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The synthetic kinetics and underwater acoustic absorption properties of novel epoxyurethanes and their blends with epoxy resin

Weihong Sun · Xin Yan · Xi Zhu

Abstract Reaction kinetics between isocyanate-terminated prepolyurethane (PPU) and glycidol using dibutyltin dilaurate (DBTDL) as a catalyst was investigated by monitoring the change in the intensity of the absorbance peak of NCO stretching band at $2{,}270$ cm^{-1} on Fourier transform infrared spectrum at different temperatures. The results indicated that the reactions of TDI- and IPDI-type PPU with glycidol followed second-order kinetics, and their activation energies could be efficiently reduced by DBTDL. For TDI-type PPU, the reaction activation energies were 80.37 kJ mol^{-1} without catalyst, 49.86 kJ mol^{-1} with 0.1 % of DBTDLs, and 37.85 kJ mol^{-1} with 0.2 % of DBTDLs, respectively. For IPDI-type PPU, the reaction activation energies were 69.16 kJ mol^{-1} without catalyst, 63.05 kJ mol^{-1} with 0.1 % of DBTDLs, and 55.57 kJ mol^{-1} with 0.2 % of DBTDLs, respectively. This corresponding TDI- and IPDI-type epoxyurethane (EPU) were blended with epoxy resins (EPs) and cured by the Michael adduct of ethlylenediamine with butyl acrylate (molar ratio = 1:1) curing agent, to prepare EPU/EP blend elastomers for underwater acoustic absorption materials. The TDI-type EPUs had good acoustic absorption properties and the average acoustic absorption coefficient of TDI-type EPU was 0.75, the maximum acoustic absorption coefficient was 0.94; the EPUs blended with E-51 EP had better acoustic absorption properties than those from E-44; and the EPU from PPG-2000 had better underwater acoustic absorption properties than that from PPG-1000.

Keywords Epoxyurethane · Polyurethane prepolymer · Glycidol · FTIR · Kinetics · Activation energy · Elastomers · Underwater acoustic property

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Introduction

Nowadays, epoxy resin (EP) is widely used as adhesives, coatings, electric-insulation materials and matrix resins due to its excellent adhesion property, good dimensional and chemical stability, and room-temperature curing. However, the cured EP is usually rigid and brittle in nature, and for this reason, its toughening by elastomers has been extensively studied in the last decades. Polyurethane has excellent abrasion resistance, good adhesion and mechanical properties, and good damping ability [1–3]. Its isocyanate-terminated prepolymer is usually employed to toughen EP by grafting, copolymerizing and forming interpenetrating polymer networks [4–10], but the prepolymer has high activity and poor storage stability. The amino-terminated polyurethane prepolymer as a curing agent is also utilized to toughen EP, but the curing reaction at room temperature is very slow [11, 12].

The polyurethane prepolymer or diisocyanate, which is blocked by reactive-hydrogen blocking agents such as phenols, caprolactams, diketones, alcohols, and amines, has good storage stability but higher deblocking temperature [13–15], and it is usually used as a high-temperature curing agent for coatings and a toughening agent for EP and phenolic resin [16–19].

Epoxyurethane (EPU), a glycidyl-terminated polyurethane prepolymer, which has the characteristic properties of polyurethane and EP, offers some distinct advantages such as good storage stability, room-temperature curing, and miscibility with EP, and it is usually used as an adhesive [20–24] and a toughening agent for EP [25–28]. Its synthesis usually includes two-step reactions: the reaction between diisocyanate and polyether/polyester diol to form an isocyanate-terminated polyurethane prepolymer, and the reaction between the isocyanate-terminated polyurethane prepolymer and glycidol [22, 25, 27, 28]. The second reaction is the key step for preparing an EPU successfully. However, few studies pay much attention to improving the efficiency of the reaction between the isocyanate-terminated polyurethane prepolymer and glycidol. As we all know, tertiary amine and organic tin are usually used as catalysts for manufacture of polyurethane [29, 30]. In this article, the reaction kinetics between isocyanate-terminated prepolyurethane (PPU) and glycidol using dibutyltin dilaurate (DBTDL) as a catalyst is investigated by FTIR. Meanwhile, this EPU is mixed with EP in various mass ratios and cured with an ethlylenediamine/butyl acrylate (BA) adduct to prepare EPU/EP blend elastomers, and the underwater absorption properties of the elastomers are reported.

