Polymer Bulletin 56, 563–569 (2006)
DOI 10.1007/s00289-006-0519-1

Polymer Bulletin

Synthesis and properties of poly-isocyanate energetic curing agent

Zheng Xiaodong [a], Qiu Shaojun [b](✉), Feng Limin [a], Wang Mintao [a], Li Hongli [a], Gan Xiaoxian [a], Zhang Zhizhong [a]

[a] Xi'an Modern Chemistry Research Institute, Xi'an 710065 China,
[b] School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an 710072 China
Fax: +86-29-88492642; E-mail: shaojqiu@yahoo.com

Received: 8 November 2005 / Revised version: 16 January 2006 / Accepted: 18 January 2006

Summary

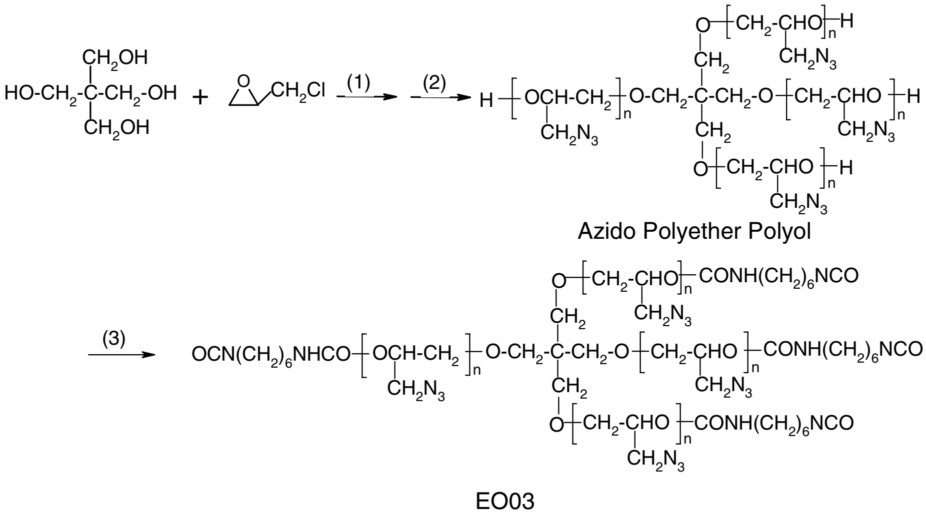
Two tetrafunctional poly-isocyanate energetic curing agents with different molecular weight (EO03-1 and EO03-3) were synthesized via reaction of azido polyether polyol with hexamethylene diisocyanate (HDI). The reaction conditions and post processing steps were investigated. There was an exothermic peak at 252.89 ^{o}C referring to the thermal decomposition of azido group in differential scanning calorimetry (DSC) plot of EO03-3 and the glass transition temperature (*Tg*) was found at –47.13 ^{o}C. Thermal decomposition peak of GAP/EO03-3 elastomer was found to be at 254.56 ^{o}C and the *Tg* was found at –45.78 ^{o}C. To estimate the potential utility of EO03 in solid rocket propellants, an nitric acid ester, triethylene glycol dinitrate (TEGDN), was added to GAP/EO03-3 system as an energetic plasticizer. It was homogeneous even as the amount of TEGDN was equal to GAP/EO03-3 system and *Tg* of GAP/EO03-3/50%TEGDN was found at –69.08 ^{o}C. Mechanical properties of GAP/EO03 and GAP/EO03-3/chain extender were also studied.

Introduction

In the manufacture of solid rocket propellant, a polymeric substance, mostly azido hydroxy-terminated prepolymer, is frequently employed as a binder to hold together fuel and oxidizer compounds of the propellant. The addition of curing agents to these prepolymers causes cross-linking between the functional groups of the prepolymer, resulting in a polymer. The physical properties of the polymers vary with the degree of cross-linkage and this degree would be varied by the amount and type of the curing agents added. In general, it is desired to cure the prepolymer to a degree such that the resulting polymer has the physical properties of an elastomer.

However, the mechanical property of the azido solid rocket propellant is weak because of the structure of azido binder [1-4]. Employing suitable energetic curing agents is one of the practical ways to improve the energetic level, physical integrity and other technical performances of solid rocket propellants. And some two or three functional group energetic poly-isocyanate curing agents have been developed [5-7].

In this study, a novel tetrafunctional poly-isocyanate energetic curing agent, EO03, is introduced and the chemical equation is shown in Scheme 1.



