Polyglycidyl nitrate (PGN)-based energetic thermoplastic polyurethane elastomers with bonding functions

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ABSTRACT: PGN-based ETPUEs were synthesized using mixture of chain extenders including 1, 4-butanediol and Diethyl Bis(hydroxymethyl)malonate (DBM). Through the special chain extenders DBM, the –COOR was introduced into the energetic thermoplastic polyurethane elastomers (ETPUEs) and further enhances the adhesion between ETPUE and nitramine solid ingredients in propellants. From the analysis, with the percentage of DBM increasing, the work of adhesion (W_a) between nitramine solid ingredients and ETPUEs increased and the maximum stress (σ_m) of ETPUEs decreased on the other hand. In order to test the bonding functions of different ETPUEs, the RDX/ETPUE propellants were prepared and the stress–strain curves of all propellants were tested. The results showed that the ETPUE-75 with 75% DBM can prevent the dewetting and improve the mechanical properties of propellants. The ETPUE prepared with chain extender including 1, 4-butanediol and DBM were valuable for application in propellants. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 2015, 132, 42026.

INTRODUCTION

Propellant is mainly composed of solid ingredients like oxidizers, metallic fuels, and other minor additives and polymer binder. The oxidizer in the propellants is to provide necessary oxygen for complete combustion of the fuel. An important kind of oxidizers is nitramine solid ingredients, such as hexogeon (RDX), cyclotetramethy-lene tetranitramine (HMX) and hexanitrohexaazaisowurtzitane (CL-20).[1]

The binders of solid propellants provide a matrix to bind the solid ingredients together. They give desired shape and structural integrity to the propellants. Conventional binders which used cross-linked elastomers are difficult to dispose and usually cause environmental problems. There has been profound interest to develop thermoplastic elastomers (TPEs) as suitable candidate for binder applications. TPEs avoid a process that involves curing reactions and hence has no pot life, and they are recyclable. Of the several forms of TPEs, thermoplastic polyurethane elastomers (TPUEs) have been extensively researched as binders of solid propellants.[2] TPUEs have unique morphology and properties. They typically exhibit a two-phase morphology because of the incompatibility of the soft and hard segments. The mechanical strength of the TPUEs is determined by the agglomeration of the hard segments, and the flexibility is because of the soft segments. The unique phase separation morphology of polyurethane makes it a good thermoplastic elastomer and a good kind of binders.[3] Energetic thermoplastic polyurethane elastomers (ETPUEs) have been widely studied because high energy and excellent properties.[4–6]

The poly (glycidyl nitrate) (PGN) with nitrato group is a good kind of macro glycol of ETPUE because of its high energy, high density, and high oxygen content.[7] In 1950, PGN was first synthesized.[8] The development of PGN was delayed because of the hazardous processes of monomer preparation, purification, and polymerization. It took years to recover its synthetic investigation. Until 1990s, commercial production of PGN was started and the researches of its application were begun.[9] Until now, there has been little research on the PGN-based ETPE. Emmanuela Diaz et al. synthesized the PGN-based ETPUEs using PGN and 4, 4-methylene diphenyl isocyanate (MDI) and studied the heats of combustion of them.[10] Zaijuan Zhang et al. synthesized the PGN-based ETPUEs using PGN and hexamethylene diisocyanate (HMDI) and studied the thermal decomposition behavior of PGN-based ETPUE.[11] Further research on PGN-based ETPUEs in this area would be needed.

Because of the incorporation of the considerable amount of solid energetic materials, dewetting behavior have become serious problems in solid propellants. When the adhesion between solid ingredients and ETPUE is not particularly strong, the
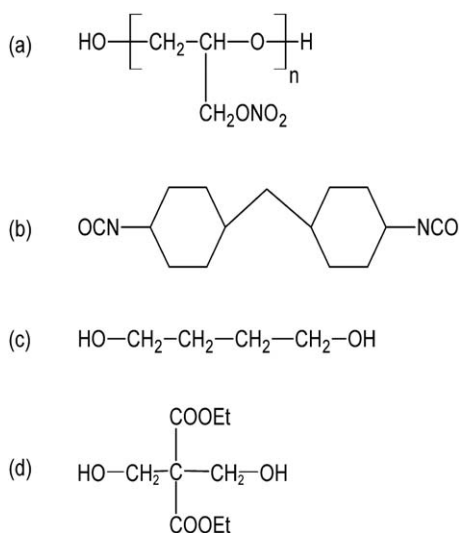
Figure 1. Chemical structure of (a) PGN, (b) HMDI, (c) BDO, and (d) DBM.

dewetting occurs rather suddenly.[12] The ETPUE with bonding functions itself is hoping to be produced to enhance the interactions of binder and solid ingredients. And they can decrease the dewetting and improve the mechanical property of propellants.