Experimental

Materials

Polypropylene glycol with a molecular weight of 2,000 or 1,000 (PPG-2000 or PPG-1000, Yueyang Petrochemical company) was dewatered at 110 °C under reducing pressure. 2,3-epoxy-1-propanol (Glycidol, Shanghai Jingchun Chemicals Co., Ltd.) was purified by vacuum distillation. 1,4-toluene diisocyanate (TDI, Wuhan Jiangbei Chemical Reagent Factory), isophorone diisocyanate (IPDI, Shanghai JingChun

Chemicals Co., Ltd.) and DBTDL (Shanghai Chemical Reagent Co., Ltd.) were used as received, bisphenol A type EP (with an epoxy value of 0.51 equiv or 0.44 v/100 g, YueYang Petrochemical Co., Yueyang, China), ethylenediamine (Tianjin Thailand Chemical Reagent Factory, Tianjin, China), BA (; Tianjin Institute of Chemical Reagent Research, Tianjin, China), The Michael adduct of ethlylenediamine with BA (molar ratio = 1:1) was used as a curing agent for EP and EPU.

Methods

Synthesis of NCO-terminated polyurethane prepolymer

TDI or IPDI was added into a 1-L three-neck flask equipped with a stirrer, a condenser, a dropping funnel, and a drying tube, then PPG-2000 or PPG-1000 or PTMG-2000 was added to the flask by dropping funnel under stirring (the molar ratio of NCO/OH is 2/1) and the reaction between them was kept for 3 h at 348 K in order to obtain PPU. The contents of NCO groups were determined by dibutylamine titration method.

Reaction kinetics of the PPU with glycidol

10 g of TDI- or IPDI-type PPUs homogeneously mixed with 0.63 g or 0.60 g of glycidol and 0, 0.1, and 0.2 % of DBTDL catalysts (mass ratio to PPU). The mixture was coated on two KBr discs and then the discs were laid in a SYD TC-L1 temperature controller (Eurotherm Company) joined with a Spectrum BX II FTIR spectrometer (PerkinElemer Company). FTIR absorption spectra were recorded at different temperatures and time intervals. The intensities of the NCO absorption band at $2{,}270$ cm^{-1} and the characteristic peak at $1{,}108$ cm^{-1} were obtained by calculating the peak area.

Synthesis of PU prepolymer blocked with glycidol (epoxyurethane) and preparation of the EPU/EP blend elastomers

TDI- or IPDI-type NCO-terminated polyurethane prepolymer was added into a 2-L three-neck flask equipped with a stirrer, a condenser, a dropping funnel, then glycidol (molar ratio of OH to NCO = 1.1/1) was added to the flask by dropping funnel under stirring and kept for 5 h at 333 K with 0.1 % of DBTDLs to give the blocked prepolymer. Amines can react with the epoxy groups in EPs and EPUs at lower temperature. Hence, the PU prepolymer blocked by glycidol and EP can be simultaneously cured and form an inter-crosslinked EPU/EP network in the presence of the curing agent (polyamine) at room temperature. EPU and EP with weight ratios of 100/0, 90/10, 80/20, and 70/30 were heated in an oven at 323 K for 1 h and mixed well under stirring, and then degassed in vacuo for about 30 min (until bubbling ceased). After degassing was stopped, the curing agents with 9 % of the mixture weights were added to the mixture and mixed under stirring at a lower rate. The final mixture was degassed in vacuo and then poured into a columniform

Teflon mold and cured for 24 h at room temperature to give the composite samples with diameters of 56.2 mm and thicknesses of 40 mm.

Measurements of underwater acoustic properties

The underwater acoustic properties were measured on a +57 pulse tube and corresponding equipments (as shown in Fig. 1) according to Chinese Standard GB/T14369-1993. The frequency is from 2 to 12 kHz, and the water temperature is 26 °C except the water temperature contrast experiment. The experimental set and a detailed description were given in Ref. [19].

