Studies on Chain Extension of a Novel Bio-Based Engineering Elastomer Using 4,4-Diphenyl Methane Diisocyanate as a Chain Extender

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ABSTRACT: A novel hydroxyl-terminated bio-based engineering elastomer (BEE) was synthesized from four bio-based monomers by adding excess diol. Then the BEE was chain extended in Haake torque rheometer with 4,4-diphenyl methane diisocyanate (MDI) as chain extender. The molar ratio of NCO/OH, reaction temperature and reaction time of the chain-extension reaction were studied, and the optimum condition was determined by the gel permeation chromatography (GPC), soxhlet extraction, and fourier transform infrared spectroscopy (FTIR) results. After chain extension, (i) the number-average molecular weight of BEE became about 3.5 times of the original BEE, (ii) the thermal stability was improved and the crystallization rate was lower, (iii) and the mechanical properties were significantly improved with nano-SiO$_2$ as reinforcing filler. The chain-extended BEE would have potential wide applications in engineering field. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40756.

INTRODUCTION

Recently, biobased polymers from renewable resources have received considerable interests due to environmental concerns and sustainable development.[1–7] Some bio-based polymers have exhibited excellent properties and replaced petroleum-based polymers in many fields.[8–12] Elastomer plays a very important role in our daily life. However, rare reports were concerned about bio-based elastomers with practical significance. Our lab first raised a bio-based engineering elastomer (BEE) with comprehensive performances from large-scaled biomass by using melting condensation polymerization.[13] The BEE has been demonstrated as an outstanding tougher to PLA.[14] Moreover, we have already found some other applications of the BEE and our lab are proceeding on pilot tests of the BEE. In this case, a high molecular weight of BEE is essential to ensure the material with good processing properties and excellent performance for industrial applications.[15] Unfortunately, the number-average molecular weight of the BEE is a little low due to the limitation of the melting polycondensation method.

During the melting polycondensation reaction, the system viscosity usually increases with increasing molecular weight of the sample, and with certain value of viscosity, the sample will climb onto the stirrer (so called Weissenberg effect) to stop the further reaction. Therefore, it is really hard to obtain a polymer with favorable high molecular weight during the melting polycondensation reaction process. Many works were focused on the increase of the molecular weight of these polymers.[16] Of which, chain extension is the most efficient way. Chain extension methods have been used on PET,[17,18] PLA,[19] and PBS.[20] The most common chain extenders reported are bi- and multifunctional epoxies,[21] diisocyanates,[22] dianhydrides,[23] bis-oxazolines,[24] diol, and diamine.[25] The multifunctional chain extender usually leads to crosslinking structures of the products, which are not suitable for the secondary processing of rubbers. Therefore, bi-functional chain extenders are favorable for rubbers. When the bi-functional compounds are reacted with low molecular weight elastomers, they form bridges between two chains of the elastomers, increasing the molecular weight significantly.

Table I. Variables of Chain Extension Reaction

| Variables	nNCO/OH	Time/min	Temperature (°C)
	1 : 1, 1.5 : 1, 2 : 1, 3 : 1, 4/1	2, 4, 6	60, 80, 100

For the BEE products, hydroxyl-terminated BEE can be obtained by adding excess diol,[26] which can be used for chain extension reaction. Isocyanate compouds, such as hexamethylene diisocyanate (HDI), toluene diisocyanate (TDI), 4,4-diphenyl methane diisocyanate (MDI), are proved to be effective chain extenders to the hydroxyl-terminated polymers.[27–29] Among these isocyanate chain extenders, TDI and HDI have higher reactivity than MDI, thus have higher toxicity and need stricter reaction conditions. To make a convenient way to the chain extension reaction of BEE to increase its molecular weight and improve its properties,[30] MDI with a relative low toxicity was used.[31]

In this study, a novel hydroxyl-terminated BEE was first synthesized from five bio-based monomers, by adding more stoichiometric ratio of diol to diacid. Then, MDI was used as a chain extender to react with the hydroxyl group of BEE in a Haake torque rheometer. After chain extension reaction, the molecular weight of BEE increased significantly and some properties of the chain-extended BEE were also improved, which was helpful for a wide industrial application.

