

Synthesis, Characterization, and Properties of Polyols from Hydrogenated Terpinene–Maleic Ester Type Epoxy Resin

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ABSTRACT: Three kinds of polyfunctional polyols with hydroxyl values of 180–320 mg/g were prepared by the reaction of hydrogenated terpinene–maleic ester type epoxy resin with secondary amines (diethylamine, *N*-methylethanolamine, and diethanolamine), and the chemical structures were characterized by Fourier transform infrared spectroscopy and NMR spectroscopy. These polyols were used in place of commonly used polyols to prepare two-component polyurethanes when reacted with polyisocyanates. The crosslinking reactions of the polyols with polyisocyanate could be catalyzed by the tertiary amine groups included in the polyols, and the reaction rate was affected by hydrochloric acid and the polarity of the solvents. The mechanical, water-resistance, and chemical-resistance properties of the crosslinked products of the polyols were evaluated by standard tests, and the thermal properties were

examined by differential scanning calorimetry and thermogravimetric analysis. The results show that these epoxy-urethane polymers, with glass-transition temperatures (T_g 's) in the range -5 to 37°C , had good thermally resistant properties, and the temperatures at 5% weight loss were in the range 235 – 280°C . All of the polymers formed transparent, strong, flexible films, with good chemical-resistance properties and excellent impact strengths of greater than 50 cm, a flexibility of 0.5 mm, adhesions of 1–2, and pencil hardnesses of HB–2H. The larger OH functionality and OH value of the polyol resulted in higher T_g and pencil hardness values and better alcohol resistance and thermal stability in the crosslinked product of the polyol. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 2894–2901, 2009

Key words: polyurethanes; resins; synthesis

INTRODUCTION

Hydrogenated terpinene–maleic ester type epoxy resin (HTME), which is an alicyclic epoxy resin with an endocyclic structure, was synthesized from the raw material turpentine or dipentene.¹ Like commonly used epoxy resins, HTME has many excellent properties after curing, such as thermal and chemical stability, adhesion, and mechanical properties,² and could be widely used in the fields of coatings, adhesives, composite materials, and so on. However, also similar to commonly used epoxy resins, HTME is rather brittle and presents poor deformability when it is cured with a stoichiometric amount of common curing agents because of its highly crosslinked structure and cohesion. Its poor fracture toughness greatly limits the use of epoxy resin in many applications demanding a high-impact tough-

ness. At present, many efforts have been made to improve the toughness of cured epoxy resin. One approach is the modification of epoxy resin with some unreactive or reactive liquid rubber, such as polysulfide rubber,³ carboxyl-terminated butadiene–acrylonitrile rubber,^{4–6} or amine-terminated butadiene–acrylonitrile rubber.^{7,8} However, these rubbers lack heat resistance because of the double bond, and modification with these rubbers leads to low thermal stability of the cured epoxy resin in high-temperature conditions. Polyurethane is another polymer material with excellent properties, especially a high flexibility. Epoxy resin can be toughened with polyurethane by all kinds of methods. So, a novel kind of polymer material with diversified properties is formed, which can be called an *epoxy-urethane material*.

In this study, three kinds of polyols were synthesized by HTME with secondary amines [diethylamine (DeA), *N*-methylethanolamine (MEA), and diethanolamine (DEA)], and they were used in place of commonly used polyols, such as poly(ether glycol)s and poly(ester polyol)s, to prepare two-component polyurethanes. The reactivity of these three polyols crosslinked with polyisocyanate, and the mechanical, chemical-resistance, and thermal properties of the crosslinked products were examined. These

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crosslinked products, which can be called *epoxy-urethane polymers*, combined the rigidity and weatherability of the saturated terpinene alicyclic epoxy resin (HTME) with the flexibility and tenacity of the polyurethane perfectly. The purpose of this study was to provide a favorable theoretical basis for the toughening technology of epoxy resin, and the application of a renewable resource of forest products for the preparation of specialty polymers.

EXPERIMENTAL

Materials

The base material was an epoxy resin (HTME) with an endocyclic structure and an epoxy value (EV) of 0.37 mol/100 g, which was synthesized from the hydrogenated product of terpinene-maleic anhydride and epichlorohydrin, as reported elsewhere.¹ DeA, MEA, and DEA were chemically pure and were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The polyisocyanate was EC385, a derivative of 1,6-hexamethylene diisocyanate with an NCO content of 14%, and was supplied by Shanghai Siwo Chemical Co., Ltd.

Synthesis of the polyols from HTME

A 500-mL, four-necked flask equipped with a stirrer, dropping funnel, thermometer, condenser, and heating mantle was charged with HTME (Shanghai, China) and the solvent (ethanol). Then, a stoichiometric amount of DEA, MEA, or DeA was added slowly with constant stirring when the temperature was raised to 40°C. The reaction was continued for 2–3 h at 60–70°C, and a yellow transparent product was obtained after the solvent was distilled.