Results and discussion

EPU can be prepared by two-step reactions as shown in Scheme 1. The second reaction kinetics for the formation of EPU can be determined on FTIR spectroscopy by monitoring the changes in intensity of the absorption band at 2,270 cm^{-1} for the NCO stretching vibration. The characteristic peak at 1,108 cm^{-1} for C–O–C stretching vibration was selected as internal standard peak to ensure that the quantitative results are independent of the thickness of the sample, because it kept unchanged in the whole reaction process. Based on Lambert–Beer law, the absorbances for the NCO and C–O–C stretching absorption bands are given by:

$$A_{t_{(NCO)}} = \varepsilon_{(NCO)} \cdot c_t \cdot d \tag{1}$$

$$A_{t_{(C-O-C)}} = \varepsilon_{(C-O-C)} \cdot c_0 \cdot d, \tag{2}$$

where A represents the absorbance, ε is the molar extinction coefficient, and d is the thickness, c_0 and c_t are the concentrations of the NCO groups at the initial time and t time, respectively. The Eq. 3 can be derived from the Eqs. 1 and 2:
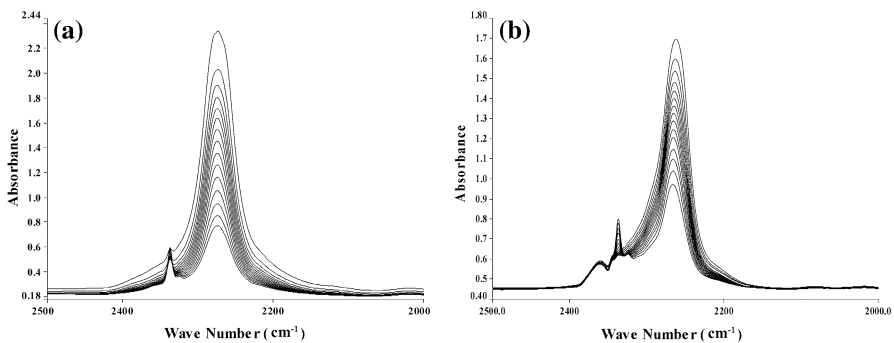

Fig. 1 Evolution of NCO band at 2,270 cm^{-1} in the reaction process between TDI-type (**a**) and IPDI-type (**b**) PPUs and glycidol at 318 K with 0.2 % of DBTDLs

$$\frac{A_{t(C-O-C)}}{A_{t(NCO)}} = \frac{\varepsilon_{(C-O-C)}}{\varepsilon_{(NCO)}} \cdot \frac{c_0}{c_t}. \tag{3}$$

If $t = 0$, the Eq. 4 can be deduced as:

$$\frac{A_{0(C-O-C)}}{A_{0(NCO)}} = \frac{\varepsilon_{(C-O-C)}}{\varepsilon_{(NCO)}}. \tag{4}$$

The conversion (α) of disappearance of the NCO groups is given by:

$$\alpha = \frac{c_0 - c_t}{c_o} = 1 - \frac{c_t}{c_0} = 1 - \frac{A_{t(NCO)}}{A_{t(C-O-C)}} \cdot \frac{A_{0(C-O-C)}}{A_{0(NCO)}}. \tag{5}$$

For a second-order reaction, the kinetic equation is given as follows:

$$-\frac{dc}{dt} = kc^2, \tag{6}$$

where k is the second-order reaction rate constant. The integrated form is given by

$$c_0 k t = \frac{\alpha}{1 - \alpha}. \tag{7}$$

The Eq. 7 indicates that $\alpha/(1 - \alpha)$ versus t is linear and the slope of this line is $c_0 k$. Based on Arrhenius' equation, $\ln(c_0 k)$ versus $1/T$ is a linear equation shown as

$$\ln c_0 k = -\frac{E_a}{RT} + \ln A + \ln c_0, \tag{8}$$

where A is pre-exponential factor, R is ideal gas constant (8.314 J K^{-1} mol^{-1}), and E_a is the activation energy, which can be obtained from the line slope.