Scheme 1. Synthesis of EO03. (1) $BF_3 \cdot OEt_2/C_2H_4Cl_2$, 47±2 °C; (2) NaN_3/DMF, 87±2 °C; (3) HDI, 80±2 °C

Experimental

Materials

All reagents were of analytical quality and the organic solvents were dried over 4A molecular mesh. GAP (Mn=4500, 28.89 mgKOH/g) and triethylene glycol dinitrate (TEGDN) were dried at 50 °C for 72 h in vacuum.

Instruments

FTIR spectrum was recorded for neat samples on a Nicolet-60SXR-FTIR spectrometer in the frequency range 400-4000 cm^{-1}. Molecular weights were determined on a WATERS 150 GPC. Tetrahydrofuran (THF) was the elution solvent with a 1 mL/min flow rate at 35 °C. The glass transition temperature (*Tg*) were determined using PE DSC-2C at a heating rate of 10 °C/min. The thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on TGA 2950 and DSC 2910 at a heating rate of 20 °C/min and 10 °C/min respectively. The N_2 flow rate was 25 mL/min.

The mechanical properties of elastomers were determined according to GB/T 528-1992 by Instron 4500 at 20 °C. The tensile strength (σm) and elongation at break (εm) were measured by using a 500 mm/min cross-head speed.

Synthesis of EO03-3

Azido polyether polyol was synthesized as described previously [8] and the molecular weight was found to be 844 by GPC. Hexamethylene diisocyanate (HDI, 135 g, 0.8 mol) was heated to 80 °C and ethyl acetate solution of dibutyltin dilaurate (0.05 M, 1 mL) was added, and then the azido polyether polyol (84.4 g, 0.1 mol) was added dropwise. After adding the azido polyether polyol, the solution was stirred for an additional 6 h at 80±2 °C. Then dry n-hexane (1500 mL) was poured into the mixture and continuous extraction was selected to separate the excess HDI for 72 h [9]. The transparent russety viscous liquid, EO03-3, was got by reduced pressure distilling, yielded 93.6%.

Synthesis of EO03-1

Using a similar procedure to that of EO03-3. The molecular weight of the starting azido polyether polyol was found to be 1870 by GPC.

Determination of NCO%

The isocyanate eqmvalent weight was determined by reaction with excess dibutylamine, followed by back titration with standardized HCl [10].

Preparation of elastomers

The testing elastomers were prepared by the one-pot method. The ingredients were mixed together at once and allowed to cure at 50 °C for 96 h. The dumbbell-shaped specimens were cut from the vulcanized sheets. Five specimens were measured for each composition.

Results and discussion

Synthesis of EO03-3

The influence of HDI amount on the NCO% of EO03-3 is shown in Table 1. When NCO/OH (mol ratio) is more than 4/1, the NCO% shows a good agreement between the calculated and the measured values of EO03-3. There are probably some by-products of cross-linking when NCO/OH (mol ratio) is 3/1. It indicates that EO03-3 is close to the ideal structure.

Table 1 Influence of HDI amount on the NCO% of EO03-3

NCO/OH(mol. ratio)	Mw(calculated)	Mw(found)	NCO%(calculated)	NCO%(measured)
3/1	1516		11.08	9.41
4/1	1516	1436	11.08	10.35
6/1	1516		11.08	10.41

The reaction of HDI with alcohol is rather slow without catalyst when isocyanate group links to the aliphatic skeleton. In general, higher temperature would increase the reaction rate. Unfortunately, such method suffers from several shortcomings. It would be the danger of energetic material decomposition besides the formation of branched by-products. In this study, the reaction is carried at 80±2 °C for the sake of safety and moderate reaction rate.

It has been reported that the excess HDI was distilled in vacuum [7]. Honestly, there was potential danger in this procedure. In this study, continuous extraction is selected to remove the excess HDI. Being an extraction solvent, *n*-hexane has following advantages:

·favorable dissolution of HDI
·insolubility of EO03
·lack of reactive and
·low boiling point.

The influence of the excess HDI on post processing is summed up in Table 2 and the Run 2 is acceptable.

Table 2 Influence of the excess HDI on post processing

No.	NCO/OH/(mol. ratio)	Reaction time /h	Post processing time /h	Yield /%
Run 1	3/1	6	46	89.1
Run 2	4/1	6	72	93.6
Run 3	6/1	6	106	93.8

FTIR spectrum is shown in Figure 1 and the result indicates the characteristic absorptions of urethane and isocyanate groups and there are no other obvious differences from the azido polyether polyol. It suggests that the polymer chain remained except HDI reacting with the end OH groups of the azido polyether polyol.