Crosslinking reaction of the polyols from HTME with polyisocyanate

The polyols from HTME were dissolved in ethyl acetate with a concentration of 40% (w/w). Then, polyisocyanate (EC-385, ca. 85% w/w) was added to the polyol solution with constant stirring at an NCO/OH ratio of 1.1 : 1. We obtained films by casting the mixed systems on tin plates or glass, letting them cure in an oven at 60°C for 4 h, and then maintaining them at room temperature for 4 days.

Measurements

The EV and OH value of the products were obtained by chemical analysis in terms of the standard methods HG2-741-72 and GB 7383-87, respectively. Fourier transform infrared (FTIR) analysis was performed on a MAGNA-IR 550, Nicolet Co. (Madison, WI) ¹³C-NMR analysis was performed on a DRX-500

(Bruker) with CD₃CN (Switzerland) as solvent. Viscosity was measured by an NDJ-8S digital display rotational viscosimeter (Shanghai Precision Scientific Instrument Co., Ltd., Shanghai, China). The mechanical, water-resistance, and chemical-resistance properties of the films were evaluated according to standard tests (impact strength, GB 1732-93; adhesion, GB 1702-93; flexibility, GB 1731-93; pencil hardness, GB 6739-96; and resistance to liquids, GB 9274-88). Differential scanning calorimetry (DSC) thermograms were recorded with a PerkinElmer Diamond differential scanning calorimeter (USA) at a heating rate of 20°C/min under a nitrogen gas flow at 20 mL/min. Thermogravimetric analysis (TGA) was performed with a Netzsch STA 409 PC/PG thermogravimetric analyzer (Germany) at a heating rate of 20°C/min under a nitrogen atmosphere.

RESULTS AND DISCUSSION

Characterizations of the polyols from HTME

The structures of HTME and the polyols from HTME are shown in Figure 1. The major technical parameters of the polyols from HTME, including EV, OH value, and softening point, were obtained by chemical analysis according to standard methods and are shown in Table I. Because of the low chemical activity of DeA reacting with the oxirane ring of HTME, the residual EV of the HTME-DeA polyol synthesized under the same conditions was comparatively large, in contrast with that of the other two adducts. The ethyl groups combined with the nitrogen of DeA were electron-donating groups, which led to a low chemical activity in the active hydrogen of DeA.

Compared with the FTIR spectra of HTME in Figure 2, the FTIR spectra of the polyols showed evidence of almost complete epoxy group consumption because they lacked or presented only residual bands at 908 and 1020 cm⁻¹, and the characteristic absorption peaks of OH at 3100–3600 cm⁻¹ of the adducts were all evidently strengthened. These results suggest that the reaction of epoxy groups with NH groups effectively took place. Also, the C–O bond stretch absorption peaks of primary hydroxyl groups at 1035 cm⁻¹ appeared in the spectrum of the HTME-DEA and HTME-MEA polyols but did not appear in the spectra of the HTME-DeA polyol. The C–O bond stretch absorption peaks of secondary hydroxyl groups at 1065 cm⁻¹ were all strengthened in the spectrum of the three adducts in contrast to that of HTME. These results corresponded to the structural features of the target adducts.

The ¹³C-NMR spectra of HTME and the polyols from HTME are shown in Figure 3. In the ¹³C-NMR