Effects of catalyst and temperature on conversion of NCO group

The evolution of NCO band at 2,270 cm^{-1} in the synthetic process of EPU at 318 K is shown in Fig. 1 (the dosage of the catalyst DBTDL is 0.2 %). It can be seen that the absorbance intensity of the NCO band decreases as the reaction time increases due to the reaction between the NCO groups in PPU and hydroxyl groups in glycidol. As known, catalysts and temperature have obvious effects on the reaction
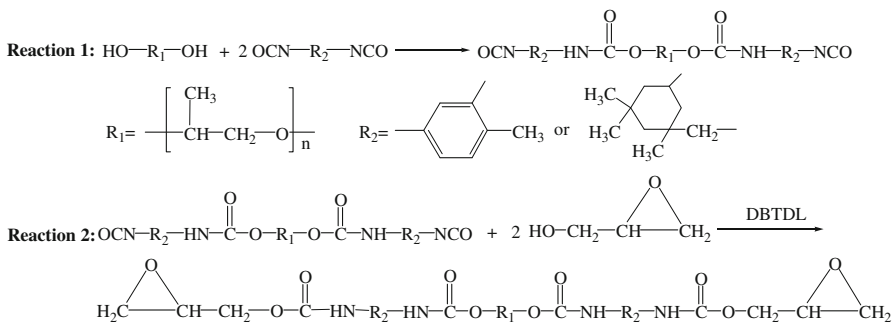
Scheme 1 Synthetic reactions of epoxyurethane

rate. Organometallic compounds such as DBTDL, stannous octoate, and metal acetylacetonates were referred to as effective catalysts for the reactions between isocyanates and alcohols owing to their Lewis acid behavior and coordinating capacity to diisocyanates or alcohols [29–32]. They can activate the reaction groups by increasing the electrophilic reactivity of isocyanate groups and nucleophilic reactivity of hydroxyl groups so as to promote the reactions dramatically. Figure 2 and 3 show the effects of catalyst DBTDL and reaction temperature on the conversion of the NCO groups in TDI- and IPDI-type PPUs, respectively. It can be seen that the conversion at the same time intervals increases as the amount of DBTDL and reaction temperature is increased. The results indicate that DBTDL can efficiently increase the conversion of the NCO groups for preparing the EPU.

Kinetic equation and activation energy of the reaction of PPU with glycidol

Figures 4, 5 and 6 show the plots of $\alpha/(1 - \alpha)$ versus reaction time for the NCO group in the absence of catalyst DBTDL and in the present of 0.1 and 0.2 % of DBTDLs at different temperature, respectively. It can be seen that all plots of $\alpha/(1 - \alpha)$ versus t are considerably good linear. This indicates that the reaction between the NCO groups in PPU and the hydroxyl groups in glycidol using DBTDL or not is a second-order reaction. The $c_0 k$ values from the slopes of the straight lines are listed in Table 1. The plots of $\ln(c_0 k)$ versus $1/T$ are basically linear as shown in Fig. 7. The activation energy and the Arrhenius' equation for the reaction with adding different dosages of DBTDLs can be obtained from linear fitting, and listed in Table 2. The results show that the activation energy for the reaction between the NCO groups in PPU and the hydroxyl groups in glycidol decreases as the dosage of the catalyst DBTDL increases, and DBTDL can obviously reduce the reaction activation energy.
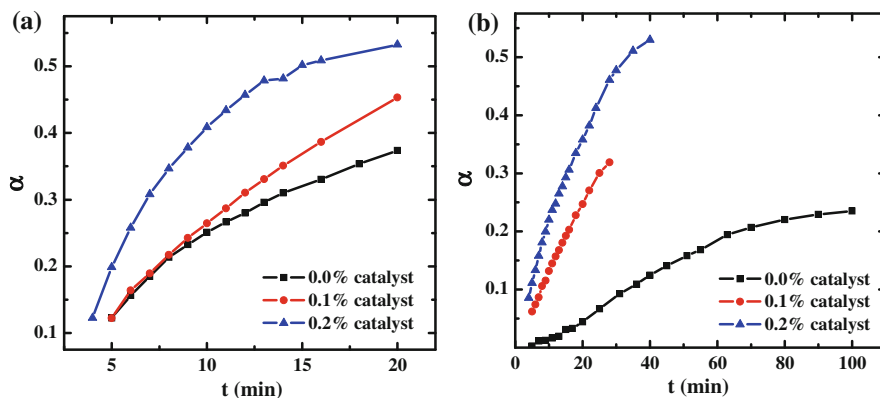