EXPERIMENTAL

Materials

Sebacic acid (SeA) (purity 99.0%) was purchased from Guangfu Fine Chemical Institute of Tianjin. Itaconic acid (IA) (purity 99.0%), succinic acid (SA) (purity 99.0%), 1,3-propanediol (PDO) (purity 99.0%), and 1,4-butanediol(BDO) (purity 99.0%) were all obtained from Alfa Aesar. Tetrabutyl orthotitanate (TBOT), hydroquinone and phosphorous acid were
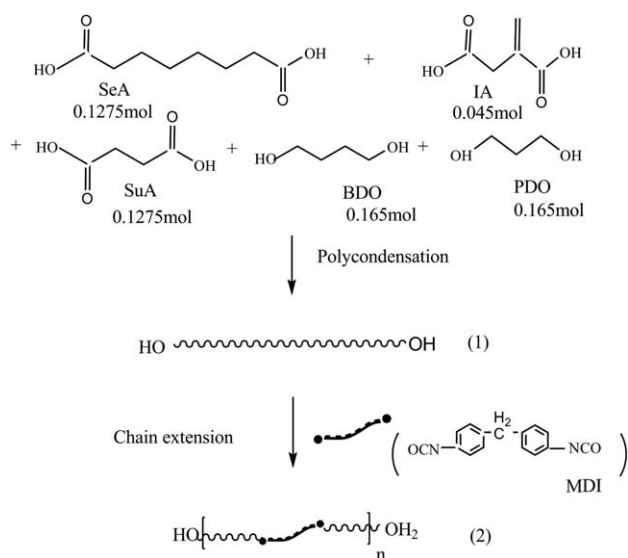
Figure 1. The synthesis of bio-based engineering elastomers and chain extension on it.
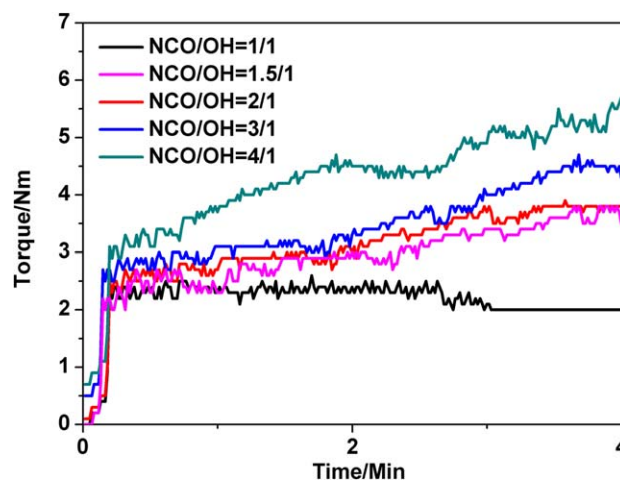
Figure 2. Torque-time curves of different NCO/OH molar ratios. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

supplied by Fluka, Beijing Yili Fine Chemicals, and Sinopharm Chemical Reagent, respectively. 4,4′-diphenylmethane diisocyanate (MDI) were bought from Yantai Wanhua Polyurethanes. SiO$_2$ VN3 was purchased from Qingdao Degussa Chemical. DCP and other chemicals were bought from HWRK Chemical, China.

Characterization

Molecular Weight. The molecular weights of chain extended BEEs were determined by GPC measurements on a Waters Breeze instrument equipped with three water columns (Styragel HT3_HT5_HT6E) at 25°C using tetrahydrofuran (THF) as the eluent (1 mL/min) and a Waters 2410 refractive index detector. Polystyrene standard was used for calibration. The results of the GPC is part of sol.

Value of Hydroxyl Groups. The hydroxyl numbers were determined by standard titrimetric method.[32] P-toluenesulfonic acid was used as the catalyst and acetic anhydride in ethyl acetate as the acetylating reagent.

$$\text{Hydroxyl value} = [(V_0 - V_1) \times C \times 56.1]/m, \text{ mg KOH /g BEE} \quad (1)$$

C is the concentration of NaOH (mol/L); V_0 is the consumption of NaOH of the blank sample (mL); V_1 is the consumption of NaOH of the sample (mL), M is the weight of sample (g).