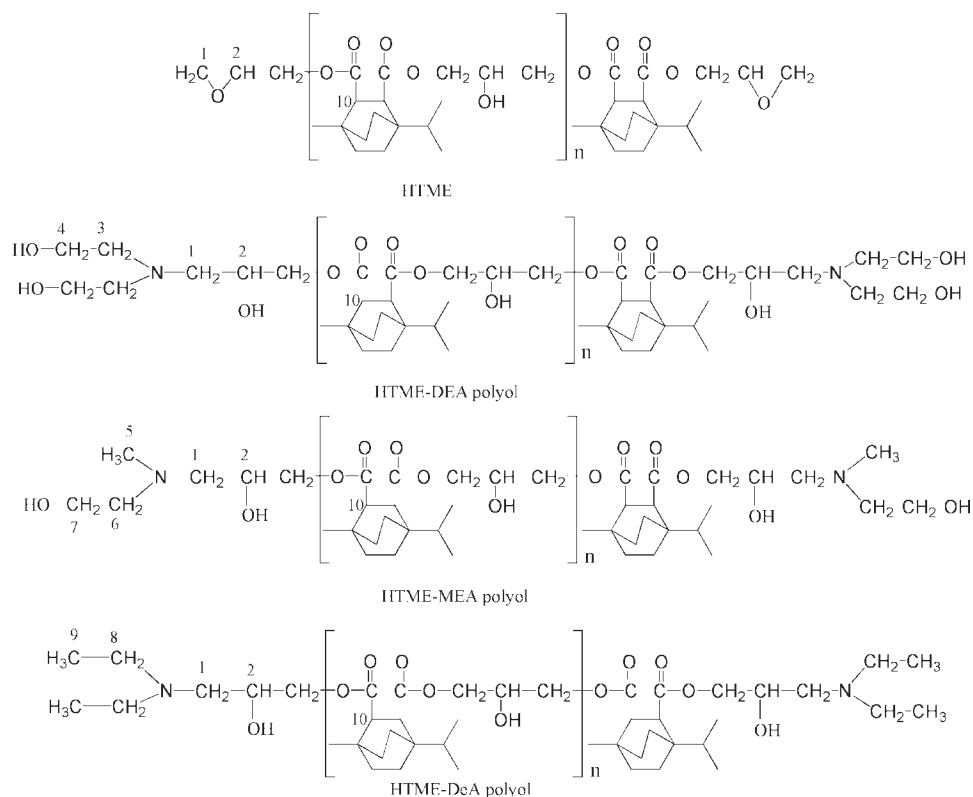


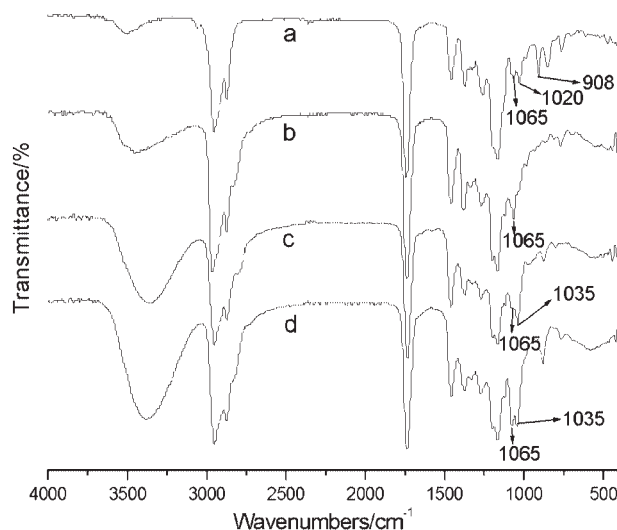
Figure 1 Structures of HTME and the polyols.

spectra of HTME, the characteristic peaks of the secondary carbon (C-1) and tertiary carbon (C-2) of epoxy groups appeared at chemical shifts of 44.5 and 49.5 ppm,^{9,10} respectively, and the peaks of C-10 and C-2 overlapped at 49.5 ppm according to refs.⁹ and¹⁰ and integral quantities of carbon. However, in the spectra of the polyols from HTME, the signals at 44.5 ppm almost completely disappeared, and the signals at 49.5 ppm were weakened (the residual signals belonged mostly to C-10). It was indicated that the chemical shifts of C-1 and C-2 changed after the

epoxy groups reacted with amino groups. The new peaks appearing in the spectra of the polyols can be discussed according to the chemical structures of the polyols (Fig. 1) and integral quantities of carbon. The quantity ratio of C-3, C-4, and C-1 in the HTME-DEA polyol was 2 : 2 : 1. According to the integral quantities of carbon in the ¹³C-NMR spectra of the HTME-DEA polyol, the peaks at 57.6, 59.8,

TABLE I
Technical Parameters and Appearance of the Polyols
from HTME

HTME-DEA polyol	
EV (mol/100 g)	0.006019
OH value (mg/g)	300 ± 20
Appearance	Pale yellow solid
Softening point (°C)	46
HTME-MEA polyol	
EV (mol/100 g)	0.006842
OH value (mg/g)	250 ± 10
Appearance	Yellow, transparent solid
Softening point (°C)	40
HTME-DeA polyol	
EV (mol/100 g)	0.02590
OH value (mg/g)	200 ± 10
Appearance	Yellow, transparent solid
Softening point (°C)	37



a:HTME; b:HTME-DeA polyol; c:HTME-MEA polyol; d:HTME-DEA polyol

Figure 2 FTIR spectra of HTME and the polyols from HTME.

