

Synthesis, Characterization, and Properties of Novel Polyetherester Polyols and Developed Polyurethanes

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Received 28 March 2006; accepted 29 May 2006

DOI 10.1002/app.24871

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Three kinds of cyclic anhydrides, which stand for aliphatic anhydride, aromatic anhydride, and anhydride containing double bond: succinic anhydride, phthalic anhydride, and maleic anhydride have been copolymerized with propylene oxide and low molecular weight polyoxypropylenediol via ring-opening copolymerization initiator by double metal cyanide complex catalyst to synthesize a series of polyetherester (PEE) polyols. The structure of the obtained copolymers was confirmed by several analysis methods. Three kinds of polyetherester polyurethane (PEEPU) were thus synthesized by polymerization of as-synthesized PEE polyol with 4,4'-diphenylmethane

diisocyanate. The mechanical properties of the obtained PEEPU were tested. The results showed that the mechanical properties of three polyurethanes are different based on their structure and composition. The inducing of the rigid phenyl group in the soft segment can improve the mechanical strength remarkably. The influences of ester content in soft segment and the hard segment content on the mechanical properties of PEEPU were studied. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 417–424, 2007

Key words: elastomers; polyetherester; polyurethane; mechanical properties

INTRODUCTION

Polyurethane (PU) elastomers have excellent abrasion resistance and the properties of both rubber and plastics. They are becoming more and more important as engineering materials. It has been well known that conventional PUs obtained from polyether polyols have excellent characteristics with respect to various physical properties such as impact resilience, low temperature characteristics, weather resistance, and economical advantages. However, they are inferior in the strength, abrasion resistance, and heat resistance to PUs obtained from polyester polyols.^{1–5}

Accordingly, it has been desired for many years to improve the strength and heat resistance while maintaining the various physical properties of the polyether polyols and to produce at low cost PU suitable as an elastomer material or as a thermoplastic urethane. However, satisfactory PU has not yet been obtained.

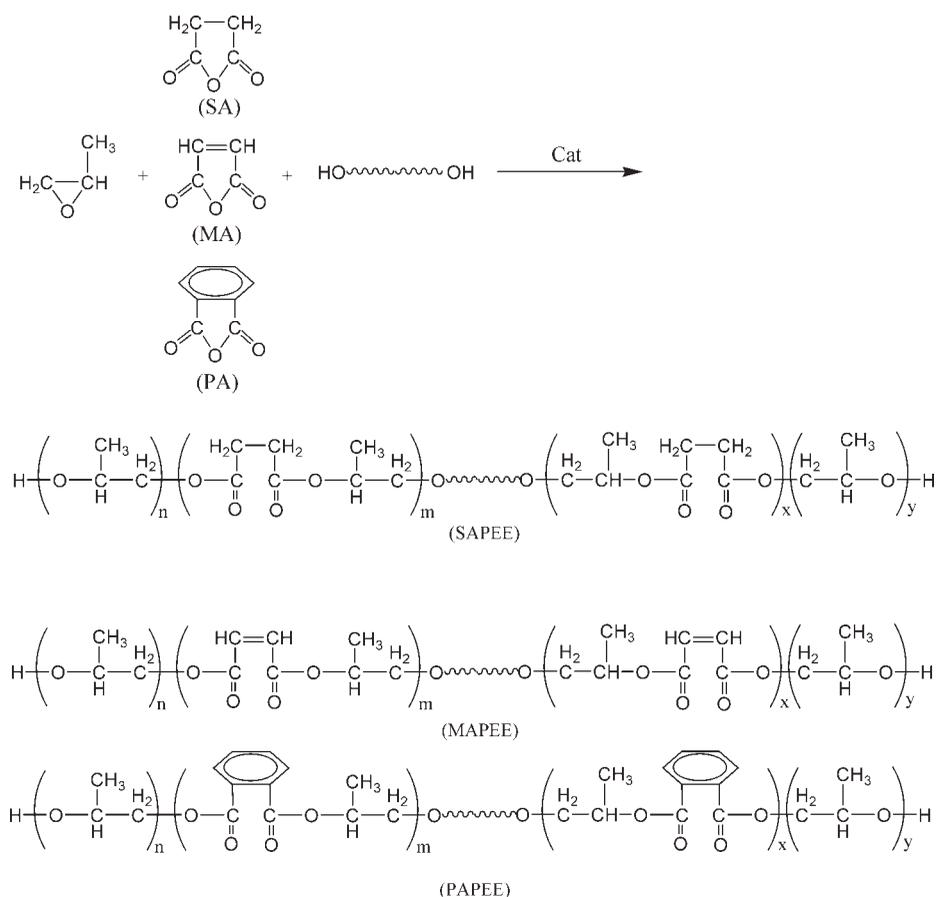
To overcome the above drawback, it has been proposed to employ a modified polyether polyol obtained by esterification of a usual polyether polyol, or to employ a polyol mixture obtained by mixing a polyether polyol and a specific polyester polyol.^{6,7} However, the physical properties such as strength and