Table II. GPC Data and Gel Contents of the C-BEE with Different NCO/OH Molar Ratios

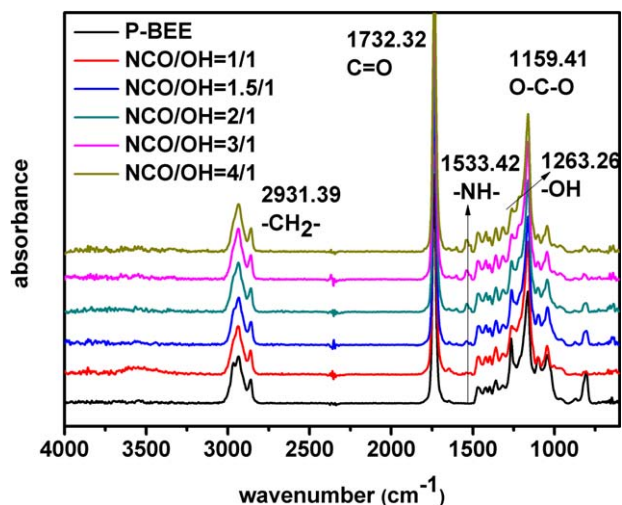| Sample	M_n	M_w	PDI	Gel content (%)
P-BEE	24,785	50,248	2.02	2.16
NCO/OH = 1 : 1	31,734	105,674	3.33	3.32
NCO/OH = 1.5 : 1	56,072	198,427	3.54	5.29
NCO/OH = 2 : 1	86,716	224,702	2.59	8.67
NCO/OH = 3 : 1	42,045	156,490	3.72	35.96
NCO/OH = 4 : 1	32,770	104,254	3.18	76.26

Figure 3. The IR spectra of different molar ratio of NCO/OH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Thermal Stability. The measurements of sample weight loss were carried out on a STARe system TGA/DSC1 thermogravimeter (Mettler-Toledo International, Switzerland) with a cooling water circulator. The testing was done under a flowing nitrogen atmosphere (10 mL/min). All the samples used in the thermogravimetric measurements were similar in weight (10 ± 1 mg) and heated from 30 to 800°C at a heating rate of 10°C/min.

Glass Transition Temperature. DSC thermograms of the samples were recorded by DSC1 Instruments (Mettler-Toledo International, Switzerland), and data was analyzed by Stare software. The temperature was first raised to 100 at 10°C/min, allowed to stay there for 5 min to eliminate any thermal history and moisture from the sample, and then lowered to -100 at 10°C/min. The nitrogen flow was 50 mL/min, and the weight of sample was about 5 mg. Both cooling and heating scans were recorded for analysis.

Cure Characteristics. The cure characteristics were measured on a Disc Rheometer (P355B2, Beijing Huanfeng Chemical Industry, China) at 160°C.

Mechanical Properties. The mechanical properties of all samples were measured at 25°C according to ASTM D638 with a CMT4104 electronic tensile tester (SANS, China) at a crosshead speed of 500 mm/min. The dumbbell shaped samples ($25 \times 6 \times 2$ mm^3) were prepared according to ASTM standard.

Fourier Transform Infrared Spectroscopy. FTIR spectra of the samples were recorded on a TENSOR27 (Bruker Optic GMBH,

Table III. GPC Data and Gel Contents of the C-BEE at Different Temperatures

Sample	M_n	M_w	PDI	Gel content (%)
60°C	44,858	158,742	3.53	6.35
80°C	86,716	224,702	2.59	8.67
100°C	15,504	92,927	5.99	37.82

Table IV. GPC Data and Gel Contents of the C-BEE Under Different Reaction Time

Sample	M_n	M_w	PDI	Gel content (%)
2 min	35,540	134,240	3.77	3.22
4 min	86,716	224,702	2.59	8.67
6 min	56,337	151,011	2.68	12.86

Germany) Fourier transform infrared spectrophotometer equipped with a smart orbit diamond attenuated total reflection (ATR) accessory. Interferograms were Fourier transformed by using cosine apodization for optimum linear response.