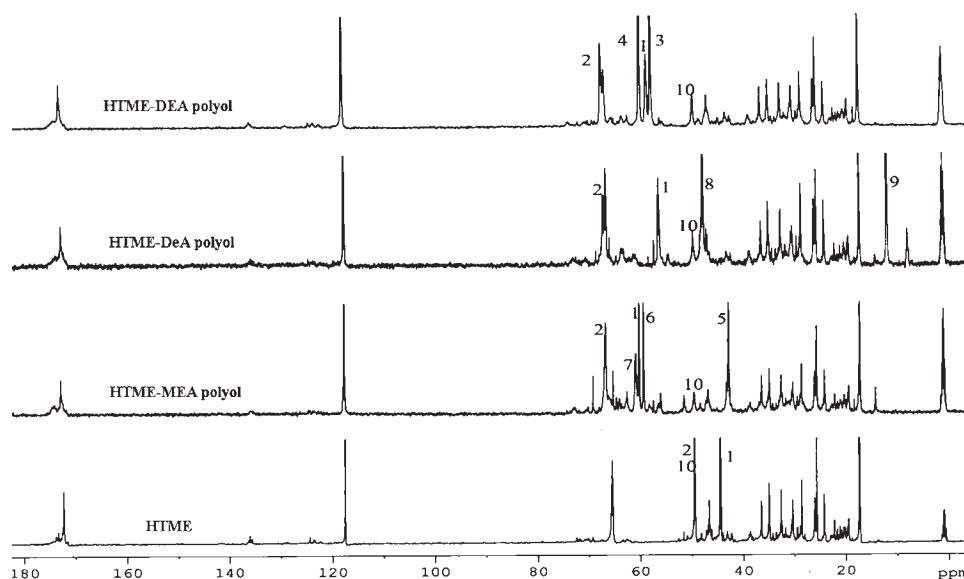


Figure 3 ^{13}C -NMR spectra of HTME and the polyols from HTME.

and 58.5 ppm could be ascribed to C-3, C-4, and C-1, respectively, and the peak of the tertiary carbon (C-2), which attached to a hydroxyl group, appeared at 67.4 ppm. In the ^{13}C -NMR spectra of the HTME-MEA polyol, the peaks at 61.1, 59.4, and 42.8 ppm were assigned to C-7, C-6, and C-5, respectively, and the signals of C-1, which attached to N, and C-2, which attached to a hydroxyl group, appeared at 60.8 and 66.7 ppm, respectively. The quantity ratio of C-8, C-9, and C-1 in the HTME-DeA polyol was 2 : 2 : 1. According to integral quantities of carbon in the ^{13}C -NMR spectra of the HTME-DeA polyol, the peaks at 47.6, 11.9, and 56.3 ppm could be ascribed to C-8, C-9 (primary carbon of ethyl), and C-1, respectively, and the peak of the tertiary carbon (C-2), which attached to a hydroxyl group, appeared at 67.2 ppm. Other signals in the ^{13}C -NMR spectra of the polyols corresponded to those of the raw material HTME.¹

Characterization of the crosslinking reaction of the polyols from HTME

The polyols synthesized by HTME with secondary amines reacted with polyisocyanates quickly at room temperature in the catalyzation of tertiary amine groups in the structures of the polyols themselves. Obviously, the change that accompanied the crosslinking reaction of the polyols from HTME with the polyisocyanates was the viscosity change of the reaction solution. The effects of the used polyol type, catalyst, and solvent polarity on the crosslinking reactions was studied by the observation of the change in the solution viscosity under different reaction conditions. Relationships between the properties

of the crosslinking reaction and the structural features of the polyols were also examined by this viscosity research.

In this study, a solution was prepared by the mixture of the polyols from HTME (ca. 40% w/w in solvent) with the polyisocyanate EC385 (a derivative of 1,6-hexamethylene diisocyanate, ca. 85% w/w) with the NCO/OH ratio maintained at 1.1 : 1. Then, the viscosity of the solution, which was varied with the time under different reaction conditions, was determined by the NDJ-8S digital display rotational viscosimeter at 25°C.

The crosslinking reaction of the polyols with polyisocyanates could be catalyzed by both alkaline compounds and acidic compounds as a result of the high unsaturation of the isocyanate group ($-\text{NCO}$), which contained electropositive carbon with electronegative nitrogen and oxygen atoms.¹¹ The tertiary amine groups included in the polyols from HTME could accelerate proton transfer from alcohols to isocyanates so that crosslinking reactions of the three polyols from HTME with polyisocyanate were all catalyzed by the polyols themselves. Particularly in the HTME-MEA polyol, when it was mixed with polyisocyanate, the solution gelled immediately at room temperature because the steric hindrance effect of the methyl group on MEA resulted in a strong alkalinity and high catalytic activity of the tertiary amine groups included in the HTME-MEA polyol. Generally, acidic compounds can also catalyze the crosslinking reaction of $-\text{NCO}$ with $-\text{OH}$ by the protonation of isocyanate groups. However, when strong alkali catalysts lead to very short gelation times of the solution of polyols and polyisocyanates, acidic compounds may slow the chain propagation