Many studies on structure–property relationships of polyurethanes were focused on chain extenders.[13] They give the special physical properties to polyurethane through the special chain extenders.[14,15] Based on the above ideas, in this article, a chain extender diethyl bis(hydroxymethyl)malonate (DBM) with ester group (-COOR) was introduced into the PGN-based ETPUEs.[16] The induced effect of -COOR and –NO$_2$ gives ETPUEs bonding functions and further enhances the adhesion between ETPUE and nitramine solid ingredients.

EXPERIMENTAL

Materials

Polyglycidyl nitrate (PGN; $\overline{Mn}$: 4770 g/mol; OH equivalent: 0.454 mmol/g; Liming Research Institute of Chemical Industry, Henan China) was used after vacuum drying for 2 h at 90°C. Hexamethylene diisocyanate (HMDI; Bayer (Germany); NCO equivalent: 7.6234 mmol/g) was used as received. Catalyst was prepared by dissolving Dibutyltin Dilaurate (DBTDL; Beijing Chemical Plant) into dibutyl phthalate. 1, 4-butanediol (BDO; Beijing Chemical Plant; OH equivalent: 22.22 mmol/g) was used after vacuum drying for 4 h at 85°C. Diethyl Bis(hydroxymethyl)malonate (DBM) was made in our laboratory and obtained with a purity of 97.6% using isopropyl ether recrystallization. The OH equivalent of DBM is 9.09 mmol/g.[17] RDX was provided by Baiyin Yinguang Chemical Material Factory.

Synthesis

Synthesis of PGN-Based ETPUEs. The PGN-based ETPUEs were synthesized using mixture of chain extenders including BDO and DBM (Figure 1). The synthesis process was illustrated in Figure 2.

As Figure 2 shows, the hard segments consist of hexamethylene diisocyanate (HMDI) chain extended with BDO and DBM. The

soft segment is polyglycidyl nitrate (PGN). The dosage of raw materials can be decided in the three following formulas:

$$R = \frac{7.6234 * m_{HMDI}}{0.454 * m_{PGN} + 22.22 * m_{BDO} + 9.09 * m_{DBM}}$$

$$wt \% B = \frac{m_{HMDI} + m_{BDO} + m_{DBM}}{m_{HMDI} + m_{BDO} + m_{DBM} + m_{PGN}} \quad m_i, \text{ mass.}$$

$$x\% DBM = \frac{m_{DBM}}{m_{BDO} + m_{DBM}}$$

The "R" was mole ratio of –NCO and –OH and in this article the $R = 1$. The "wt % B" was hard segment content by weight and in this article the wt % $B = 30\%$. The "$x\%$ DBM" was the mass fraction of DBM in the mixture of chain extenders. The sample with $x\%$ DBM was named as ETPUE-x. In this article the mass fraction of DBM was 0%, 25%, 50%, 75%, and 100% in the mixture, respectively.

In this article, the synthesis process of PGN-based ETPUEs is divided into three primary processes: (1) a certain amount of PGN, HMDI, and catalyst (the mass fraction to total materials was 1%) was added into reactor. The mixture was stirred and kept for 2 h at 90°C in the nitrogen atmosphere. (2) The different proportional chain extender (BDO and DBM) was added to mixture at 60°C, and reacted for 3–5 min. (3) The product was poured in a mold to cure at 100°C for around 10 h. Finally the PGN-based ETPUEs with different proportional chain extender were obtained.

