, Sweden).

Azide content of the copolymers was determined by iodometric titration<sup>7</sup> method, wherein the corresponding azido compounds were reduced to the amines, and liberated iodine was titrated with sodium thiosulphate. From the titre reading, the amount of azide present in the copolymer was calculated using the equation



### RESULTS AND DISCUSSION

The copolymers of BAMO and AMMO in various molar ratios were synthesized successfully. They were characterized by IR and  $^1\text{H-NMR}$ . The IR spectra of BAMO-AMMO copolymer (80 : 20) showed stretching vibrations at 3434, 2882, 2102 and 1104  $\text{cm}^{-1}$  corresponding to  $-\text{OH}$ ,  $\text{C-H}$ ,  $-\text{CH}_2\text{N}_3$ , and  $\text{C-O-C}$ , respectively. The  $^1\text{H-NMR}$  spectra of BAMO-AMMO copolymer (80 : 20) (Fig. 1) showed



**Figure 3** TG curve of BAMO-AMMO copolymer (50 : 50).

TABLE II  
Characteristics of BAMO-AMMO Copolymers (TPEs)

Copolymer ratio BAMO-AMMO	Molecular weight $\bar{M}_n\bar{M}_w$	Polydispersity	Hydroxyl value mg of KOH/g	$T_g$ ( $^{\circ}\text{C}$ )	Melting point ( $^{\circ}\text{C}$ )
Poly-BAMO	6247, 18,678	2.99	18.6	-30	78
80 : 20	3431, 5200	1.5	32	-36	56
50 : 50	1200, 1600	1.3	93	-43	41
20 : 80	3064, 4475	1.46	36	-51	9
Poly-AMMO	1000, 1738	1.7	112	-30	liquid

TABLE III  
Rheological Properties of *P*-BAMO, *P*-AMMO, and the Copolymers

Copolymer ratio BAMO-AMMO	Temp. of measurement ( $^{\circ}\text{C}$ )	Storage modulus at crossover $G'$ (Pa)	Crossover frequency (Hz)	Viscosity (cPs)
Poly-BAMO	80	—	—	Solid at RT
80 : 20	75	$2.6 \times 10^{+2}$	17	1000 (Solid at RT)
50 : 50	50	$8.8 \times 10^{+3}$	7	20000
20 : 80	30	$3.73 \times 10^{+3}$	17	15500
Poly-AMMO	30	$6.5 \times 10^{+3}$	28	10400

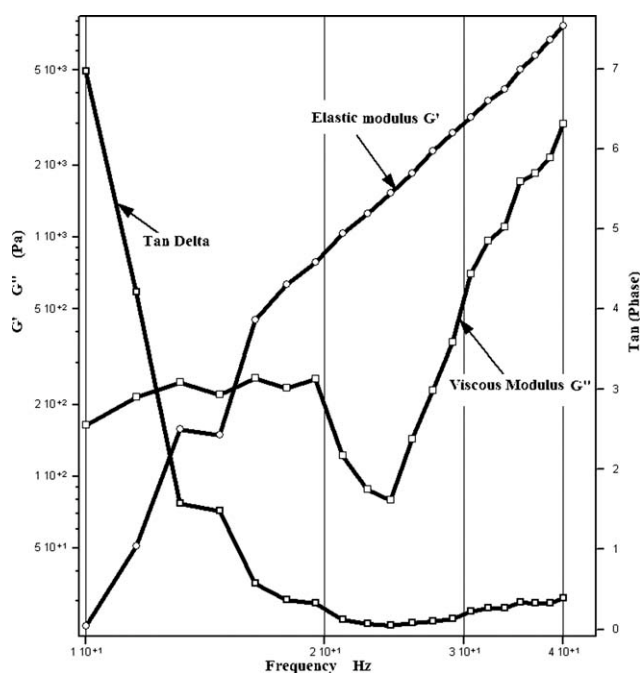


Figure 4 Crossover of  $G'$  and  $G''$  with frequency variation in BAMO-AMMO (80 : 20) copolymer.

signals at  $\delta$  0.93 (s, 3H)  $-\text{CH}_3$  group of AMMO,  $\delta$  1.6 ( $-\text{CH}_2$  of butanediol),  $\delta$  3.2–3.65 (m) for  $-\text{CH}_2-\text{N}_3$  and  $-\text{CH}_2-\text{O}$  of AMMO and BAMO.

Azide content of the all the polymers was estimated by iodometric method, and the experimental values were found to be in agreement with the calculated values (Table I). Therefore, it can be inferred that the polymers synthesized had the same molar ratio of the monomers to that of feed ratio.

Thermal analyses of the samples were carried out to determine their thermal stability as well as decomposition pattern. DSC of all BAMO-AMMO copolymers

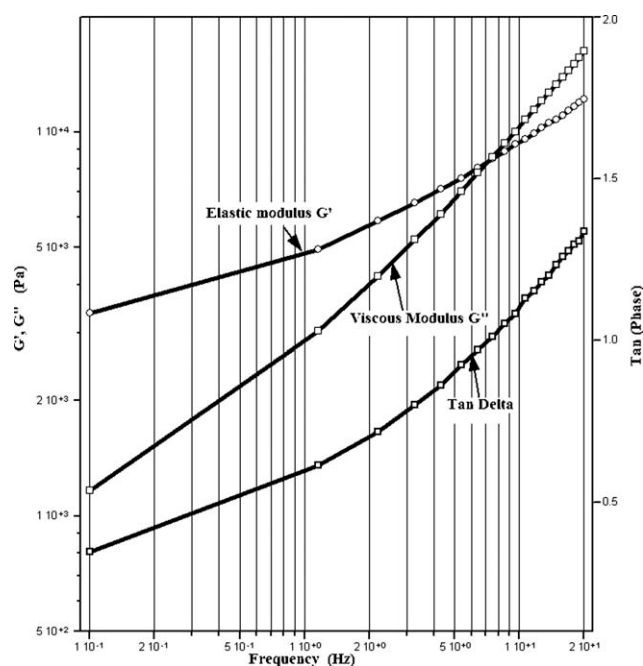


Figure 5 Crossover of  $G'$  and  $G''$  with frequency variation in BAMO-AMMO (50 : 50) copolymer.