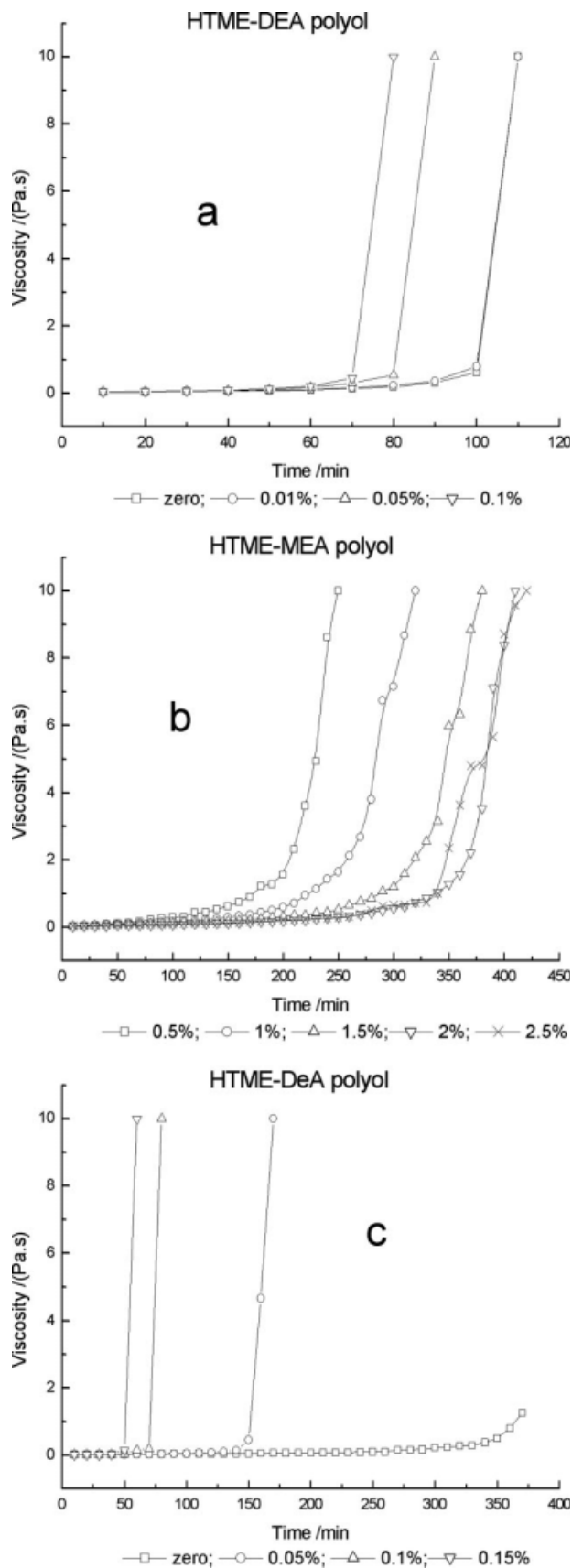


Figure 4 Effects of hydrochloric acid on the crosslinking reactions.