Synthesis of RDX/ETPUE Propellants. The RDX/ETPUE propellants were prepared with the following steps: The ETPUE was dissolved in tetrahydrofuran, and the RDX was introduced in the ETPUE solution at 80% weight percentages. Then the tetrahydrofuran was evaporated. Finally the mixture of ETPUE and RDX was mixed on open mill and tableted by flat-panel curing. The propellant of ETPUE-x was named as RDX/ETPUE-x.
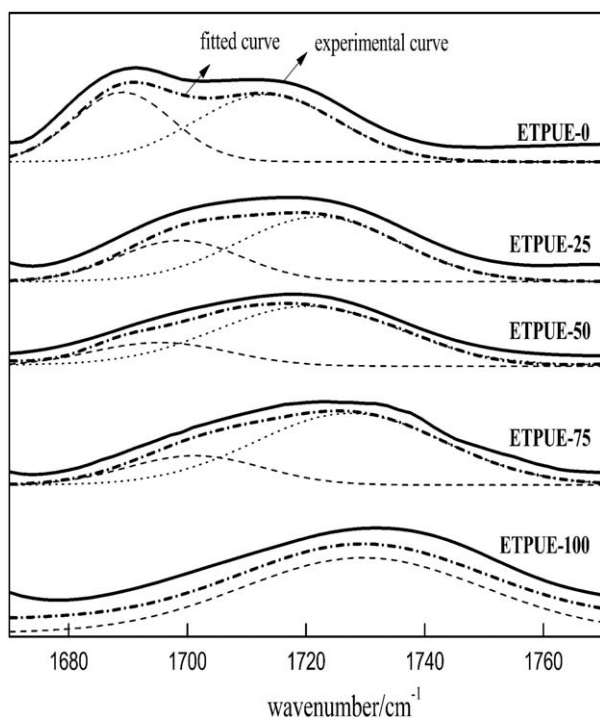
Measurements

Fourier transform infrared spectra were recorded on FTIR (Nicolet FTIR- 8700, Thermo) with a wavenumber resolution of 4 cm^{-1} and a single average of 32 scans at room temperature. Each sample for infrared analysis was obtained with Attenuated Total Reflection (ATR).

The molecular weights ($\overline{Mw}$ and $\overline{Mn}$) and the polydispersity index (PDI $= \overline{Mw}/\overline{Mn}$) were obtained using GPC (LC-20A, Shimadzu). The operating temperature was 40°C, the mobile phase was THF, the flow rate was 1.0 mL/min and the raw data were calibrated using a universal calibration with polystyrene standards.

Thermo gravimetric analysis was carried out in TGA analyzer (TGA/DSC1SF/ 417-2, Mettler Toledo) at heating rates of 10°C/min from room temperature to 600°C in a nitrogen atmosphere (40 mL/min).

Differential scanning calorimetric analysis (DSC) was made over the temperature range from −100°C to 150°C on Mettler DSC1 with a 10 K/min heating rate in a nitrogen atmosphere (40 mL/min). 2–5 mg of each sample was placed in a small confined aluminum cell.

Figure 2. The synthesis process of PGN-based ETPUEs with different proportional chain extender.

The contact angle was measured using OCA contact angle analyzer (Datephysics). The drop volume was 2 μL and the drop flow was medium speed. The surface free energy was calculated using the contact angle measurement software SCA20.

The stress–strain test of dumb-bell specimens was measured by using a tensile testing machine (Instron-6022, Shimadzu) at a constant strain rate of 100 mm/min and at room temperature. The dimensions of the samples were 20 mm (neck area length) x 4 mm (width) x 2 mm (thickness).

RESULTS AND DISCUSSION

Molecular Weight Analysis
The number-average molecular weight ($\overline{Mn}$) and polydispersity index (PDI; $\overline{Mw}/\overline{Mn}$) of synthesized PGN-based ETPUEs were tested by GPC. The $\overline{Mn}$ of prepared ETPUEs were between 20,000 and 32,000 g mol^{-1} and the PDI were between 1.83 and 2.13.

FTIR Analysis
Figure 3 showed the infrared spectra of synthesized PGN-based ETPUEs with different proportional chain extender. According to the references, the polyurethane syntheses were successful in making no residual -OH and -NCO groups and appearance of

Figure 3. FTIR spectra of ETPUEs.

Figure 4. Curve fitting for carbonyl region of ETPUEs.

urethane. In Figure 3, the infrared spectra of ETPUEs did not show the -OH absorption band of PGN and -NCO absorption band of HMDI at 3450 and 2265 cm^{-1}.[18,19] The absorption bands at 3340 cm^{-1} were assigned to -NH stretching of urethane. Also the characteristic peaks of -ONO$_2$ group from PGN at 1634 and 1279 cm^{-1} were shown.[20,21] Those results proved the structure of the ETPUE.