elongation of the PU obtainable from such a polyol are inadequate.

Furthermore, in a case where a modified polyether polyol, having the terminals esterified, is to be produced, it has been very difficult to conduct the synthesis by the same catalyst according to the conventional techniques.⁸ Namely, if a strong basic catalyst is used for the terminal esterification, it is unavoidable to obtain a polyol having a very wide molecular weight distribution and a substantial amount of by-products containing short chain polyester components because of the ester exchange reaction, which substantially reduces the impact resilience, compression permanent set, etc. of the flexible PU foam obtainable from such a polyol.⁶ This has been a problem that must be solved. Double metal cyanide (DMC) complexes catalysts discovered are well-known catalysts for epoxide polymerization.^{9–12} The catalysts are highly active, and give polyether polyols that have low unsaturation and narrow molecular weight distribution (MWD) compared with similar polyols made using basic (KOH) catalysis.

In this article, three kinds of anhydrides: succinic anhydride (SA), phthalic Anhydride (PA), and maleic anhydride (MA), representation of different category: aliphatic anhydride, aromatic anhydride, and anhydride containing double bond, were selected for this investigation. We select Zn/Co double metal cyanide complexes as catalyst and use three kinds of cyclic anhydrides mentioned above and propylene oxide as polymerization monomers to prepare copolymers

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Scheme 1 Structures and reactions of the ring-opening copolymerization of three anhydrides.

containing ether and ester links in the macromolecular chain by ring-opening copolymerization. All polyols were purified with low MWD and then characterized by a variety of methods. Further, they were reacted with 4,4'-diphenylmethane diisocyanate (MDI) to obtain PUs designated as SAPEEPU, MAPEEPU, and PAPEEPU. The effect of structure and functionality of the polyols on the properties of their PUs was studied.

EXPERIMENTAL

Materials

The three kinds of anhydrides were purchased from Shanghai Chemical Reagent Company of Chinese Medicine Group. Propylene oxide and low molecular polyoxypropylene diol initiator DL-400 (M.W.: 400; M.W. Distribution: 1.02) was purchased from the third factory of Tianjin Petroleum Chemical Industry Company, and the double metal cyanide complex catalyst was prepared in our laboratory.¹³

1,4-Butanediol (BDO) was purchased from Bayer, Germany. 4,4'-Diphenylmethane diisocyanate (4,4'-MDI) was received from Yantai Wanhua Polyurethane without any further purification. All the other chemicals were of analytical grade and were used without further purification.

Copolymerization

In the following section a description of the synthetic procedures adopted in the present work is given. The general scheme of the reactions used for derivatization to the polyetherester (PEE) polyols is summarized in Scheme 1.

Copolymerization of polyetherester polyol

The copolymerization reactions were conducted in a 300 mL stainless steel autoclave, which is equipped with a manometer, external electrical heating, mechanical stirring, a thermocouple, and a water cooling coil. The heterogeneous mixture of solid anhydride, catalyst, and the low molecular polyoxypropylene diol initiator were weighed into the vessel. Then the autoclave was flushed with nitrogen for about 20 min after capping while stirring and the temperature of system was rising. At the same time pump liquid propylene oxide was added into the autoclave. The onset of the reaction was revealed by a progressive increase in temperature and pressure and its completion assessed by the observation of a drastic decrease in pressure down to a constant low level corresponding to the set temperature.