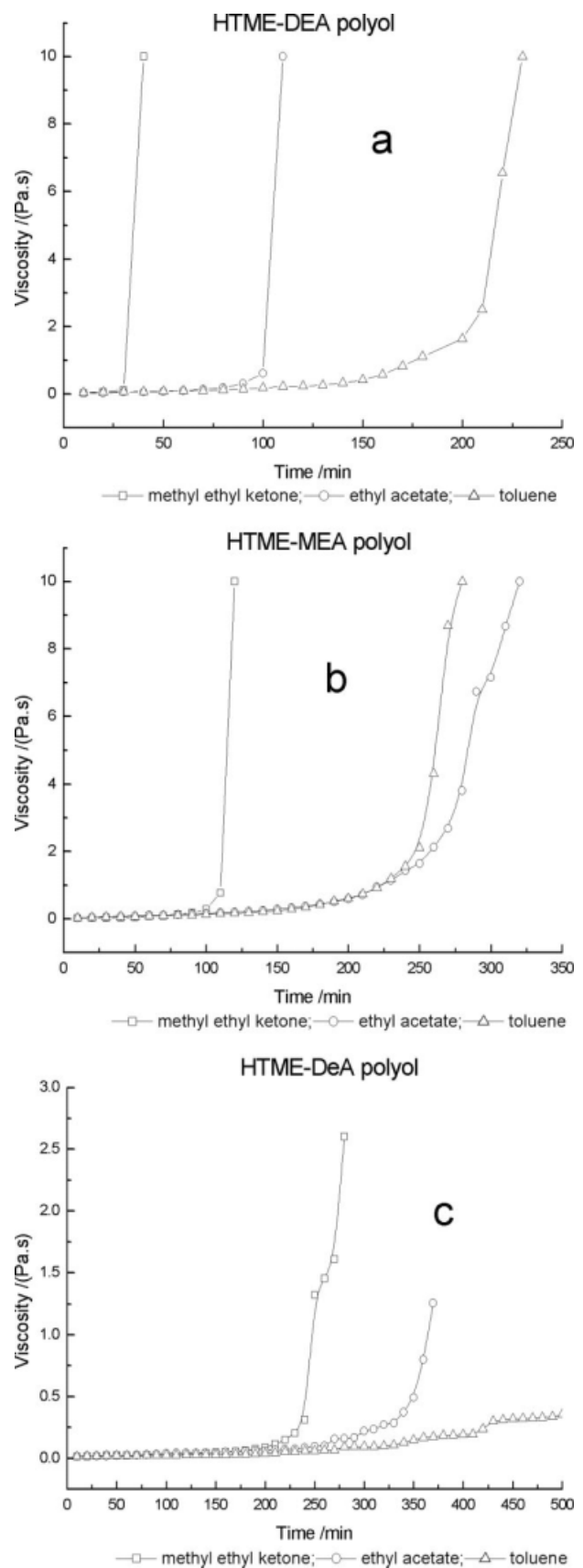


Figure 5 Effects of the polarity of solvents on the crosslinking reactions.



Scheme 1 Formation of urethane.

of the crosslinking reaction.¹² In this study, the effects of hydrochloric acid on the crosslinking reactions of the polyols from HTME with a polyisocyanate crosslinker (EC385) were examined by the determination of the change in the viscosity of the solutions prepared as discussed previously, and the results are shown in Figure 4. Hydrochloric acid obviously inhibited the reaction of the HTME–MEA polyol with the polyisocyanate crosslinker, and the inhibition was more distinct as the amount of hydrochloric acid increased to a certain extent [Fig. 4(b)]. The gelation time was prolonged from immediate gelation originally to a gelation of 7 h by the addition of 2% w/w hydrochloric acid based on the polyol component at 25°C. However, the reaction rate of the polyisocyanate crosslinker with the HTME–DEA or HTME–DeA polyol, which contained tertiary amine groups with a strong steric hindrance effect and slight alkalinity, was accelerated by hydrochloric acid [Fig. 4(a,c)]. Particularly in the HTME–DeA polyol, which only had secondary hydroxyl groups with low chemical activity, the acceleration by hydrochloric acid was even more distinct [Fig. 4(c)].

Commonly used polyols react with polyisocyanates at a slower rate in organic solvents with stronger polarities because the solvent molecules with strong polarities can associate with the OH groups of the polyols and form hydrogen bonds, which leads to a slow reaction rate.¹² However, in our study of the effect of the solvent polarity on the crosslinking reactions of the polyols from HTME with the polyisocyanate EC385, a different phenomenon was observed (Fig. 5). The reaction rate was the fastest when the reaction (without hydrochloric acid) of the HTME–DEA or HTME–DeA polyol with the polyisocyanate EC385 took place in methyl ethyl ketone, next in ethyl acetate, and the slowest in toluene, which had the weakest polarity by comparison with the other two organic solvents [Fig. 5(a,c)]. The reason for this phenomenon may be that the solvent with a strong polarity promoted the acceleration of the proton to transfer from alcohols to isocyanates by tertiary amine groups. As for the HTME–MEA polyol, when it reacted with the polyisocyanate EC385, the reaction rate had to be controlled by the addition of hydrochloric acid, which affected the solvent effects again. The reaction rate was still fastest in methyl ethyl ketone, then toluene, and slowest in ethyl acetate, as shown in Figure 5(b).