Soxhlet Extraction. A 1 g sample of each chain extended BEE was extracted for 24 h with 300 mL of refluxing tetrahydrofuran in a Soxhlet extractor. After extraction, the resulting solution was concentrated by rotary evaporation. Then the soluble fraction and insoluble fraction were dried in a vacuum oven at 100°C, and the insoluble solids were weighed. Calculation formula:

$$X = \frac{W_3 - W_2}{W_1} \times 100\% \qquad (2)$$

X is the gel content; W_2 is the quantity of the package; W_1 is the quantity of the original sample; W_3 is the quantity of wrapped residues after extraction.

Synthesis of Hydroxyl-Terminated Bio-Based Engineering Elastomers

Sebacic acid (0.1275 mol), succinic acid (0.1275 mol), and itaconic acid (0.045 mol), 1,3-propanediol (0.165 mol), 1,4-butanediol (0.165 mol), retarder phosphorous acid (0.01 wt %), and hydroquinone (0.04 wt %) were added into a 100 mL three-neck flask in turn. The system was first purged with high purity nitrogen, stirred at 250 rpm, and heated to 180°C for prereaction about 2 h. Then the temperature of the system was decreased at lower than 50°C to add the catalyst tetrabutyl titanate (0.05 wt %). The reaction was then processed at 220°C in a high vacuum environment, which was sealed and vacuumized to -0.1 Pa for about 4–5 h until the Weisenberg effect was found. The obtained product was light-yellow elastomer named P-BEE (pre-BEE) and the number-average molecular weight of the product was about 24,785. Products obtained had the similar degree of polymerization. All the original BEE was premixed in the two-roll mill to ensure a single molecular weight for the chain-extension experiment. That is to say, the value of OH groups of the original BEE was similar. Thus we listed one titrimetric result and molecular weight for all the P-BEE products.

Table V. DSC Data of the C-BEE and P-BEE

Sample	T_g^a (°C)	T_c^a (°C)	T_m (°C)	T_g^b (°C)	ΔH_m (J/g)	ΔH_c^a (J/g)
P-BEE	-55.98	-37.99	7.25	-63.49	-28.99	12.24
C-BEE	-53.64	-17.86	5.39	-57.22	-20.76	16.85

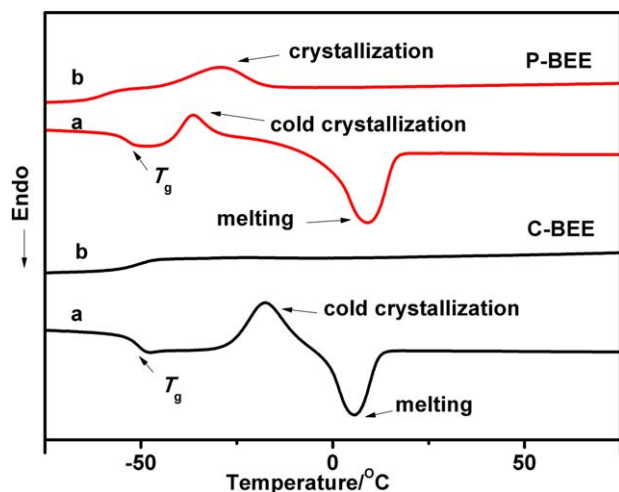[a] Heating curve.
[b] Cooling curve.

Figure 4. DSC thermograms (a) heating curve and (b) cooling curve of the BEE and chain extended BEE. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Chain Extension of BEE in Haake Torque Rheometer

The chain extension was carried out by one-step addition polymerization process in Haake torque rheometer. P-BEE (50 g) was cut into small pieces and added into the Haake torque rheometer. The premix temperature was 60°C and the rotating speed was 20 round/min (rpm). Then, different variables of MDI were added, and then the P-BEE and MDI were premixed for 1 min. After that, the temperature was increased to a certain value, and the rotating speed was increased to 60 rpm. The chain-extended product was named C-BEE (chain-extended BEE). Variables studied in the experiment are shown in Table I. Since the influence of rotating speed on the chain extension was not obvious in this study, the rotating speed of chain extension was set as 60 rpm.