Fig. 2 Effect of catalyst dosage on conversion of the NCO groups in TDI-type (a) and IPDI-type (b) PPUs at 308 K
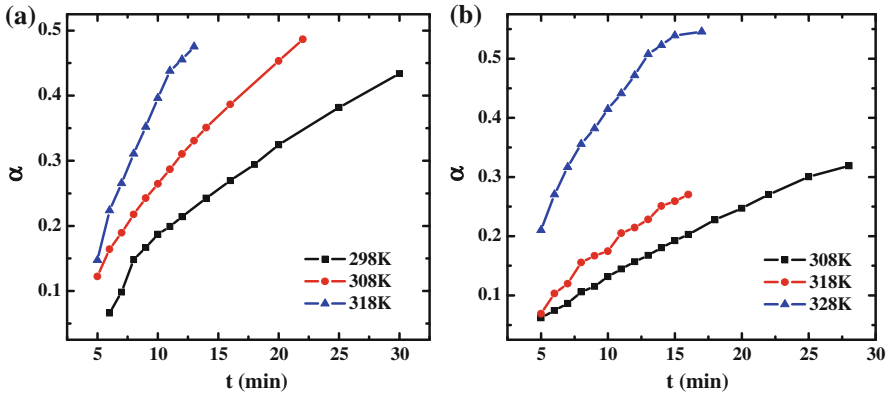
Fig. 3 Effect of reaction temperature on conversion of the NCO groups in TDI-type (**a**) and IPDI-type (**b**) PPUs with 0.1 % of DBTDLs
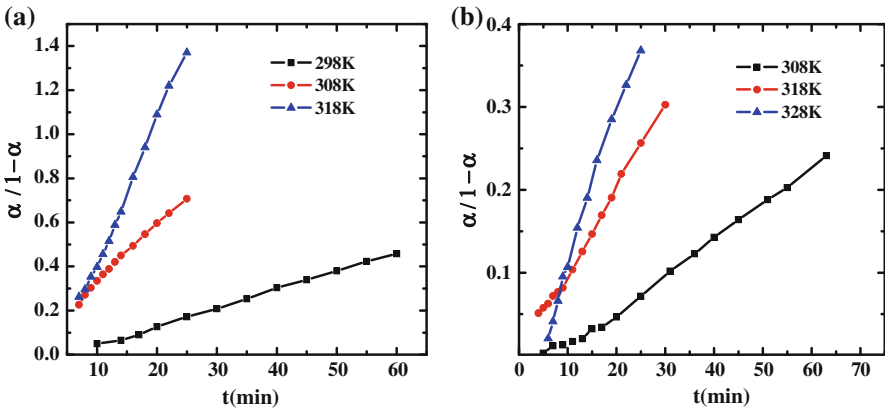

Fig. 4 Plots of $\alpha/(1-\alpha)$ versus t for the NCO groups in TDI-type (**a**) and IPDI-type (**b**) PPUs without DBTDLs