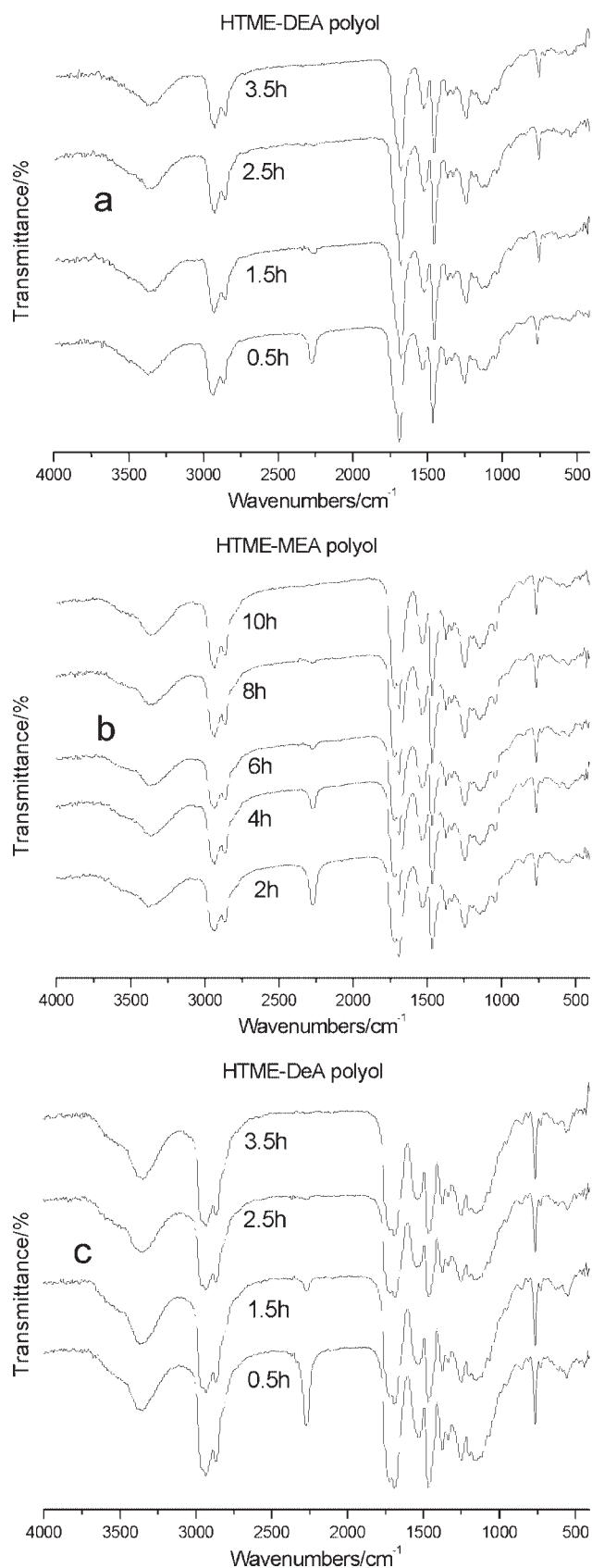


Figure 6 FTIR spectra of the crosslinked products cured for different times.

TABLE II
Properties of the Crosslinked Products of the Polyols from HTME

Item	HTME-DEA polyol	HTME-MEA polyol	HTME-DeA polyol
Surface drying time (h) at 25°C	1	2	0.5
Hard drying time (h) at 25°C	2.5	5.5	2
Appearance	Brilliant, transparent	Brilliant, transparent	Brilliant, transparent
Gloss (60°)	92.2	86.3	91.4
Impact strength (50 cm)	Pass	Pass	Pass
Adhesion (grade)	2	1	1
Flexibility (mm)	0.5	0.5	0.5
Pencil hardness	H-2H	H	HB
Water resistance (4 days)	Pass	Pass	Pass
Alkali resistance (4 days, 3% NaCO ₃)	Pass	Pass	Pass
Salt-water resistance (4 days, 3% NaCl)	Pass	Pass	Pass
Alcohol resistance (5 h, 50% C ₂ H ₅ OH)	Pass	Pass	Pass

Analysis of the crosslinking processes with FTIR spectra

The crosslinking reactions of polyols with polyisocyanates are processes of the consumption of -NCO and -OH groups and the formation of -NHCOO- (urethane) groups (Scheme 1).

To investigate these crosslinking processes, FTIR spectra were used to observe the change in the -N=C=O stretch absorption peaks, which are strong and acute in IR spectra.¹³

The FTIR spectra of the crosslinked products cured for different times at 60°C with the NCO/OH ratio maintained at 1.1 : 1 are shown in Figure 6. The change in the -N=C=O group stretch absorption peaks at about 2270 cm^{-1} were obvious. With increasing reaction time, the -NCO peaks became weaker and disappeared at last. The region between 3100 and 3600 cm^{-1} was dominated by a broad band assigned to hydroxyl absorption. It did not change a lot with the consumption of the hydroxyl group because the N-H bond of the forming

-NHCOO- group, whose sharp absorption was centered approximately at 3320 cm^{-1} , interfered with the observed change of -OH group absorption peaks in the IR spectra. At the beginning, the crosslinking reaction was very fast, and then, it slowed with decreasing amount of the activity groups, which might have been partly trapped by the crosslinked network as the reaction proceeded. The crosslinking reaction of the HTME-DEA or HTME-DeA polyol with polyisocyanate was fast and came to a close after 3.5 h at 60°C [Fig. 6(a,c)]; it was catalyzed by tertiary amine groups included in themselves. However, the crosslinking reaction of the HTME-MEA polyol with polyisocyanate finished after 10 h at 60°C [Fig. 6(b)], and it was slowed by the addition of 1% w/w hydrochloric acid.

