

# Preparation of Flexible Epoxy Resin Containing Polyurethane Segments

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**Abstract.** Epoxy resin is applicable for adhesives, coatings, electronic packaging, composite materials and other fields. In this paper, an original flexible epoxy resin (FEP) was synthesized by introducing polyurethane segments into the main chain. The formation of FEP was characterized using FTIR and <sup>1</sup>H MNR methods. Subsequently, the bonding properties of the FEP/bisphenol A diglycidyl ether (DGEBA) blends were studied, and 4,4'-diaminodiphenylmethane (DDM) was used as a curing agent. The results showed that the introduction of FEP made a great improvement for T-peel strength, while the lap shear strength at different temperature increased firstly and then decreased with the increasing of FEP content.

## 1. Introduction

Epoxy resin has been widely used in many industrial applications, such as adhesives, coatings and composite materials for many years [1-2]. Similar to other thermosetting resins, the cured epoxy resin shows a brittle behavior due to high crosslink density. The commonly approach used to improve the toughness of epoxy resins is the incorporation of second phase particles, such as rubber elastomer, thermoplastic polymer, inorganic nanoparticle, liquid crystalline polymer, and hyperbranched resin reported in many papers [2-5].

In recent years, polyurethane (PU) has attracted much research attention due to its versatile applications. Generally, PU was composed of polyether or polyester “soft” segments and a varieties of isocyanate (-NCO)-based “hard” segments [6]. It was found that the modified epoxy resin with PU elastomer showed a good toughness and low temperature performance because of the formation of an interpenetrating network structure. The urethane groups (-NHCOO-) in the PU molecular chain also play a positive impact on mechanical strength, impact resistance and bonding strength of epoxy resin. However, the traditional PU is sensitive to moisture for the existence of free -NCO groups, and the corresponding modified epoxy adhesive exhibits a poor storage stability [7]. Therefore, in this work,

a polyurethane prepolymer capped with glycidyl was synthesized and used to toughen epoxy resin. On one hand, it showed good compatibility with epoxy resin as the existence of co-crosslinking reaction. On the other hand, it was expected that the toughness of epoxy resin could be significantly improved by the flexible polyether chain of PU.

## 2. Experimental Methods

### 2.1. The synthesis of hydroxymethyl phenyl glycidyl ether (MPEP)

The raw materials, 4-hydroxybenzyl alcohol (MP, 0.1 mol), epichlorohydrin (ECH, 0.2 mol) and potassium carbonate (0.12 mol) were placed into a three-necked flask equipped with a mechanical stirrer, reflux condenser and thermometer, and butanone (80 mL) was added as a solvent. The reaction mixture was stirred at 80 °C for 40 h, and the excess ECH and solvent were then removed by vacuum distillation. A yellowish transparent liquid was obtained. The synthesis route of MPEP is shown in Figure 1(a).

### 2.2. The synthesis of polyurethane prepolymer

Polyether polyol ( $M_2$ ,  $M_n=2000$ ) was degassed and dried in a round flask under high vacuum at 110 °C for 3 h. After the temperature was cooled to 80 °C, a certain amount of toluene-2,4-diisocyanate (TDI) (molar ratio of TDI and  $M_2$  is 2.0) was then added dropwise, and the reaction was continued for another 3 h at 80 °C protected by dry nitrogen gas. The reaction process was monitored by FTIR technique to obtain a polyurethane prepolymer. The reaction route is shown in Figure 1(b).

### 2.3. Preparation of flexible epoxy resin containing polyurethane segments (FEP)

one equivalent of as-prepared polyurethane prepolymer and two equivalents of MPEP were added into a reaction kettle equipped with a nitrogen inlet. The mixture was continuously mixed at 80 °C until the -NCO groups disappeared. The synthesis route of FEP is shown in Figure 1(c).