The traces of unreacted polyol were vacuum-extracted, then the autoclave was flushed with

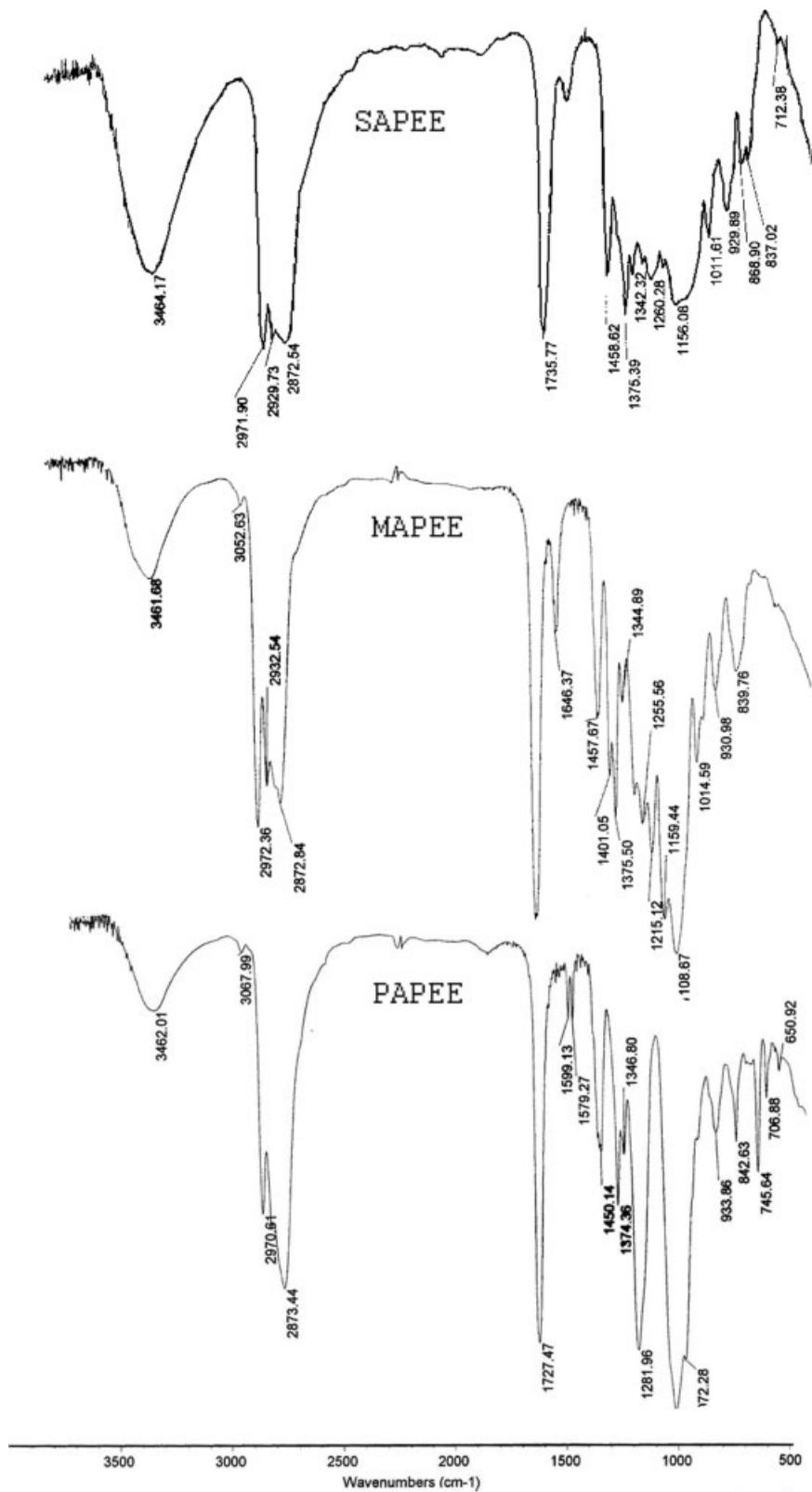


Figure 1 IR spectra of three polyetherester polyols.

nitrogen and thereafter, the contents of the vessel were allowed to reach room temperature under stirring.

Condensation polymerization of polyetherester polyurethane

To study the suitability of using the synthesized PEE polyols in the preparation of polyurethanes (PUs), each of the above three kinds of the polyol was reacted with 4,4'-diphenylmethane diisocyanate (MDI), respectively. After they were added in the amount as identified, the mixture was maintained under stirring in a round-bottom flask and purged with N₂ at 80°C for 3 h to obtain a prepolymer. Then chain extender 1,4-butanediol was added in an amount as identified. After ~1 min of intense mixing, the reacting mixture was cast onto a preheated tray and annealed for 2 h at 110°C. Finally the PEEPU was allowed to cool to room temperature.