Hydrogen bonding in ETPUEs, which reflect the microphase separation, has an important effect on the properties of the elastomer.[22] One of the most useful methods of studying the hydrogen bonding was FTIR. In these ETPUEs, the carbonyl absorption included the absorption of amide and DBM, and they all belong to the hard segment. Traditionally, the hydrogen bond between –NH and carbonyl of hard segment can reflect the aggregation ability of hard segments. So we studied the infrared spectra of the carbonyl of hard segment.

In Figure 4 the infrared spectra of the carbonyl stretching region are shown for various proportional chain extenders. The spectra could be fitted with two Gauss lines.[23] The results of curve-

fitting the carbonyl stretching region of ETPUEs were shown in Figure 4 and Table I. As shown in Table I, the hydrogen bonding carbonyl decreases as the amount of DBM in chain extender increased. The steric hindrance of the bulk ester side chain leads to the difficulty of hydrogen bonding. After adding DBM, the distance between the hydrogen bonding sites along the chains increased which lead to the decreased hydrogen bonding and aggregation ability of hard segments.

DSC Analysis

The glass transition temperature of ETPUEs is correlated with the lowest application temperature. So it is important to study the glass transition temperature of ETPUEs. Figure 5 and Table II show the DSC results of PGN-based ETPUEs with different proportional chain extender. Two glass transition temperatures were found for ETPUEs. The first is the glass transition temperature of soft segment (Tgs) and the second one is the glass transition temperature of hard segment (Tgh). The Tgs of all ETPUEs are lower than −30.0°C and indicate that the PGN-based ETPUEs have good low temperature properties. Upon further analysis, we may find that the Tgs shifted to higher temperature and the Tgh shifted to lower temperature with the percentage of DBM increasing. The two glass transition temperatures were closer to the middle, which indicated that the compatibility of soft and hard segment was increased. This was because of the reduced hydrogen bond between hard segments which was proved by FTIR.

TGA/DTG Analysis

Thermal decomposition could be correlated with the processing temperature of ETPUEs.[5,24] So it is necessary to understand the thermal decomposition process of PGN-based ETPUEs.

Figure 6 shows the thermal curves of ETPUEs with different proportional chain extender recorded at a heating rate of 10 K/min. The initial 5% weight loss for total ETPUEs occurs around 190°C which showed that the PGN-based ETPUEs have good thermal stability. The DTG curves of ETPUEs showed that as the percentage of DBM is increased, the thermal transition around 270°C became apparent and the stage around 327°C became weak. This indicates that with the percentage of DBM increasing, the decomposition of hard segment moved to lower temperature. This is also because the accumulation between hard segments was weaker.

Interfacial Characteristics

The adhesion between nitramine solid ingredients and ETPUEs has important effects on the mechanical properties of propellants.

Table I. Results of Curve Fitting for Carbonyl Region of FTIR Spectra for ETPUEs

Samples	Bonded carbonyl		Free carbonyl		
	Wavenumber (cm^{-1})	Peak area	Wavenumber (cm^{-1})	Peak area	Ratio of hydrogen bonding (%)
ETPUE-0	1689.1	0.97	1713.4	0.68	58.8
ETPUE-25	1698.7	0.67	1722.1	0.72	48.2
ETPUE-50	1695.4	0.46	1720.4	0.76	37.7
ETPUE-75	1701.2	0.36	1727.4	0.82	30.5
ETPUE-100	–	–	1732.8	–	–

Figure 5. The DSC thermograms of ETPUEs.

Figure 6. (a) TGA and (b) DTG curves of PGN-ETPUEs.
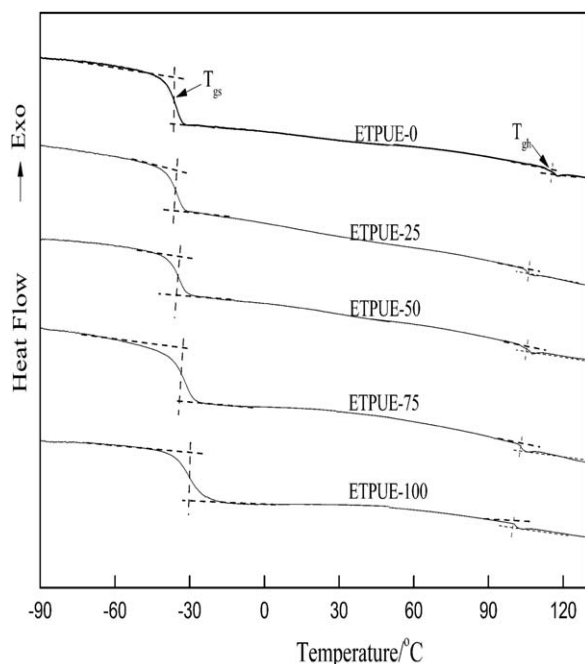
In this article, the work of adhesion between nitramine solid ingredients and ETPUEs was tested by measurement of contact angle. Through the contact angle analysis, the surface free energy of ETPUEs was calculated.