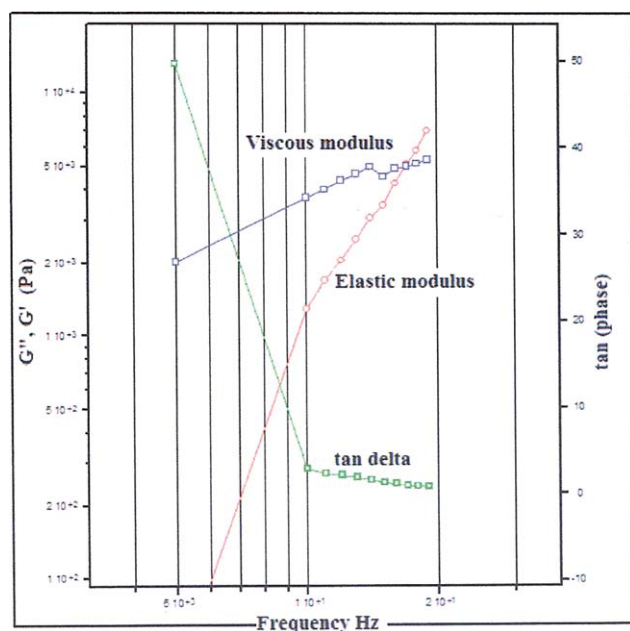
showed  $T_{\text{max}}$  close to that of poly-BAMO because of the decomposition of methyl azide group at about  $252^{\circ}\text{C}$ . A typical DSC curve of the BAMO-AMMO copolymer (80 : 20) is illustrated in Figure 2. TG studies of copolymers showed three-step weight loss, the cleavage of azide structure being the first step of decomposition similar to homo polymers.<sup>5,8</sup> TG curve of BAMO-AMMO copolymer (50 : 50) is illustrated in Figure 3.

Impact and friction sensitivity values of the copolymers were greater than 170 cm ( $h_{50}$ ) and 30 kg, respectively. Sensitivity data revealed that these copolymers are insensitive to impact and friction stimuli.

All polymers were characterized for hydroxyl value (OH value), glass transition temperature, and melting point as given in Table II. It is observed from the table that as BAMO content (crystalline) in the copolymer decreases, its glass transition temperature as well as melting point also decreases.

Rheological studies were carried out on the above polymers (Table III). They were tested for stress/shear rate variation to find out linear viscoelastic region (LVER). Crossover of elastic ( $G'$ ) and viscous moduli ( $G''$ ) with frequency variation and viscosity in LVER region were also determined. The crystalline nature of poly-BAMO plays a vital role in rheological characterization. As poly-BAMO, BAMO-AMMO (80 : 20) and BAMO-AMMO (50 : 50), are solid at ambient temperature, rheological properties were studied after melting the polymer.

Poly-BAMO showed very high elastic modulus than viscous modulus as expected, as it contains symmetrical hard block through out. Therefore, initially, it showed shear thinning nature and then dilatant-type behavior (i.e., at higher frequency or higher shear rate, viscosity increases). It may be because of structure of the polymer getting separated at higher frequency and pendent symmetrical azide groups become more prominent for resistance to flow, which in turn leads to increase in viscosity. Same trend was observed in case of BAMO-AMMO copolymer (80 : 20) (Fig. 4). But other copolymers showed directly dilatant-type nature (Figs. 5 and 6). It was observed that the viscosity



**Figure 6** Crossover of  $G'$  and  $G''$  with frequency variation in AMO-AMMO (20 : 80) copolymer. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

decreased from BAMO-AMMO (50 : 50) to Poly-AMMO with the increase in AMMO content (Table III), but elastic modulus did not show any trend as the polymers were tested at different temperatures.

The crossover frequency in case of Poly-AMMO was observed at  $\sim 28$  Hz, whereas in copolymer 20 : 80 crossover took place at 17 Hz. LVER region of Poly-AMMO started from 40 Pa stress onwards. In case of solid polymers (Poly-BAMO, copolymers 80 : 20 and 50 : 50) did not show any trend for initial  $G'$  and  $G''$  values, as they were tested above their melting point. In case of copolymer 50 : 50 crossover took place at 7 Hz in which elastic modulus is more than viscous modulus in initial stage. But in case of copolymer 80 : 20 crossover took place at 17 Hz in which initial viscous modulus is more than elastic modulus. Its LVER region was above 150 Pa in shear rate variation.

## CONCLUSIONS

Polymers and copolymers of BAMO and AMMO in various molar ratios have been successfully synthesized. The homopolymers and copolymers were characterized by spectral and thermal methods. Also molar ratio of BAMO and AMMO in copolymers was supported by chemical analysis (azide content). BAMO-AMMO copolymer (80 : 20) realized during this work, offers attractive features for use as ETPE in futuristic propellants and explosives. It is more viscous than elastic in nature at lower shear rate. It has got broad LVER region to facilitate mixing of ingredients and initially no shear thickening is taking place even at higher shear rate.

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