Properties of the crosslinked products

The crosslinked products, which could be called *epoxy-urethane polymers*, had excellent impact strength, adhesion, flexibility, and water-resistance and chemical-resistance properties, as shown in Table II. These

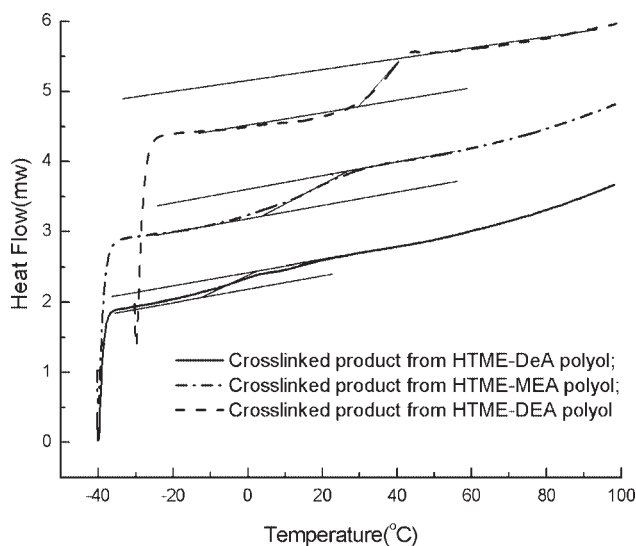


Figure 7 DSC curves of the crosslinked products.

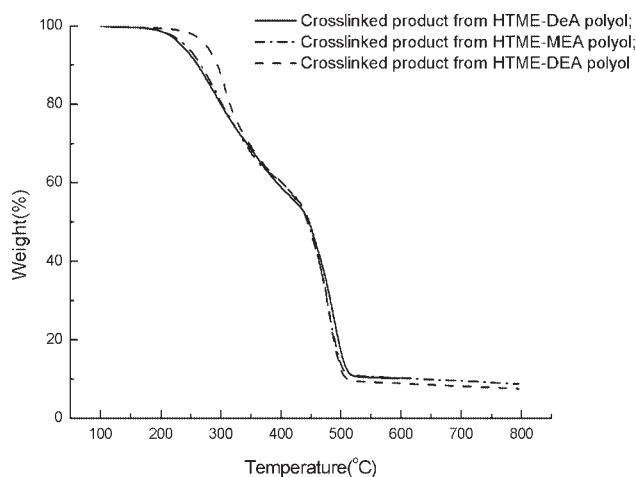


Figure 8 TGA curves of the crosslinked products.

epoxy-urethane polymers modified the epoxy resin and polyurethane with each other successfully. The drying time of the HTME-MEA polyol crosslinking system was relatively long compared to those of the other two polyols because of the addition of 1% w/w hydrochloric acid. The pencil hardness and alcohol resistance of the crosslinked products were in accordance with the OH functionality and OH value of each polyol, and the larger OH functionality and OH value of the polyol led to better properties in the crosslinked products. Because the larger OH functionality and OH value resulted in a higher crosslinking density, the rigidity and alcohol resistance of the crosslinked products were improved.¹⁴

The glass-transition temperatures (T_g 's) of the crosslinked products were examined with DSC (Fig. 7). As shown, the larger OH functionality and OH value of the polyol resulted in a higher T_g of the crosslinked product of polyol, with the product from the HTME-DEA polyol with the highest T_g at 36.5°C, the next product from the HTME-MEA polyol with its T_g at 16.1°C, and the product from the HTME-DeA polyol with the lowest T_g at -5.5°C. The greater extents of crosslinking made it more difficult for the products to expand, and higher temperature was needed to obtain enough free volume for glass transition. Also, there was no evidence of multiple thermal transitions in each DSC curve, which consequently indicated good compatibility in the crosslinked systems and no major bulk phase separation.

TGA was used to investigate the thermal stability of the crosslinked products of the polyols (Fig. 8). The crosslinked products of the polyols had good thermal-resistance properties, and the temperatures at 5% weight loss (T_d) were all above 230°C. The larger functionality and OH value of the polyol also resulted in a better thermal stability in the crosslinked product of the polyol. The product from the HTME-DEA polyol had the highest T_d at 276°C because of its highest crosslinking density, and the T_d values of the products from the HTME-MEA and HTME-DeA polyols were 242 and 235°C, respectively. The degradation patterns of the crosslinked products were all the same: a two-stage weight loss pattern. The prestage degradation was correlated with the decomposition from the $-\text{NH}-\text{CO}-\text{O}-$

(urethane) linkage, and the second stages of the three products were almost the same, with temperatures ranging from 450 to 500°C, which was attributed to the thermal decomposition of the epoxy resin (HTME) structure.

CONCLUSIONS

Three kinds of polyols with different OH functionalities and OH values were synthesized by HTME with secondary amines and were characterized by FTIR and ¹³C-NMR spectra. The reactivity of these polyols crosslinked with polyisocyanate were examined by viscosity testing and FTIR spectra. Then, the appropriate curing conditions of the crosslinking reactions were obtained. The mechanical, water-resistance, and chemical-resistance properties of the crosslinked products of the polyols from HTME with polyisocyanate were evaluated according to standard tests, and the thermal properties were examined with DSC and TGA. The results show that the crosslinked products, which could be called *epoxy-urethane polymers*, had excellent impact strengths, flexibilities, and chemical-resistance and thermal-resistance properties.

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