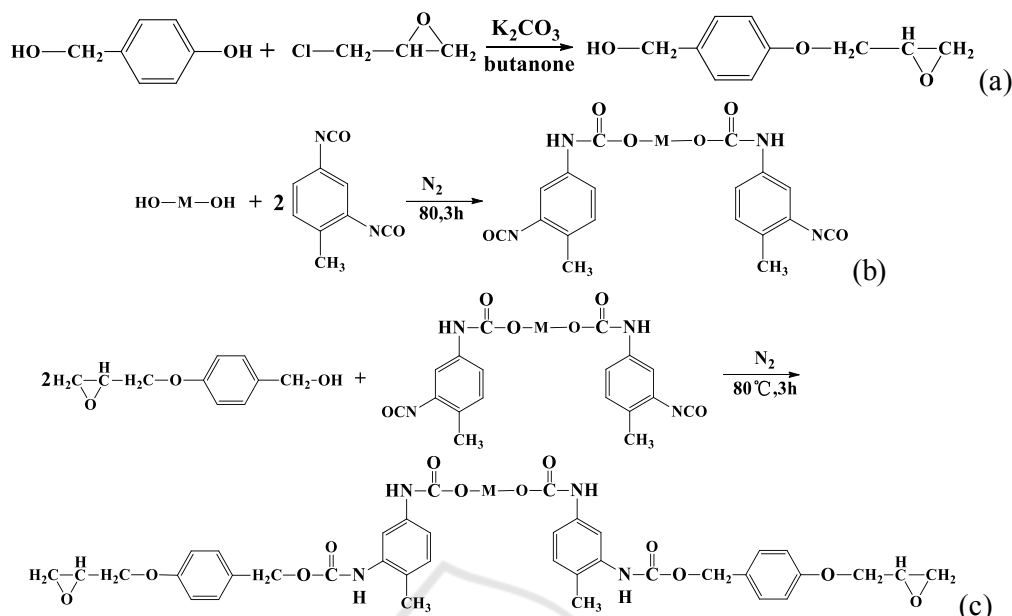
### 2.4. Preparation of DGEBA/FEP blends

The FEP/DGEBA ratios of 0%, 20%, 40%, 60% and 80% by mass of DGEBA were used. The resin blends containing stoichiometric amount of DDM curing agent were polymerized gradually at 80 °C for 1 h, 120 °C for 2 h and 150 °C for another 2 h in an oven.

### 2.5. Characterization and measurements

The structure of the as-prepared monomer was verified by  $^1\text{H}$  NMR (Bruker AVANCE-500 nuclear magnetic resonance spectrometer) with a proton frequency of 400 MHz. The solvent was deuterated chloroform and tetramethylsilane (TMS) was used as an internal standard. Fourier transform infrared (FTIR) spectra were recorded by a Bruker-VECTOR22. The samples were brushed on a potassium bromide window and the FTIR spectra were obtained at a resolution of  $4\text{ cm}^{-1}$  at room temperature.

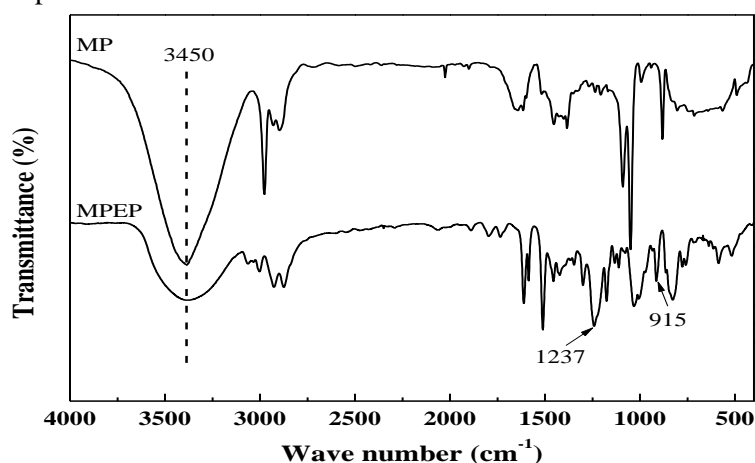
The lap shear strength (LSS) test specimens were prepared according to GB/T 7124-2008. The aluminium alloy plates (2024-T3) were used as adherend in this study, which were polished with a 80 grade emery paper and then cleaned with ethyl acetate prior to bonding. The T-peel strength (T-PS) were tested by an electro-mechanical testing machine (Instron 5969) at room temperature. The test speed is 100 mm/min.