The fundamental equation which relates the interfacial tension between solid and liquid (γ_{SL}) to solid surface tension (γ_S), liquid surface tension (γ_L), and the contact angle (θ) between a drop of liquid and the solid surface is given by the well-known Young 's equation: $\gamma_{SL} = \gamma_S - \gamma_L \cos\theta (\theta > 0)$. The polar molecule would have two terms making up its surface tension, dispersion force (d) and dipolar interaction (p), so that $\gamma_s = \gamma_s^d + \gamma_s^p$ where γ_s^d and γ_s^p are the dispersion and dipolar contributions to the total surface tension. The contact angle and the calculated surface free energy using SCA20 were listed in Table III.

The surface free energy of RDX, HMX, and CL-20 was theoretical values.[26] The γ_s of them is 41.81, 49.76, and 42.65 mJ m^{-2} separately. The γ_s^d of them is 24.17, 45.63, and 40.61 mJ m^{-2} separately.

The interfacial tension (γ_{s1s2}) and work of adhesion (W_a) between three different nitramine solid ingredients and ETPUEs were calculated by the following equations, separately. The γ_{s1s2} and W_a results of theoretic calculation were listed in Table IV:

$$\gamma_{S1S2} = \gamma_{S1} + \gamma_{S2} - 2\sqrt{\gamma_{S1}^d}\sqrt{\gamma_{S2}^d} - 2\sqrt{\gamma_{S1}^p}\sqrt{\gamma_{S2}^p} \qquad (1)$$

$$W_a = 2\sqrt{\gamma_{S1}^d}\sqrt{\gamma_{S2}^d} + 2\sqrt{\gamma_{s1}^p}\sqrt{\gamma_{S2}^p} \qquad (2)$$

where γ_{s1s2} is the interfacial tension between s1 and s2; γ_{s1} and γ_{s2} are the surface tensions of s1 and s2 separately; γ_{S1}^d and γ_{S2}^d are the dispersion surface tensions of s1 and s2 separately; γ_{S1}^p and γ_{S2}^p are the dipolar surface tensions of s1 and s2 separately.

As shown in Table IV, with the increasing of percentage of DBM of the ETPUEs the γ_{s1s2} between three solid ingredients and ETPUEs decreased and the W_a improved generally. The W_a value between three solid ingredients and ETPUEs containing -COOR (ETPUE-25, ETPUE-50, ETPUE-75, and ETPUE-100) are greatly improved compared with ETPUE-0. This showed that PGN-ETPUEs synthesized with mixture extender including DBM have bonding functions themselves.

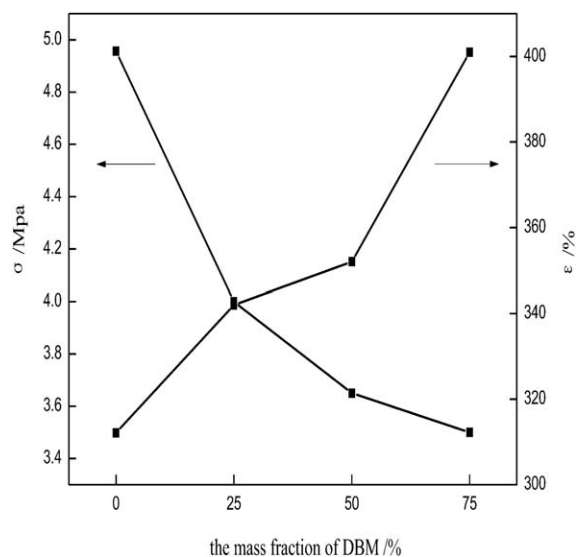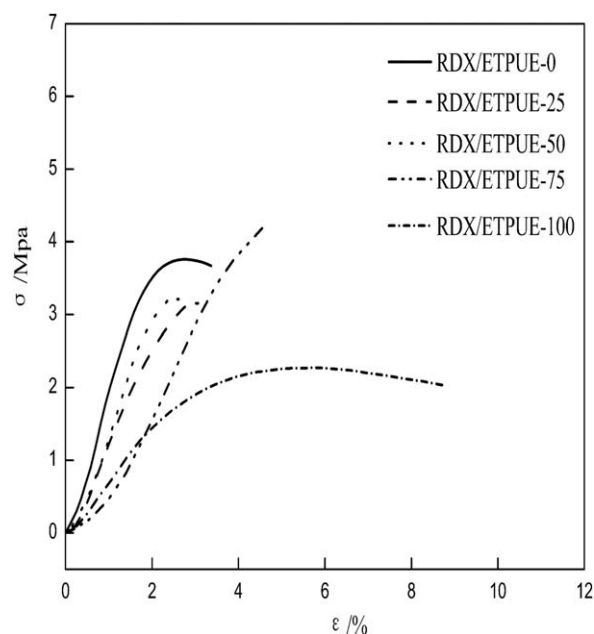**Mechanical Properties of ETPUEs**

