

# Synthesis and Characterization of Thermoplastic Polyurethanes as Binder for Novel Thermoplastic Propellant

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**ABSTRACT:** Two series of thermoplastic polyurethanes (TPUs), which used nitroester plasticizable tetrahydrofuran-ethylene oxide random copolyether as soft segment and adduction products of isophorone diisocyanate (IPDI) and toluene diisocyanate (TDI) with 1,4-butanediol as hard segments respectively, were successfully synthesized as binders for novel thermoplastic propellant. Mechanical tests and DSC techniques were applied to make characterizations of the polymers in order to choose candidate materials. Results shown that the TPU based on IPDI with fraction of the hard segment around 45% will meet requirements of propellant in terms of mechanical properties and glass transition of the soft segment phase. The results were further manifested in detail by quantitative studies of the degree of microphase separation as well as hydrogen bonding within the hard segment domain based on the equations established through FTIR and DSC analyses. It was found that mixing of two phases, which mainly referred to the amount of the hard segment dissolving into the soft segment phase, was as little as 10% in IPDI series TPUs, whereas it was almost up to 30% in TDI series. This indicated that better phase separation was achieved in IPDI series TPU. By contrast, studies of hydrogen bonding in domain revealed that the domain of TPUs prepared with TDI was much oriented in comparison with that with IPDI, which indicated higher processing temperatures. The results were raised by the melting index results under required conditions. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2961–2966, 2002; DOI 10.1002/app.2324

**Key words:** thermoplastic polyurethanes; thermoplastic propellant; microphase separation; hydrogen bonding

## INTRODUCTION

Since Butler<sup>1</sup> first introduced thermoplastic polyurethanes (TPE) into thermoplastic propellants as binder after careful studies of series of TPE during the 1980s, considerable attention has been attracted in this area; many candidate materials,<sup>2,3</sup> such as Karton G, have been successfully applied to prepared thermoplastic propellant.

However, most TPEs developed thus far still cannot satisfy the users in many ways. The high melting viscosity of TPEs during processing in most propellants has to be prepared through tedious techniques and, more importantly, greatly restricts the loading capacities and the subsequent energetic performances of the complex systems greatly. Therefore, we considered it would be a good key to this problem simply to introduce an energetic plasticizer, such as nitroester, into a nitroester plasticizable TPE binder system, to improve energetic performance and lower melting viscosity simultaneously.

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**Table I** Summary of Mechanical Properties of TPU

Weight Fraction Of Hard Segment (%)	TPUs Prepared With IPDI			TPUs Prepared With TDI		
	$\sigma_m$ /MPa	$\epsilon_m$ /%	$\sigma$ ( $\epsilon = 250\%$ )/MPa	$\sigma_m$ /MPa	$\epsilon_m$ /%	$\sigma$ ( $\epsilon = 250\%$ )/MPa
40	4.97	692	1.88	1.60	924	—
45	8.34	636	3.96	3.10	834	1.19
48	8.52	448	4.25	3.76	453	2.40
50	6.92	352	4.89	6.49	366	—

Several years of studies<sup>4</sup> in our laboratory have clearly proved that introducing an ethylene oxide unit into the chain of polytetrahydrofuran can significantly improve the compatibility of the oligomer with nitroester; when the molar ratio of the two monomer units approaches 1, a random sequence structure is achieved. This makes the polymer exhibit low crystallinity at low temperature and has appropriate compatibility with nitroester at the same time. We therefore considered that thermoplastic polyurethanes (TPU) based on the random copolyether as a soft segment would be good candidate materials for thermoplastic propellant. Attempts have therefore been made in this article to synthesize two series of TPUs using the random copolyether as soft segment and reaction products of IPDI and TDI with 1,4-butanediol as hard segments, respectively. Characterizations and especially quantitative studies of microphase separation and hydrogen bonding within the hard segment domain were also carried out in detail.

## EXPERIMENTAL

### Materials

Tetrahydrofuran-ethylene oxide copolyether, comprising the polymer chain with a unit ratio of ethylene oxide and tetrahydrofuran of 50/50, was supplied by Liming Institute of Chemical Engineering. Isophorone diisocyanate and toluene diisocyanate were commercial products from BASF Corporation Ltd., and 1,4-butanediol was purchased from Beijing Chemical Industry. All the materials were used without further purification.