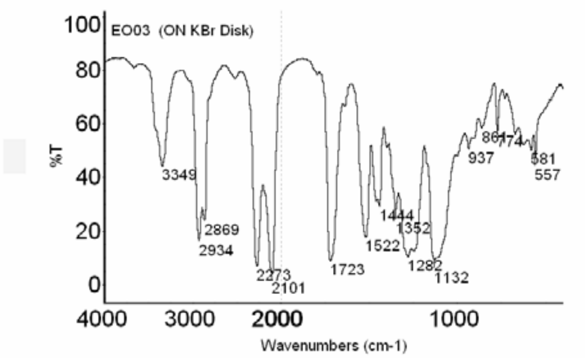


Figure 1. FTIR spectrum of EO03-3

Thermal properties of EO03-3

There is a peak at 252.89 °C in the ranging of 200-300 °C from Figure 2, which corresponding the decomposition of azido group. And the glass transition temperature (*Tg*) is found to be –47.13 °C (Figure 3).

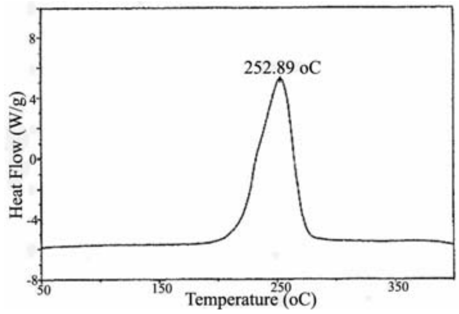


Figure 2. DSC plot of EO03-3

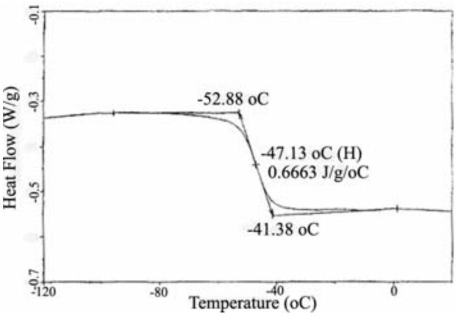


Figure 3. Glass transition temperature of EO03-3

Application of EO03-3

Thermal properties of GAP/EO03-3 elastomer

There is a decomposition peak at 254.56 °C from DSC plot of the polyurethane elastomer based on GAP/EO03-3 (Figure 4) and it is subtly different from that oberserved for EO03-3. For instance, the *Tg* of GAP/EO03-3 elastomer is –45.87 °C as shown in Figure 5, and is slightly higher than *Tg* of GAP/N100, (-47.03 °C). The results indicate that the structure of EO03-3 was branched and same as N100, which is known to have average functional group numbers of 3.65-3.70 [11].

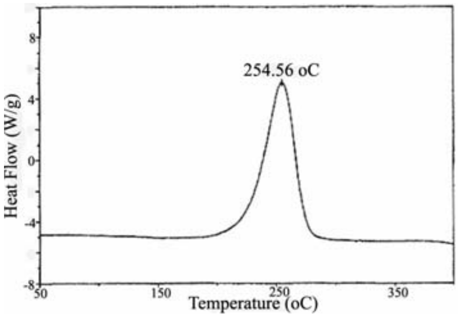


Figure 4. DSC plot of the GAP/EO03-3 elastomer

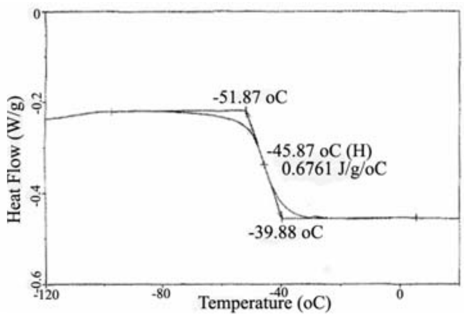


Figure 5. Glass transition temperature of GAP/EO03-3 elastomer

Compatibility of GAP/EO03-3 with TEGDN

An energetic nitric acid ester plasticizer, triethylene glycol dinitrate (TEGDN) was added to GAP/EO03-3 system, having 15%, 30% and 50% of mass ratio, respectively. The experiments results are shown in Table 3.

Table 3. Compatibility of GAP/EO03-3 with TEGDN

(GAP+EO03-3)/g	TEGDN/g	TEGDN/%	Appearances after 3 weeks	Tg/ °C
21.25	3.75	15	Transparent, no separation	
17.5	7.5	30	Transparent, no separation	
12.5	12.5	50	Transparent, no separation	-69.08

It is homogeneous even as the amount of TEGDN is equal to GAP/EO03-3 system. The results indicate that the system would be single-phase as long as the weight content of TEGDN is below 50%. There are two peaks found to be at 213.05 ^{o}C and 250.89 ^{o}C in DSC plot of GAP/EO03-3/50%TEGDN (Figure 6). The two exothermic peaks are attributed to the thermal decomposition of TEGDN and azido groups respectively. The *Tg* of GAP/EO03-3/50%TEGDN is found at –69.08 ^{o}C and there is only one glass transition region in Figure 7.