The mechanical properties of binders affect the mechanical properties of the final propellants. Thus it is necessary to study the mechanical properties (tensile strength and elongation at

Table II. The Glass Transition Temperature of ETPUEs

Samples	Tgs (°C)	Tgh (°C)
ETPUE-0	−36.4	114.8
ETPUE-25	−35.6	105.7
ETPUE-50	−34.7	105.5
ETPUE-75	−33.4	102.8
ETPUE-100	−30.2	100.7

Table III. The Contact Angle and Surface Free Energy of ETPUEs

Samples	Water (deg)	Formamide (deg)	γ_s (mJ m^{-2})	γ_s^d (mJ m^{-2})
ETPUE-0	104.9	95.8	11.76	8.01
ETPUE-25	100.5	91.0	14.05	9.34
ETPUE-50	98.8	89.2	14.96	9.81
ETPUE-75	97.3	87.3	15.95	10.54
ETPUE-100	94.7	85.0	17.23	10.85

Table IV. The γ_{s1s2} and W_a of ETPUEs and Nitramine Solid Ingredients (RDX, HMX, and CL-20)

	RDX		HMX		CL-20	
Samples	γ_{s1s2} (mJ m^{-2})	Wa (mJ m^{-2})	γ_{s1s2} (mJ m^{-2})	Wa (mJ m^{-2})	γ_{s1s2} (mJ m^{-2})	Wa (mJ m^{-2})
ETPUE-0	9.48	44.09	15.42	46.10	12.80	41.61
ETPUE-25	7.58	48.28	13.71	50.10	11.55	45.15
ETPUE-50	6.91	49.86	13.19	51.53	11.21	46.40
ETPUE-75	6.30	51.46	12.40	53.31	10.57	48.03
ETPUE-100	5.43	53.61	12.23	54.76	10.68	49.20

Figure 7. The mechanical properties of ETPUEs (the ETPE-100 was too soft to test the mechanical properties).

Figure 8. The stress–strain curves of RDX/ETPUE.

break) of ETPUEs. The mechanical properties of ETPUEs were shown in Figure 7. With the increasing of DBM, the elongation at break (ε_b) increased and the maximum stress (σ_m) decreased. Combining the FTIR analysis results, the reason was weakened hydrogen bonding between hard segments.

Mechanical Properties of RDX/ETPUE

The mechanical properties of propellants are the combining results of mechanical properties of ETPUEs and the work of adhesion between solid ingredients and ETPUEs.

The stress–strain curves of all five propellants were shown in Figure 8. Yield occurred in stress–strain curves of RDX/ETPUE-0 propellants, which was considered as one of the indicators of dewetting. The curves of RDX/ETPUE-75 propellants presented no yield and its mechanical properties were higher than those of RDX/ETPUE-0. When the mass fraction of DBM in the mixture of chain extenders was 75%, the two kinds of factors worked together best. The above results showed that the ETPUE-75 can prevent the dewetting and improve the mechanical properties of propellants.

CONCLUSIONS

The adhesion between solid ingredients and binders and the properties of binders themselves jointly affect the mechanical properties of the final propellants. The Polyglycidyl nitrate (PGN)-based ETPUEs with functional –COOR groups were synthesized as binders to enhance the interactions of binders and solid ingredients. The ETPUEs were given -COOR using different proportional mixture of chain extenders including BDO and DBM which has -COOR. The analysis showed that the ability of ETPUEs to form hydrogen bond weakened with the percentage of DBM increasing and further caused the maximum stress (σ_m) of ETPUEs to decrease. On the contrary, the interfacial tension and the work of adhesion between nitramine solid ingredients and ETPUEs increased. In order to test the combining results of two factors, the RDX/ETPUE propellants with different ETPUEs were prepared. The tensile tests of propellants showed that the RDX/ETPUE-75 propellants presented no dewetting and good mechanical properties. In conclusion, the ETPUEs prepared with functional –COOR groups have bonding function and the potential applied value in propellants.