Then, the PU elastomer sheet thus obtained was left to stand for 7 days in an atmosphere having humidity 50%.

Measurement and instruments

The number average molecular weight and molecular weight distribution of the polymerization product was detected by a Waters University 1500 GPC instrument (USA) at ambient temperature. The chromatograph was calibrated with samples of PS of known molecular weight. A Shimadzu FTIR-8101 Fourier transform infrared spectrograph (Japan) was used to analyze the structure of polyols and PUs. The ¹H NMR experiments were carried out on a Bruker DRX-300 NMR spectrometer (USA) with 300.13 MHz using CDCl₃ as the solvent and at a scanning width of 10 ppm.

The hydroxyl value was determined by the pyridine-acetic anhydride method. The thermal behavior of the PU was studied on a TGA92 thermogravimetric analyzer (USA) at a heating rate of 10°C/min in N₂ atmosphere. The hardness measurements were carried out using a durometer of Shanghai, China.

Room temperature stress-strain data were taken on a XLL-250 tensile device (Shanghai, China). Dumbbell-shaped samples with a gauge length of 1 cm and width of 0.4 cm were stamped out with a die. For each tensile strength reported, at least five sample measurements were averaged.

Dynamic mechanical property of the PU was measured by a dynamic mechanical analyzer (DMTA, Rheometric Scientific Mark IV, UK). Storage modulus, loss modulus, and loss tangent (tan δ) were scanned between -100 and 200°C at a heating rate of 3°C/min.

RESULTS AND DISCUSSION

In this work, the synthesis, characterization, and properties of three different PEE polyols were undertaken. The mechanical properties of the PUs prepared from them were also evaluated. Owing to the struc-

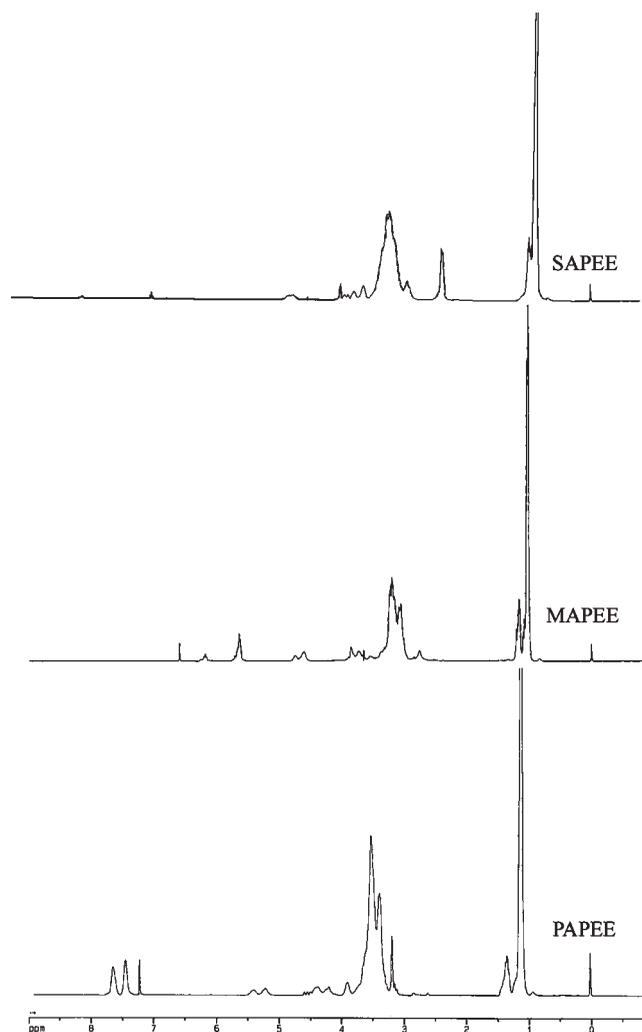


Figure 2 ¹H NMR spectra of three polyetherester polyols.

tural complexity of PEE polyol and to ensure raw material consistency, it was thought appropriate to characterize them first. Then structural characterization of the developed polyols was carried out. These results are discussed in the following sections.