The underwater acoustic absorption properties of the EPU/EP elastomers

Polymer elastomers such as Rho-C rubber [33], *Eucommia ulmoides* gum [34], polyurethanes [35] are widely used as underwater acoustic materials. Among these elastomers, polyurethanes are gained much of people's interest due to their good damping and acoustic absorption properties, excellent adhesion properties and good mechanical properties, and their damping or underwater acoustic absorption ability can be controlled by molecular design and blending with other polymers such as EP [2]. In our previous article [19], the blend elastomers from *p*-cresol blocked PU (BPU) and epoxy was used underwater acoustic absorption materials, and the results showed that the elastomers can matching with the impedance of seawater, but the ability of the acoustic wave dissipation in BPU/EP matrix itself is not so good, and the *p*-cresol, which is accompanied with the course of curing, is harmful to health.
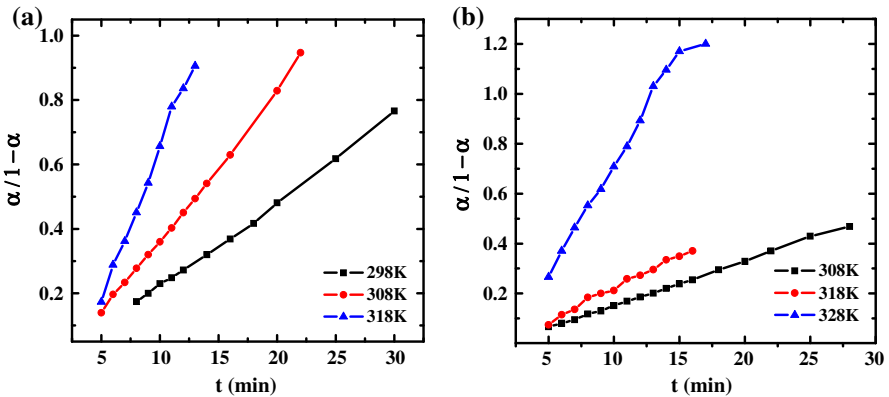
Fig. 5 Plots of $\alpha/(1 - \alpha)$ versus t for the NCO groups in TDI-type (**a**) and IPDI-type (**b**) PPUs with 0.1 % of DBTDLs
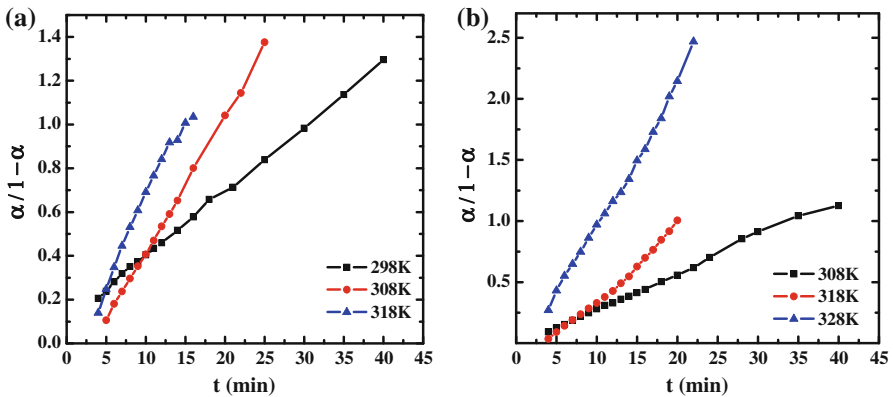

Fig. 6 Plots of $\alpha/(1 - \alpha)$ versus t for the NCO groups in TDI-type (**a**) and IPDI-type (**b**) PPUs with 0.2 % of DBTDLs

EPU has more ether bands than BPU, and EPU/EP have good damping properties [36], so now the underwater acoustic absorption and reflection properties of EPU/EP elastomers are discussed in this section.

As shown in Fig. 8, the different proportions of EPU to EP can obtain different acoustic absorption properties, the acoustic absorption properties of PU/EP = 70/30 and 100/0 are better than that of other proportions, especially in middle and high frequency, the acoustic absorption coefficient can exceed 0.8 in 4–12 kHz, the average absorption coefficient is 0.75 and the maximum value is 0.94. From Fig. 8a, we can see that there appear good middle and high frequency acoustic absorption properties when EPU/EP = 70/30 and EPU/EP = 100/0, while there shows a good low frequency acoustic absorption property when the proportion of EPU to EP is 90/10, that is because it has a higher damping loss factor when the proportion of EPU to EP is 90/10 in 2–4 kHz, so acoustic absorption coefficient of the proportion (90/10) is higher than others in low frequency.

Table 1 The c_0k values for the reactions of the NCO groups in TDI- and IPDI-type PPUs with different dosages of DBTDLs at different temperatures

DBTDL dosage	Temp. (K)	c_0k for TDI-type PPU	c_0k for IPDI-type PPU
0.0 %	298	0.0085	–
	308	0.0262	0.0041
	318	0.0650	0.0100
	328	–	0.0214
0.1 %	298	0.0266	–
	308	0.0463	0.0179
	318	0.0936	0.0265
	328	–	0.0841
0.2 %	298	0.0326	–
	308	0.0624	0.0299
	318	0.0853	0.0589
	328	–	0.1146