The synthesis and chain extension reaction are shown in Figure 1. Hydroxyl-terminated P-BEE (1) can be obtained by adding more stoichiometric ratio of diol to diacid. (2) MDI, act like a bridge, could connect two or more BEE chains to make chain-extended C-BEE.
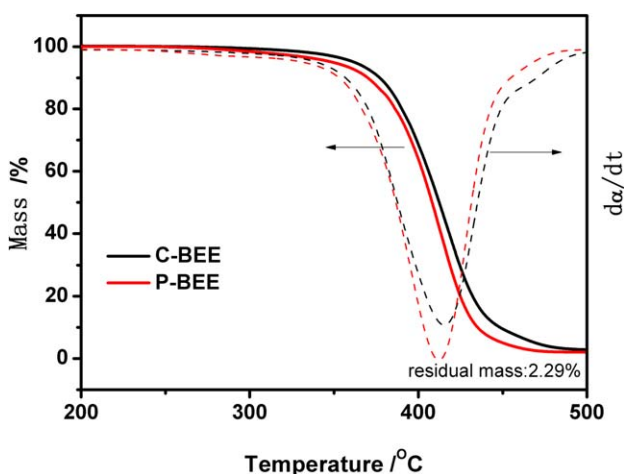

Figure 5. TGA curves of the BEE and chain-extended BEE. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
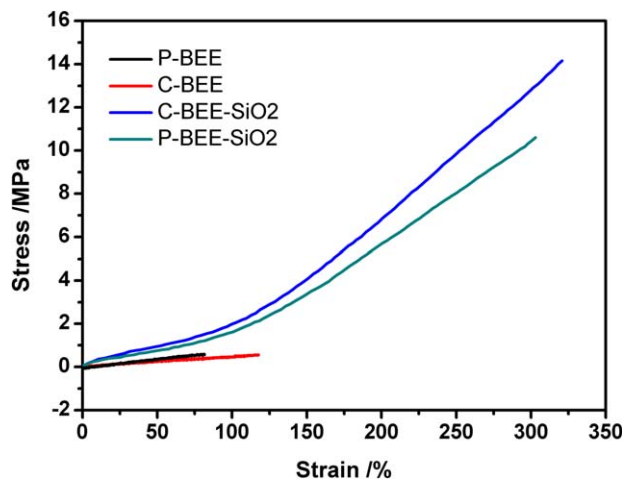

Figure 6. The stress–strain curves of BEE and chain extended BEE. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

1. Hydroxyl-terminated P-BEE.
2. Linear macromolecule formed from chain extension reaction.

Mixing and Curing of Chain-Extended BEE Compounds

The blending of chain-extended C-BEE (100 phr) with SiO_2 (VN3, 30 phr) was carried out on a two-roll mill (Φ 160 mm, Zhanjiang Machinery Factory, Guangdong Province, China) with a roller spacing of 0.5 mm. DCP (0.16 phr) was added. The ingredients were processed on the mill for about 15 min in order to obtain homogeneous compounds. The rubber compounds were then vulcanized by using a compression molding press (Shanghai Rubber Machinery Factory, Shanghai, China) for the curing time of T_{90} (as determined by a disc rheometer, P355B2, Beijing Huanfeng Chemical Technology and Experimental Machine Plant, Beijing, China) at a pressure of 15 MPa and a temperature of 160°C.

RESULTS AND DISCUSSION

Influence Factors During the Chain-Extension Reaction Between BEE and MDI

P-BEE was prepared according to Figure 1 by melting polycondensation reaction of diacid with 0.3 molar excess of diol. Excess diol was to form hydroxyl-terminated structure, and excessive 0.3 molar was found be the optimal one during the experiments. Hydroxyl numbers was determined by standard titrimetric method, and the hydroxyl value was 0.047×10^{-3} mol/g P-BEE. To investigate the best condition of chain extension reaction, the effect of molar ratios of NCO/OH, reaction time, and reaction temperature on the chain extension of P-BEE were studied.