Characterization of structure and properties of polyetherester polyols

IR analysis

Figure 1 presents the IR spectra of the three kinds of PEE polyols synthesized. It indicates that characteristic peaks of ether bond appear at around 1730, 1215, 1160, cm⁻¹, respectively, and that of the ester bond is at 1106 cm⁻¹. The band at 3462 cm⁻¹ is hydroxyl group characteristic peak. Except these common characteristics, we can also observe the distinguishing feature of three kinds of polyols. For PAPEE, it appears at the characteristic absorption peak of phenyl group at the vicinity of 3000–3100 cm⁻¹, 1600 cm⁻¹, 700–900 cm⁻¹ wave numbers.¹⁴ For MAPEE, there exists a strong sharp peak at 1646 cm⁻¹ wave number, which is the characteristic

TABLE I
Physical Parameters of Polyetheresters

Sample	Hydroxyl value (HV)	Molecular weight calculated by HV ^a	Viscosity at 25°C (mPa s)	Molecular weight got from GPC	Molecular weight distribution
1 (20% PA)	54.7	2051	1620	1980	1.05
2 (20% MA)	54.0	2081	700	2010	1.07
3 (20% SA)	52.8	2125	550	2064	1.09

^a The designed value of molecular weight is 2000.

absorption peak of C=C. In the spectrogram, we can not see the characteristic absorption peak of anhydride monomer and carboxyl group, indicating the raw material reacted quite completely, and there is no by-product ended with carboxyl group.

¹H NMR spectra of the polyetherester polyols

The ¹H NMR spectra of three kinds of PEE polyols are shown in Figure 2. All of them showed same resonance signals at vicinity of $\delta = 1.2, 3.6, 4.2, 4.5$, which are the characteristic peaks of methyl, methylene, and methine resonance. For PAPEE, we can also observe a group of peaks at $\delta = 7.5$, which is characteristic of phenyl hydrogen resonance. For MAPEE, the resonance peak of hydrogen at C=C appear at $\delta = 5.7$.

It should be noted that all the three polyether ester used here contain 15% of ester, and from the integration of the ¹H NMR, we can calculate the content of ester as 13%, which is close to the theoretical value.

In the spectra, there do not appear characteristic peaks of phthalic anhydride monomer and the carboxyl group, indicating the reaction is quite complete and there is no by-product ended with carboxyl group.

Thus, from the analysis of FTIR and NMR, we can conclude that the product is polyether ester ended with hydroxyl group as we designed.

Hydroxyl value, viscosity molecular weight and its distribution

Some important parameters, such as hydroxyl value, molecular weight, molecular weight distribution, etc., of synthesized polyether ester polyols were measured to determine their properties. The results were summar-

ized in Table I. The molecular weight distribution index of the polyether ester polyol catalyzed by the DMC catalyst is ranging between 1.05 and 1.10 indicating a uniform distribution of molecular weight. It should be stressed that such a low MWD can not be obtained by normal base catalyst. The DMC catalyst plays a key role in the polymerization process, however the mechanism is still unclear which need more detailed investigation.

From the hydroxyl value, the molecular weight can be calculated. It can be observed that the molecular weight calculated by hydroxyl value well accord with the value obtained by GPC analysis. Both the values well fit the designed value that is calculated from the content of raw materials.

Because of the large viscosity of PAPEE with big ester content (for example, the viscosity can reach 5575 mPa s when ester content is 30%), which can induce difficulty in operation and large error in characterization, we select the product with 20% of ester content for comparison. From Table I, we can see that the viscosity of three polyether ester strongly correlated with the structure of the polyether ester. The PAPEE has the biggest viscosity and then is the MAPEE, and the SAPEE has the lowest viscosity. As we know, the viscosity of polymer is correlated with the rigidity of the main chain. The larger the rigidity is, the bigger the viscosity is. It can be seen that from PAPEE, MAPEE to SAPEE, the rigidity of the main chain decreased, which caused the decrease of apparent viscosity.¹⁵

Characterization and mechanical properties of polyetherester polyurethane

Three kinds of PU were then developed from the as-synthesized polyols. The mechanical properties of these

TABLE II
The Different Mechanical Performances of Polyetherester PU and Polyether PU at the Same Content of MDI

Type of PU	NCO (%)	Hardness (Shore A)	Rebound resilience (%)	Elongation at break (%)	Tensile strength (MPa)	Tearing strength (kN/m)
PAPEE-PU	8.2	96	16	510	23.5	80
MAPEE-PU	8.2	89	8	312	19.54	60
SAPEE-PU	8.2	87	7	298	19.12	53
PE-PU	8.2	86	8	304	18.24	51

TABLE III
The Different Mechanical Properties of PAPEEPU with Different Content of Ester in Soft Segment

The ester content in soft segment (%)	Hardness	Rebound resilience (%)	Elongation at break (%)	Tensile strength (MPa)	Tearing strength (kN/m)
15	96 (Shore A)	16	510	23.5	80
20	58 (Shore D)	23	260	29.7	93
25	70 (Shore D)	35	250	34	150
30	72 (Shore D)	37	200	36.9	154

^a At the same content of hard segment content 6.54%.