Fig. 7 Plots of $\ln(c_0k)$ versus $1/T$ for the reactions of the NCO groups in TDI- and IPDI-type PPUs with different dosages of DBTDLs
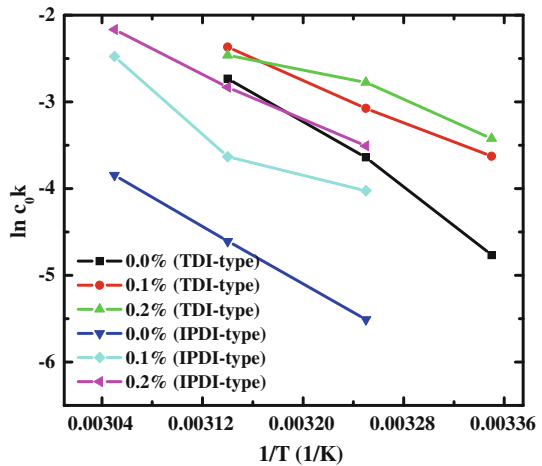

Table 2 The activation energy and Arrhenius' equations for the reactions of the NCO groups in TDI- and IPDI-type PPUs with different dosages of DBTDLs

PPU type	DBTDL dosage (%)	Arrhenius' equation	E_a (kJ mol^{-1})
TDI	0.0	$ln(c_0k) = -9667/T + 27.67$	80.37
	0.1	$ln(c_0k) = -5997/T + 16.45$	49.86
	0.2	$ln(c_0k) = -4552/T + 11.89$	37.85
IPDI	0.0	$ln(c_0k) = -8316/T + 21.51$	69.16
	0.1	$ln(c_0k) = -7583/T + 20.48$	63.05
	0.2	$ln(c_0k) = -6684/T + 18.20$	55.57

The underwater acoustic properties of different isocyanate type polyurethane and different type of EP are shown in Fig. 9, and the results show that the underwater acoustic properties of TDI-type EPU/EP elastomers are better than that of IPDI-type
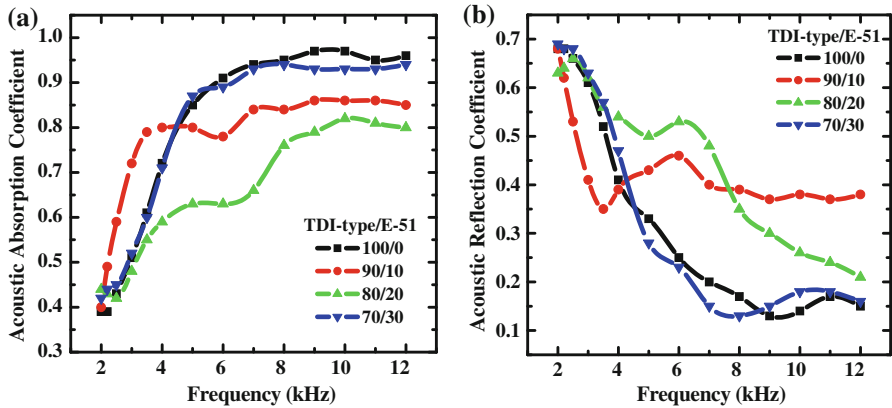
Fig. 8 Underwater acoustic properties of different weight ratios of TDI-type EPU/EP compositions: **a** acoustic absorption coefficient and **b** acoustic reflection coefficient
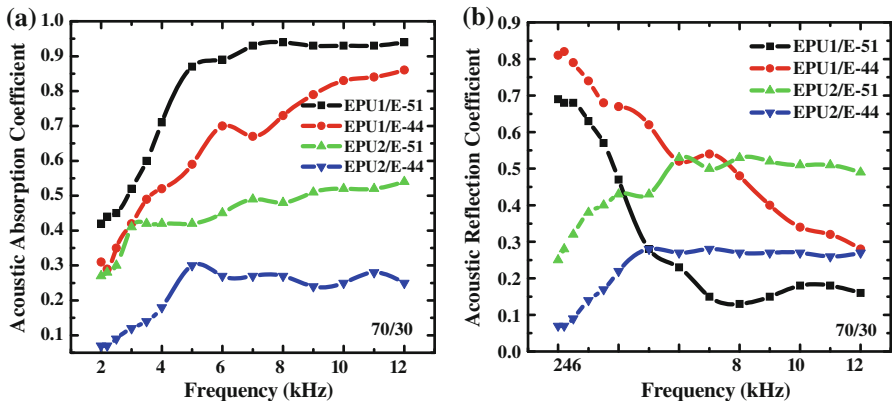

Fig. 9 The influence of different type of epoxy resin and different type of isocyanate on the underwater acoustic properties of the EPU/EP = 70/30 elastomers: **a** acoustic absorption coefficient and **b** acoustic reflection coefficient. (*EPU1* TDI-type epoxyurethane, *EPU2* IPDI-type epoxyurethane)

EPU/EP elastomers, and both the underwater acoustic absorption coefficient and the acoustic reflection coefficient in E-51 type EP composed with the same EPU are higher than that of E-44.