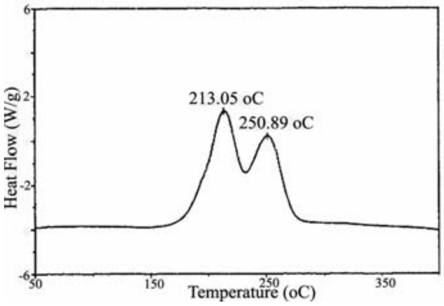


Figure 6. DSC plot of GAP/EO03-3/50%TEGDN

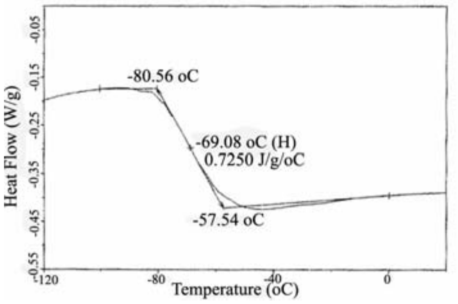


Figure 7. Glass transition temperature of GAP/EO03-3/50%TEGDN

Mechanical properties of GAP/ EO03 elastomers

Two azido poly-isocyanate curing agents with different molecular weight, EO03-1 and EO03-3, are selected to test mechanical properties of their elastomers cured with GAP and the results are shown in Table 4.

Table 4. Mechanical properties of GAP/ EO03 elastomers

Curing agent	Mw (found)	NCO/OH (mol. ratio)	σm/ MPa	εm/ %
EO03-1	2451	1.05	0.35	291
EO03-1	2451	1.10	0.37	244
EO03-1	2451	1.20	0.37	229
EO03-3	1436	1.05	0.63	157
EO03-3	1436	1.10	0.65	147
EO03-3	1436	1.20	0.67	129

Based on EO03-3/GAP system, three low molecular weight diols, ethylene glycol, butane-1,4-diol and hexane-1,6-diol are selected to be as chain extenders and mechanical properties of these three energetic elastomers are studied. The results (Table 5) suggest that *σ*m have improved slightly and εm have dropped followed the adding of the chain extenders. It would be contributed to the concentration increasing of –NHCOO- groups for the reaction of hydroxide groups with isocyanate groups.

Table 5. Influence of chain extenders on mechanical properties of GAP/EO03-3 elasomers

Curing agent	Chain extender	NCO/OH (mol. ratio)	σm/ MPa	εm/ %
EO03-3	ethylene glycol	1.20	0.74	95.6
EO03-3	butane-1,4-diol	1.20	0.75	75.0
EO03-3	hexane-1,6-diol	1.20	0.70	106.8

Conclusions

Tetrafunctional energetic poly-isocyanate curing agents (EO03-1 and EO03-3) were synthesized successfully via reaction of azido polyether polyol with HDI. Continuous extraction with n-hexane is selected to remove the excess HDI. EO03 have good physical and chemical compatibility with common energetic binder, such as GAP, and with common nitric acid ester plasticizer, such as TEGDN and the azido poly-isocyanate curing agent would improve mechanical properties of azido solid propellant. This procedure to prepare the energetic curing agent is safe and favorable to scale-up.

Acknowledgement. We thank Mr. Yu Hongjian for supplying GAP and TEGDN.

References

1. Stacer RG, Husband DM (1991) Propellants, Explosives, Pyrotechnics 16:167
2. Vasudevan V, Sundararajan G (1999) Propellants, Explosives, Pyrotechnics 24:295
3. Pang Aimin, Zhang Ruwen, Wu Jinghan (1995) Journal of Solid Rocket Technology 18:31
4. Li Ping (1998) Dissertion, Xi’an Modern Chemistry Research Institute
5. Gilman JW (1998) AFAL-T R-88-055, AD-A 202 295
6. Frankel MB, Wilson ER, Woolery DO (1990) USP 4962213
7. Frankel MB (1998) EP 0296310
8. Frankel MB, Flanagan JE, Hills E (1981) USP 4268450
9. Furniss BS, Hannaford AJ, Smith PWG, Tatchell AR (1989) Vogel's textbook of practical organic chemistry. 5th ed. John Wiley & Sons, Inc, New York
10. Hepburn C (1982) Polyurethane elastomers. Applied Science Publishers Ltd, New York
11. Li Xuli, Gan Xiaoxian, Su Yanling, Shao Chongbin (1997) Journal of Propellant Technology 18:98