PU were studied and compared with normal polyether PU.

Performance comparison with ordinary polyether PU

The three polyurethanes PAPEEPU, MAPEEPU, and SAPEEPU were prepared by mixing MDI with corresponding polyols. The mechanical properties of these PUs were measured and the results were summarized in Table II. For comparison, the properties of ordinary PU from polyether (PE-PU) were also listed in Table II.

From Table II, we can see that under the same hard segment content, the properties of PAPEEPU are better than that of ordinary PE-PU. The hardness of PAPEEPU is 11.6% higher than that of polyether PU, which should attribute to the existence of rigid phenyl group in the soft segment of PAPEEPU. Other properties such as rebound resilience, elongation at break, tensile strength, and the tearing strength are 50, 67.8, 28.8, and 56.8% higher than those of PE-PU, respectively. The reason for such increase is also due to the existence of phenyl group in soft segment. The phenyl group can arrange neatly, which makes the crystalline degree of the soft segment increase, thus

limiting the distortion of soft segment effectively and preventing the growth of the crack. As a result, the mechanical strength of the PAPEEPU elastomer increases. Moreover, the phenyl group in the soft segment also reduces the elasticity of elastomer, which displays as the increase of elongation at break.

For MAPEEPU, since only double bond exists in the soft segment, the rigidity of the soft segment does not increase remarkably, the properties of MAPEEPU increase a little, and for SAPEEPU, the properties are almost similar to that of PE-PU because there is little difference in the rigidity of soft segment.

The influence of ester content in soft segment on PU mechanical properties

From discussion above, it can be concluded that the PAPEEPU has better mechanical properties than the other two PU, thus we use it for our further study.

As discussed above, the existence of rigid ester in soft segment makes the mechanical properties improved. Thus the influences of ester content in soft segment on mechanical properties of PU were studied. Some PAPEEPU with different ester content but same soft segment content was thus synthesized for

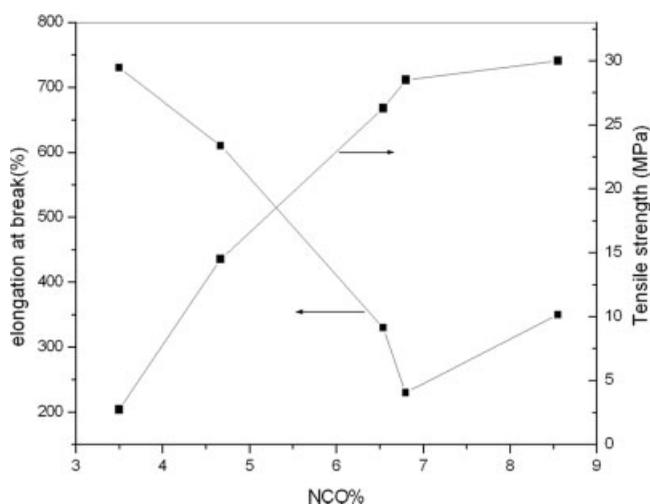


Figure 3 The effect of hard segment content on elongation at break and tensile strength.

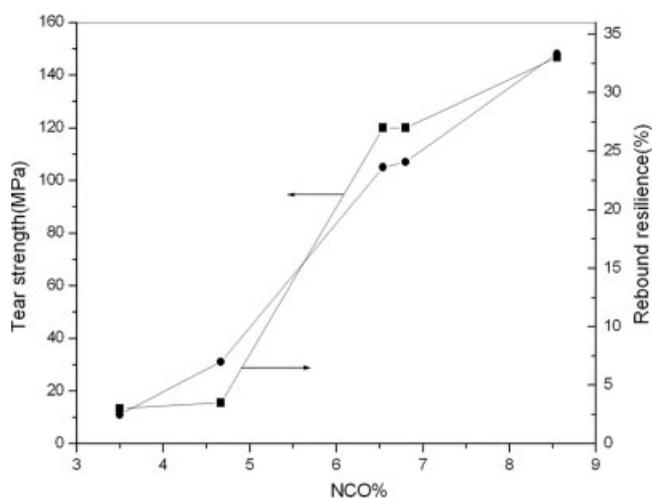


Figure 4 The variety curve of tear strength and impact elasticity with the increase of hard segment content.