Figure 10 shows the underwater acoustic absorption properties of different weight of polyether, and results show that EPU from PPG-2000 have excellent acoustic absorption properties than that from PPG-1000, that is because the former has better damping property to dissipate energy better than the latter, without any fillers and capacities, so it has a better underwater acoustic absorption property.

The acoustic property of EPU/EP in this research is better than BPU/EP shown in our previous paper [19]. EPU/EP gain higher performance of acoustic attenuation and more low acoustic reflection coefficence especially in middle and high frequency than BPU/EP elastomer. And if we added adequate porous fillers (such as
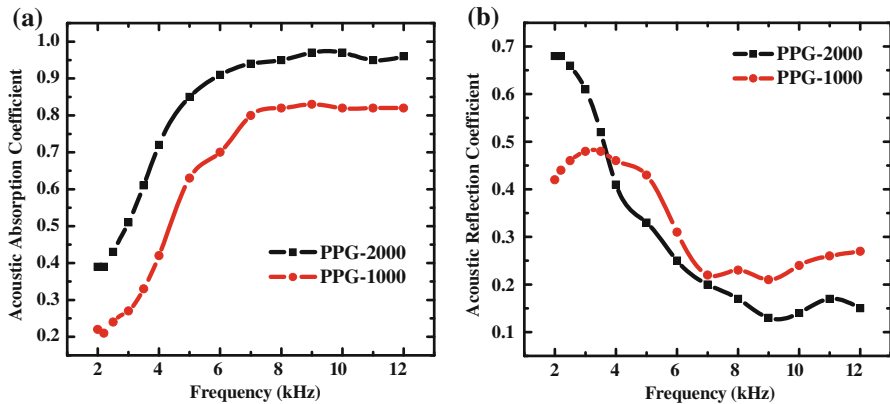
Fig. 10 Underwater acoustic absorption and reflection properties of the EPU elastomers with different molecular weight of polyether: **a** acoustic absorption coefficient and **b** acoustic reflection coefficient (*note*: isocyanate used to synthesize the epoxyurethane is TDI)

micro-balloons, voids, cavities, and particles) or acoustic absorption structures to these matrices, more enough progress on acoustic property may be achieved.

Conclusion

In summary, this article showed that considerable requirements for improving the synthetic reaction efficiency of EPUs, DBTDL was used as a catalyst for the reaction between isocyanate-terminated PPU and glycidol; then we utilized this EPU to blend with EP for synthesizing the EPU/EP elastomers for underwater acoustic absorption, and obtained good underwater acoustic absorption properties without any filler and cavity. Fourier transform infrared spectrum is performed to gain insight into the mechanism of the reaction. The reaction kinetics was studied by monitoring the change in the intensity of the absorbance peak of NCO stretching band at 2,270 cm^{-1} on the spectrum. The reaction parameters were determined by evaluating the kinetic data collected at various temperatures. The kinetic data indicated that the reactions between TDI- and IPDI-type PPUs and glycidol followed second-order kinetics, and their activation energies could be efficiently reduced by DBTDL. Activation energy of the reactions (in the absence of catalyst DBTDL and in the present of 0.1 and 0.2 % of DBTDLs) were obtained in this article. The underwater acoustic property test results shows that the underwater acoustic absorption property of TDI-type EPU blended with EP is better than IPDI-type EPU, and elastomer of the composition ratios of EPU to EP is 70/30 showed better underwater acoustic absorption property than the ratios are 80/20 and 90/10; the average acoustic absorption coefficient of EPU(TDI-type)/E-51(70/30) elastomer in 2–12 kHz is 0.75, and the low frequency maximum acoustic absorption of this elastomer is 0.44; the maximum coefficient is 0.94; The EPUs blended with E-51 EP have better acoustic absorption properties than those from E-44; and the

EPU from PPG-2000 has better underwater acoustic absorption properties than that from PPG-1000.

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