### Polymer Synthesis

The two series of TPUs with weight fractions of hard segment of 40–50% were prepared through

a melting–prepolymerization method according to previous work.<sup>5</sup>

### Characterization

Mechanical tests were carried out on Instron model 6022 universal testing machine at a cross-head speed of 100 mL/min. Infrared (IR) spectra were recorded on a Perkin–Elmer spectrometer by ATR techniques with a incidence angle of 55°. Thermal analysis was measured on a Perkin–Elmer DSC 7 instrument with a heating rate of 10°C/min.

## RESULTS AND DISCUSSION

### Characterization of Mechanical Properties

It has been well adopted that a  $\sigma_m$  value over 4 MPa along with an  $\epsilon_m$  value of greater than 400% were necessary for TPU to be well applied to thermoplastic propellant. Therefore, mechanical properties of TPUs are important factors in choosing candidate materials. The obtained results of mechanical tests were listed in Table I.

It can be seen in Table I that the mechanical properties of TPU prepared with IPDI were apparently better than those with TDI and that the IPDI series with fraction of hard segment around 45% would be good candidate materials just in view of mechanical properties.

### Thermal Analysis

The  $T_g$  results of soft segment phase measured from DSC were summarized in Table II. The data in Table II showed that TPU based on IPDI have  $T_g$  values of soft segment phase far below  $-50^\circ\text{C}$ , which were adequate for propellants consequently prepared to well stand low-temperature conditions and that the  $T_g$  values of TDI-based TPU were much higher.

**Table II**  $T_g$  of Soft Segment Phase Measured from DSC

Fraction of Hard Segment by wt %	$T_g$ of TPU With IPDI/K	$T_g$ of TPU With TDI/K
40	211.8	243.3
45	211.2	246.6
48	211.4	—
50	209.8	260.1

### Quantitative Studies of Microphase Separation

Properties of TPU largely depend on microphase separation; the degree is mainly determined by estimating mixing of hard and soft segment phase. It has been commonly assumed in research that the portion of soft segment dissolving into a hard segment domain is a negligible magnitude as compared with that of a hard segment dissolving into soft segment phase. Therefore, the degree of microphase separation can be estimated simply as the fraction of hard segment dissolving into soft segment phase.

Dissolving hard segment can increase the  $T_g$  of soft segment phase, and the change can be directly recorded from DSC measurements. Therefore, the relationship between the increment of  $T_g$  and the amount of hard segment in the mixed soft segment phase can be used to estimate microphase separation quantitatively. In achieving this, two models can be invoked. The first assumed that the increment of  $T_g$  of soft segment phase is owing to the additive effects of mixing composition as described by the copolymer equation developed by Gordon-Taylor:<sup>6</sup>

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \quad (1)$$

where  $T_g$  is the  $T_g$  of soft segment phase obtained from DSC,  $T_{g1} = 198$  k is the  $T_g$  of the copolyether oligomer, and  $T_{g2} = 390$  k for the hard segment of IPDI series,  $T_{g2} = 380$  k for the TDI series, while  $w_1$ ,  $w_2$  represent the weight fraction of soft and hard segment in the mixed soft segment and hard segment phase, respectively.

The alternative model concerns the hydrogen bonding between NH protons and ether oxygen of soft segment. In their studies of TPU Sung et al.<sup>7</sup> found, using Fourier transform infrared (FTIR) that almost all the NH groups of the hard segment are hydrogen bonded. It thus can derive

that the NH groups of the hard segment after dissolving into the soft segment phase were hydrogen bonded with the ether oxygen of the soft segment. The part of hydrogen bond that accompanies mixing will be equivalent to crosslinking of the soft segment and the effect on  $T_g$  can be estimated using equation (2) developed by DiBenedetto:<sup>8</sup>

$$\frac{\Delta T_g}{T_{g1}} = \frac{kX_C}{(1 - X_C)} \quad (2)$$

where  $k$  is a constant between 1.2 and 1.5 and is held at 1.5 in this study;  $\Delta T_g$  is the increment of  $T_g$  of soft segment caused by crosslinking and  $X_C$  is the molar fraction of ether units hydrogen bonded to urethane NH groups.

If we were to assume that the increment of  $T_g$  of soft segment phase caused by mixing and crosslinking can be simply added, then equations (4) and (5) for TPU prepared with IPDI and TDI, respectively, can be derived by converting the weight fraction in equation (1) to  $X_C$  in equation (2), according to the relationship as described in equation (3):

$$X_C = (W_2/M_2)/(W_1/M_1) \quad (3)$$

$$\frac{\Delta T_{g\text{Total}}}{T_{g1}} = \frac{2.822X_C}{1 + 0.366X_C} \quad (4)$$

$$\frac{\Delta T_{g\text{Total}}}{T_{g1}} = \frac{1.322X_C}{1.366X_C + 1} + \frac{1.5X_C}{1 - X_C} \quad (5)$$

With  $\Delta T_{g\text{Total}}$  values measured from DSC, the degrees of microphase separation of the two series of TPU calculated as fraction of hard segment dissolving into soft segment phase based on equations (4) and (5) are listed in Table III. The results in Table III show that the fractions of the hard segment dissolving into the soft segment phase are about 10% and 30% for TPU prepared with IPDI and TDI, respectively, indicating that better microphase separation was achieved in IPDI series TPU. The results were in agreement with mechanical results, presented in Table I.