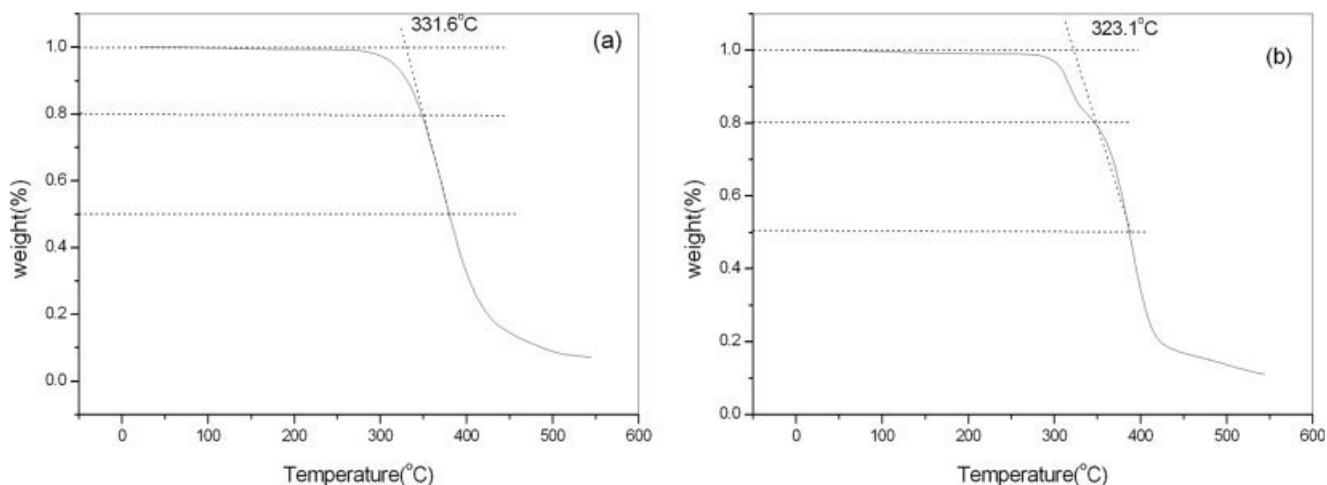


Figure 5 TG curves of synthesized PU: (a) PEEPU; (b) PEPU.

comparison. Table III listed the results obtained. It can be seen that with the increase of ester content in soft segment, the hardness, tensile strength, and tear strength increased, whereas the elongation at break decreased. Such trend is strongly related to the change of structure for different ester content. With the increase of ester content in the soft segment, the rigidity of the soft segment increase because of the increasing amount of phenyl group in the chain, which can make the PU more difficult to stretch, as a result, the mechanical strength of the PU increased. However, the increasing rigidity can also lead to the difficulty of elongation, and thus we can see that the elongation at break decreased a lot with the increase of ester content in soft segment.¹⁶

The influence of soft segment content on mechanical properties of PU

The mechanical properties of synthesized PU are also related with the content of hard segment. A series of PAPEEPU with different hard segment content were synthesized and their properties were compared. The results were shown in Figures 3 and 4, from which we can see that, the tensile strength, the tearing strength, and the rebound resilience of the PEEPU showed almost linear increase with the increase of hard segment content, whereas the elongation at break has a tendency, which decreases first and then increases a little with the increase of hard segment content. The reason for such dependence can be attributed to the change of macromolecular structure during the