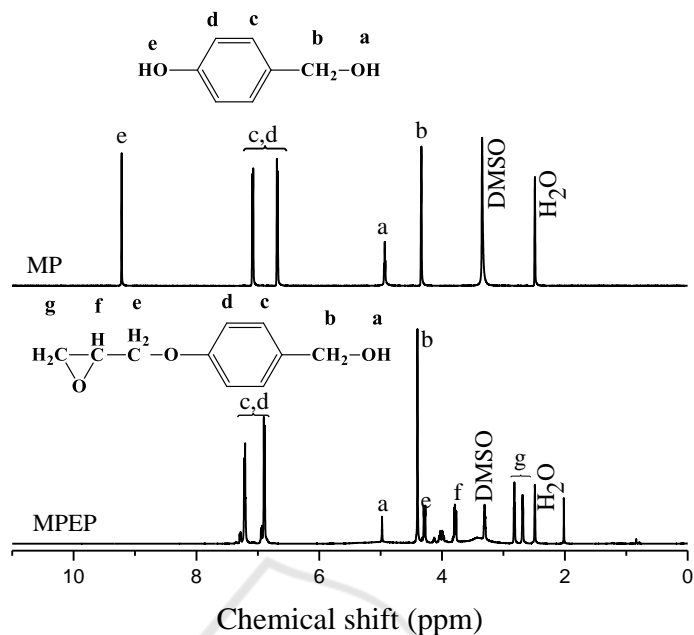
**Figure 1.** Preparation process of flexible epoxy resin containing polyurethane segments: (a) MPEP, (b) polyurethane prepolymer and (c) FEP.

### 3. Results and discussion

The FT-IR spectra of MP and MPEP are shown in Figure 2. It can be seen that MPEP exhibited the characteristic absorption at  $1237\text{ cm}^{-1}$ , which was attributed to the C-O-C stretching vibration. The characteristic absorption of epoxy ring appeared at  $915\text{ cm}^{-1}$ . Moreover, the absorption at approximately  $2863$  and  $2924\text{ cm}^{-1}$  related to the asymmetric and symmetric stretching vibrations of methylene ( $-\text{CH}_2-$ ), were also founded. As shown in Figure 3, the chemical structures of MP and MPEP were also characterized by  $^1\text{H NMR}$ . The peak observed at  $9.2\text{ ppm}$  for MP was assigned to the phenolic hydroxyl group (Ph-OH) structure, which has been disappeared for MPEP. The resonance signals of epoxide protons observed at  $3.7\text{ ppm}$  were assigned to the methylene f, and the peaks at  $2.5$  and  $2.9\text{ ppm}$  were attributed to the methylene g [8]. These results demonstrated that MPEP have the expected chemical structures.

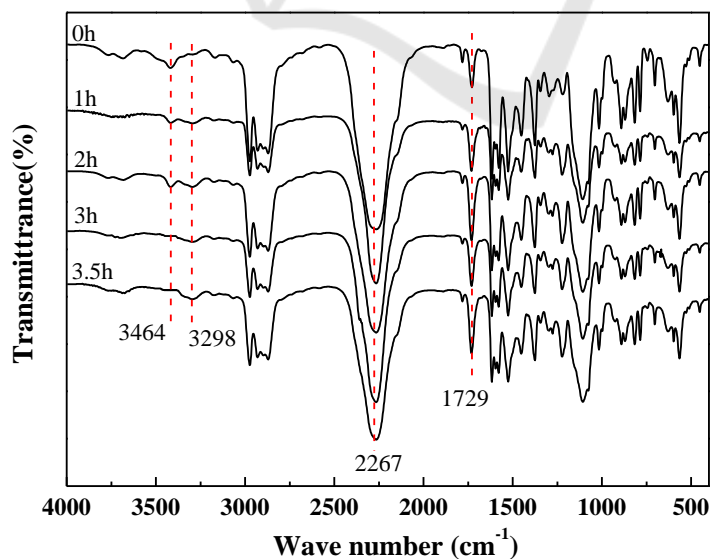


**Figure 2.** FTIR spectra of MP and MPEP.



**Figure 3.**  $^1\text{H}$  NMR spectra of MP and MPEP.

The NCO-terminated polyurethane prepolymers were synthesized by  $\text{M}_2$  and TDI. The synthetic process was continuously monitored by a FTIR spectrometer. As shown in Figure 4 the decay for the intensity of  $-\text{NCO}$  ( $2267\text{ cm}^{-1}$ ) and  $\text{Ph-OH}$  ( $3464\text{ cm}^{-1}$ ) absorption peaks can be used to monitor the conversion of functional groups during reaction. Meanwhile, the peak at  $3298\text{ cm}^{-1}$  (N-H) increased observably as the reaction time prolonged. After polymerized at  $80\text{ }^\circ\text{C}$  for 3 h, the  $\text{Ph-OH}$  characteristic peak at  $3464\text{ cm}^{-1}$  has disappeared.