### Studies of Hydrogen Bonding in Hard Segment Domain

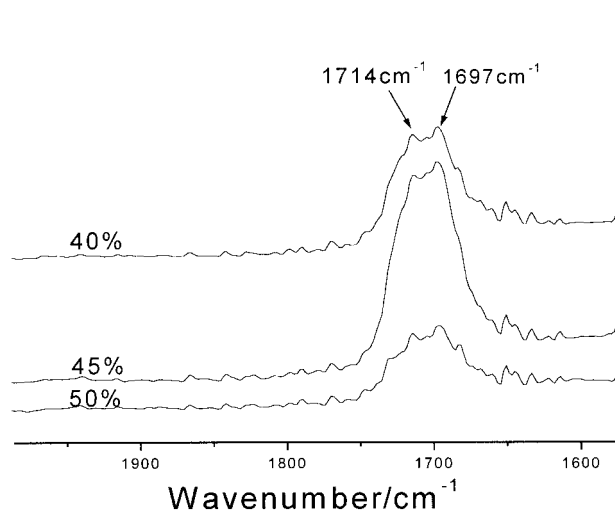
Hydrogen bonding in the hard segment domain is crucial for TPU to have good properties. Therefore, many researchers have been attracted to

**Table III Fraction of Hard Segment Dissolving into Soft Segment Phase**

Weight Fraction of Hard Segment (%)	IPDI Series TPU		TDI Series TPU	
	$\Delta T_g/K$	Fraction of Hard Segment Dissolving into Soft Segment Phase (%)	$\Delta T_g/K$	Fraction of Hard Segment Dissolving into Soft Segment Phase (%)
40	13.8	10.05	45.3	30.61
45	13.1	7.82	48.6	26.97
48	13.4	7.05	—	—
50	11.8	5.73	62.1	28.44

this study. Sung et al.<sup>7</sup> showed that almost all the NH groups of the hard segment were hydrogen bonded and, except for a small portion, were hydrogen bonded to the ether oxygen of the soft segment that accompanied mixing of the two phases. Most were hydrogen bonded in the domain with the carbonyl groups and the urethane alkoxy oxygen of the hard segment.

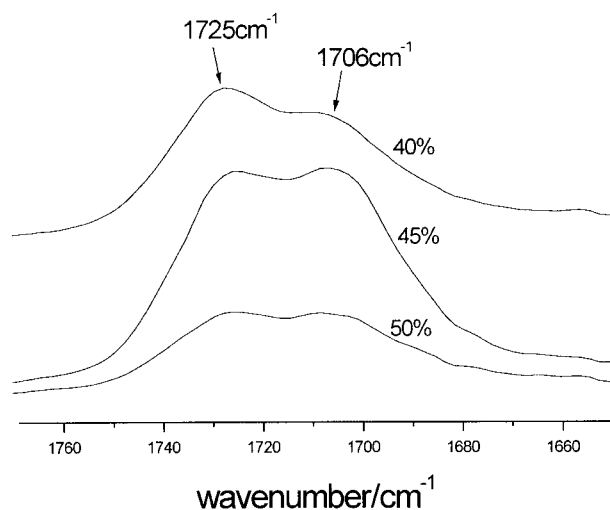
Forming of hydrogen bond of the carbonyl groups with the NH protons usually led to red shifts of the absorption bands in FTIR spectra, as illustrated in Figures 1 and 2. The carbonyl groups regions of IPDI series in Figure 1 split into two peaks, at  $1714\text{ cm}^{-1}$  and  $1697\text{ cm}^{-1}$ , corresponding to the free carbonyl groups and the hydrogen-bonded carbonyl groups, respectively, and at  $1725\text{ cm}^{-1}$  and  $1706\text{ cm}^{-1}$  for TDI series in Figure 2.



**Figure 1** FTIR spectra of the carbonyl groups of TPU based on IPDI with different weight fractions of hard segment: upper (40%), middle (45%), lower (50%), and where the peaks at  $1714\text{ cm}^{-1}$  correspond to the free carbonyl groups and at  $1697\text{ cm}^{-1}$  correspond to the hydrogen-bonded carbonyl groups.