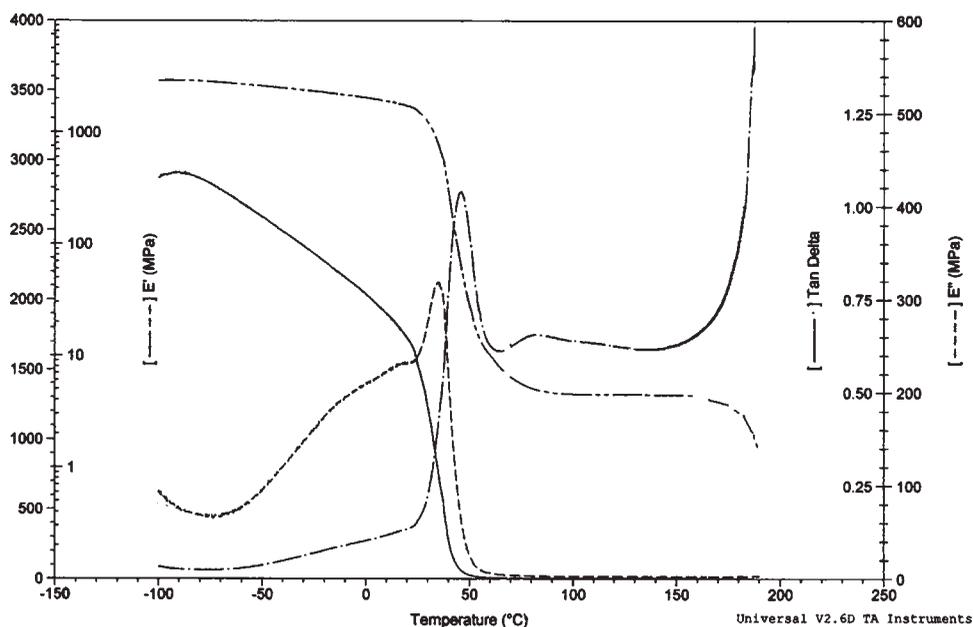


Figure 6 Dynamic mechanical properties of PAPEE-PU.

increase of hard segment content. With the increase of hard segment content, the rigid diphenylmethane moiety coupled with hydrogen bonding and dipole-dipole interaction make the PU more and more difficult to stretch as higher percentage of hard segment is incorporated. In addition, physical crosslinking made by the rigid diphenylmethane moieties also contributes to the high maximum stress with the increase of hard segment. However, at high hard segment content, the rigidity of the PU would not allow it to stretch long, and the very low degree of physical crosslinking at low percentage of hard segment is responsible for the PU break up at short elongation, which induce the decrease of elongation at break.

Thermal analysis

Figure 5 is the TG curve of polyether PU and PAPEEPU under the same hardness (Shore A 96). From the figures we can see that the decomposition temperature of PAPEEPU is 331.6°C, which is higher than that of the polyether PU (323.1°C). Moreover, in the curves it can be seen obviously that, polyether PU has two decompositions processes, but there is no obvious staggered degradation in the curve of PEEPU. This can also attribute to the existence of rigid function of the phenyl group in the soft section of the PEEPU, which causes the decomposition temperature of the soft section drawing close to that of the hard section. Such phenomenon is advantageous in enhancing the overall thermal stability of PU.

Dynamical mechanical properties of PAPEEPU

The dynamic mechanical analysis of the polymers in tensile mode helps in evaluating the viscoelastic properties of the materials. Figure 6 shows the typical dynamic mechanical curves of 15% PA content of PAPEEPU. The loss modulus peak in PAPEEPU appears to be narrow indicating the narrow distribution in crosslink density. Maxima on loss modulus-temperature curves are associated with the glass transition. The peak temperature (48°C) could be taken as a measured of the glass transition temperature of the PU. The storage modulus of PAPEEPU in the glassy state decreases slowly with increasing temperature, displaying a precipitous drop of about two orders of magnitude at T_g , followed by a steady state with the increase of temperature in the rubbery state. It should be noted that the $\tan \delta$ value of PAPEEPU can reach

1.0, which implied its good damping properties of PAPEEPU at glass transition temperature.¹⁷

CONCLUSIONS

Three kinds of cyclic anhydrides, succinic anhydride (SA), phthalic anhydride (PA), and maleic anhydride (MA) have been copolymerized with propylene oxide and low molecular weight polyoxypropylenediol via ring-opening copolymerization initiator by double metal cyanide complex catalyst to synthesis a series of PEE polyols, and three kinds of PEEPU were thus synthesized by copolymerization of as-synthesized PEE polyol with 4,4'-diphenylmethane diisocyanate and 1,4-dihydroxybutane. It is found that the mechanical properties of the PUs strongly correlated the structure and the composition of the macromolecules. The inducing of the rigid phenyl group in the soft segment can improve the mechanical strength remarkably, and both increase the ester content in soft segment and the hard segment content can increase the mechanical properties of polyurthanes.

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