**Figure 4.** FTIR spectra of polyurethane prepolymers at different time.

Figure 5 showed the FTIR spectra of the NCO-terminated polyurethane prepolymer reacted with two equivalents of MPEP for 0, 1, 2 and 3 h at 80 °C, respectively. The reaction progress was indicated by the disappearance of -NCO ( $2267\text{ cm}^{-1}$ ) gradually with reaction time, along with the simultaneous increase of broad N-H peak ( $3298\text{ cm}^{-1}$ ). The absorption peak of the -NCO group eventually become zero after 3 h. The results indicated that the alcoholic hydroxyl groups of the MPEP had completely reacted with the -NCO groups of the polyurethane prepolymers. The targeted product FEP has been successfully synthesized.

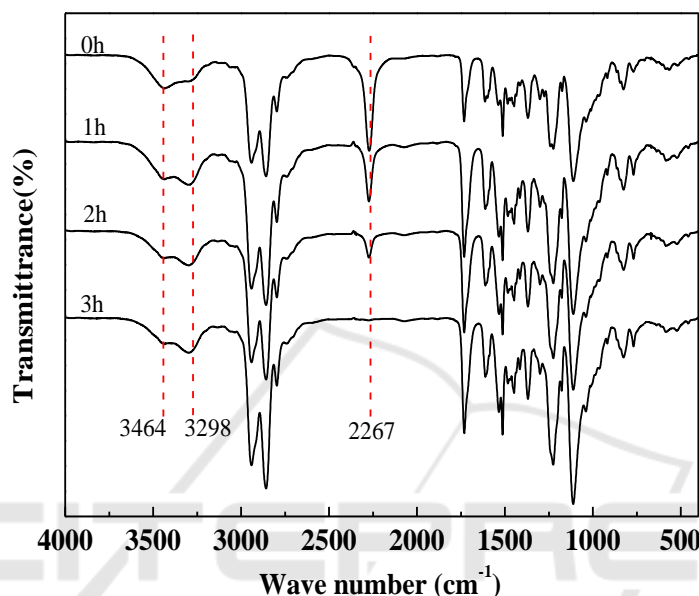


Figure 5. FTIR spectra of FEP at different time.

The adhesive properties of modified epoxy resin with different FEP contents were studied, and the results for LSS and T-PS are listed in Table 1. In general, there is a positive correlation between T-PS and toughness of resin system. For the epoxy systems the LSS at 25 °C increased gradually with the incorporation of FEP but not exceeding 60 percents, the system containing 20 phr FEP showed the highest LSS value of 31.41 MPa at 70 °C. Meanwhile, the T-PS increased abruptly with FEP content increasing. This phenomenon can be attributed that the molecular interpenetration benefits the improvement in the compatibility of DGEBA and FEP. As a result, not only does the increased molecular mass lead to a phase separation, but also that there are lots of strong chemical bonds across the rubbery phase/resin matrix interface. In other words, an increase of toughness is mainly attributed to the cavitation or shear-yielding mechanisms [9-11].

Table 1. Adhesive properties of FEP/DGEBA/DDM systems.

FEP content, phr	Lap shear strength, MPa		T-Peel strength, kN/m
	25 °C	70 °C	
0	31.02	30.43	2.31
20	34.20	31.41	5.03
40	35.21	25.86	6.98
60	37.89	19.74	8.74
80	24.78	6.31	10.37

#### 4. Conclusions

In this study, glycidyl-terminated polyurethane prepolymer FEP was prepared and characterized. The adhesive properties of DGEBA filled with varying wt% of FEP were also investigated. The results implied that the as-prepared glycidyl-terminated polyurethanes can be utilized for high performance adhesive and resin fields.

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