It has been demonstrated that the increment of extinction coefficient of carbonyl groups caused by hydrogen bond was no more than 20%. Therefore, the molar fraction of the hydrogen-bonded carbonyl groups can be estimated approximately as the ratio of absorbance of the two absorption bands. The calculated results of both series of TPU based on FTIR results are summarized in Table IV. The data presented in Table IV indicate that nearly 50% of the carbonyl groups of the hard segment within the domain were hydrogen bonded in both series of TPU.

Whereas, compared with carbonyl groups, the free urethane alkoxy oxygen along with the hydrogen-bonded urethane alkoxy oxygen was not clearly resolved in FTIR curves due to the com-



**Figure 2** FTIR spectra of carbonyl groups of TPU based on TDI with different weight fractions of hard segment: upper (40%), middle (45%), lower (50%), and where the peaks at  $1725\text{ cm}^{-1}$  correspond to the free carbonyl groups and at  $1706\text{ cm}^{-1}$  correspond to the hydrogen-bonded carbonyl groups.

**Table IV Fraction of Hydrogen-Bonded Carbonyl Groups**

Weight Fraction of Hard Segment (%)	Absorbance of Free Bonded Carbonyl Groups		Absorbance of Hydrogen-Bonded Carbonyl Groups		Fraction of Hydrogen-Bonded Carbonyl Groups	
	IPDI	TDI	IPDI	TDI	IPDI	TDI
40	0.1587	0.4630	0.1678	0.3867	51.39%	45.51%
45	0.2821	0.6987	0.3002	0.7093	51.55%	50.38%
50	0.0964	0.2482	0.1062	0.2460	52.42%	49.78%

plexity introduced by the soft ether oxygen, amide III and the asymmetric ester stretching bands along the 1000–1300-cm<sup>-1</sup> region. Accordingly, it is difficult to determinate the fraction of the hydrogen-bonded urethane alkoxy oxygen directly through FTIR as occurred in carbonyl groups. However, if we adopted the conclusion drawn by Sung et al.<sup>7</sup> that almost all the NH groups were hydrogen bonded, the fraction of hydrogen bonding between the urethane alkoxy oxygen and the NH groups within domain could still be obtained with the normalization method. The calculated results, corrected by subtracting the part of the hard segment dissolving into the soft segment phase, are summarized in Table V.

It is clearly shown in Table IV that hydrogen bonding within the domain was principally dominated by carbonyl groups and that this was especially true in the case of TPU based on TDI, in which the fractions of the hydrogen-bonded carbonyl groups were nearly up to 70%. If we postulate that a more random sequence structure can be easily achieved when fractions of the two hydrogen-bonded acceptors are much closer, we can derive that a well-ordered and crystalline domain structure will occur in TPU prepared with TDI, and that this will produce higher viscosity during processing. In order to prove this, melting index

tests were consequently undertaken. The values for TPU based on IPDI were within 0.05–0.3, whereas no products were extruded for samples based on TDI under the same conditions. Therefore, in this view, the IPDI series TPUs will be good candidate material in terms of processing temperature.

## CONCLUSIONS

In view of the applications of TPE as a thermoplastic propellant, we considered that a nitroester plasticizable TPE plasticized with nitroester would be a good binder system. Therefore, two series of thermoplastic polyurethanes based on nitroester plasticizable tetrahydrofuran-ethylene oxide random copolyether as soft segment and adduction products of isophorone diisocyanate and toluene diisocyanate with 1,4-butanediol as hard segments are, respectively, synthesized in this article. It can be concluded from mechanical tests and thermal analyses that TPU based on IPDI with a fraction of the hard segment around 45% will be a good candidate binder material in terms of mechanical properties and glass transition of the soft segment phase. Quantitative studies of microphase separation as well as hydrogen bonding

**Table V Distribution of Hydrogen Bond in Domain**

Weight Fraction of Hard Segment (%)	Distribution of Hydrogen Bond (%)			
	IPDI Series		TDI Series	
	Carbonyl Groups	Alkoxy Oxygen	Carbonyl Groups	Alkoxy Oxygen
40	57.13	42.87	65.59	34.41
45	55.92	44.08	68.99	31.01
50	55.61	44.39	69.56	30.45

within hard segment domain showed that TPU prepared with IPDI undergo less mixing of hard and soft phases, and that the domain of TPU prepared with TDI is much more oriented, indicating that higher temperature is required during processing.

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