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REFERENCES

1. Chen, F. T.; Duo, Y. Q.; Luo, S. G.; Luo, Y. J.; Tan, H. M. *Propell. Explos. Pyrot.* **2003**, *28*, 7.

2. Baoyan, Z.; Tan, H. M. *Eur. Polym. J.* **1998**, *34*, 571.

3. Kendagannaswamy, B. K.; Siddaramaiah. *J. Appl. Polym. Sci.* **2002**, *84*, 359.

4. Nair, J. K.; Reddy, T. S.; Satpute, R. S.; Mukundan, T.; Asthana, S. N. *J. Polym. Mater.* **2004**, *21*, 205.

5. Kawamoto, A. M.; Oliveira, J. I. S.; Utra, R. C. L.; Rezende, L. C.; Keicher, T.; Krause, H. *J. Aerosp. Technol. Manag.* **2009**, *1*, 35.

6. Sanghavi, R. R.; Asthana, S. N.; Karir, J. S.; Singh, H. *J. Energ. Mater.* **2001**, *19*, 79.

7. Sikder, A. K.; Reddy, S. *Propell. Explos. Pyrot.* **2013**, *38*, 14.

8. Thelen, C. J.; Meitner, J. G.; Murbach, W. J.; Van Dolah, R. W. NAVORD report 2028, NOTS 686, US Naval Ordnance, **1953.**

9. Day, R. S.; Stern, A. G.; Willer, R. L. U.S. Patent. 5, 120, 827[P].**1992.**

10. Diaz, E.; Brousseau,P.; Ampleman,G.; Prud'homme, R. E. *Propell. Explos. Pyrot.* **2003**, *28*, 101.

11. Zhang, Z. J.; Wang,G.; Luo, N.; Huang, M. H.; Jin, M. M.; Luo,Y. J. *J. Appl. Polym. Sci.* **2014**, *131*, 40965.

12. Mulage, K. S.; Patkar, R. N.; Deuskar, V. D.; Pundlik, S. M.; Kakade, S. D.; Gupta, M. *J. Energ. Mater.* **2007**, *25*, 233.

13. Blackwell, J.; Nagarajan, M. R.; Hoitink, T. B. *Polymer* **1982**, *23*, 950.

14. Liaw, D. J. *J. Appl. Polym. Sci.* **1997**, *66*, 1251.

15. Chen, K. Y.; Kuo, J. F. *Macrmol. Chem. Phys.* **2000**, *201*, 2676.

16. Kim, C. S. U.S. Patent 4,915,755[P], **1990**, 4.

17. Ferris, A. F. *J. Org. Chem.* **1955**, *20*, 780.

18. Padmavathy,T.; Srinivasan, K. S. V. *J. Polym. Sci. Polym. Chem.* **2002**, *40*, 1527.

19. Hsu, Tsai-Fa; Lee, Yu-Der. *Polymer* **1999**, *40*, 577.

20. You, J. S.; Kweon, J. O.; Kang, S. C.; Noh, S. T. *Macromol. Res.* **2010**, *18*, 1226.

21. Fei, P. L.; Lin, Y.; Gang, Y. L.; De, F. N. *Polym. Bull.* **2011**, *66*, 503.

22. Wang, X.; D, Luo, X. *Eur. Polym. J.* **2004**, *40*, 2391.

23. Ning, L.; De, N. W.; Sheng, K. Y. *Polymer* **1996**, *37*, 3577.

24. Herder, G.; Weterings, F. P.; de Klerk, W. P. C. *J. Therm. Anal. Calorim.* **2003**, *72*, 921.

25. Krabbendam-La Haye, E. L. M.; de Klerk, W. P. C.; Miszczak, M.; Szymanowski, J. *J. Therm. Anal. Calorim.* **2003**, *72*, 931.

26. Du, M. N.; Luo, Y. J.; Li, G. P. *Chin. J. Energ. Mater.* **2007**, *15*, 269.