Effects of Molar Ratios of NCO/OH. To study the effect of molar ratio of NCO/OH on the molecular weight of C-BEE, the other three conditions were fixed. The reaction temperature is 80°C, the reaction time is 4 min and the rotating speed is 60 rpm. The molar ratios of NCO/OH were adjusted from 1 : 1 to 4 : 1. During the mixing process of P-BEE and MDI in Haake torque rheometer, the torque of the mixture increased after about 2 min (shown in Figure 2), indicating the

Table VI. Mechanical Properties of P-BEE and C-BEE

Sample	Tensile strength (MPa)	Modulus at 100% elongation (MPa)	Elongation at break (%)	Shore A hardness	Density (g/cm^3)
P-BEE	0.78	–	72	–	1.281
C-BEE	0.86	0.7	117	–	1.293
P-BEE-SiO$_2$	11.2	1.7	303	67	–
C-BEE-SiO$_2$	14.3	1.8	326	73	–

chain-extension reaction was occurred from 2 min. When the molar ratio of NCO/OH is 1 : 1, the torque did not change with increasing reaction time, means the chain-extension reaction degree of P-BEE and MDI is low. When the molar ratio of NCO/OH is 4 : 1, the torque increased from the beginning, indicating a high reaction speed. In addition, the torque of the mixture increased with increasing molar ratio of NCO/OH, which is contributed by both the molecular weight and the gel content of the sample. As shown in Table II, with increasing molar ratio of NCO/OH, the molecular weight of the samples first increase then decrease while the gel contents increased continuously. The reaction degree of C-BEE can also be judged by the molecular weight of the C-BEE: Low molecular weight means that the reaction is insufficient, and with increasing molar ratio of NCO/OH, the reaction reaches saturation. This phenomenon could be explained from Figure 1. With increasing amount of MDI, the NCO group first reacted with OH group to increase the molecular weight of C-BEE, and with excess amount of MDI, the abundant NCO group would further react with the generated NHCOO group to form crosslinked structure. When the molar ratio of NCO/OH is 4 : 1, the M_n and M_w detected were only soluble low molecular weights. The number-average molecular weight of the sample with molar ratio of NCO/OH at 2 : 1 was improved significantly, about 3.5 times of the original P-BEE, and at the same time the gel content of this sample is proper for further processing.

The chemical structures of the BEE samples with different molar ratios of NCO/OH were characterized by FTIR spectroscopy (shown in Figure 3). The peaks at 2800–2935 cm^{-1}, 1732 cm^{-1}, 1533 cm^{-1}, 1263 cm^{-1}, and 1159 cm^{-1} represent methylene stretching vibration, C=O stretching vibration, N—H deformation vibration, O—H deformation vibration and O—C—O stretching vibration, respectively. With increasing molar ratio of NCO/OH, the peak intensity of N—H deformation vibration increased while the peak intensity of O—H deformation vibration decreased, which indicated the reaction of NCO and OH.

Effects of the Chain-Extension Temperature. Temperature is also an important factor of the chain-extension reaction. With low reaction temperature, the reaction degree would be low, while with high reaction temperature, the crosslinking structure would be formed. According to the reference, 80°C is a proper temperature for the reaction of NCO and OH. Thus, in this study the effect of three reaction temperatures around 80°C on the chain-extension reaction were studied. The other three conditions were fixed at NCO/OH = 2 : 1, 60 rpm, and 4 min, respectively. The GPC data and gel contents of the chain-extended C-BEE at

different reaction temperatures were shown in Table III. It can be seen that, the number-average molecular weight of C-BEE first increased, then decreased. High temperature could greatly improve the reaction degree; however, the high temperature could also increase the formation of gel content (at 100°C), which is disadvantageous for the processing of elastomers. Therefore, the optimum chain-extension temperature is 80°C.

Effects of the Chain-Extension Time. To further understand the process of chain extension reaction between P-BEE and MDI, the molecular weight and gel contents of the C-BEE products at different reaction time were also studied. The other three conditions were NCO/OH = 2 : 1, 60 rpm, and 80°C, respectively. As shown in Table IV, with increasing chain-extension time, the molecular weight of the BEE first increased then decreased, while the gel contents of the C-BEE increase continuously. That is to say, with extended reaction time, the reaction degree would increase. When the reaction time is 4 min, the molecular weight and the gel content of the C-BEE is favorable.

From the above discussion, the optimum chain-extension conditions are: reaction temperature of 80°C, molar ratio of NCO/OH = 2 : 1, and the reaction time of 4 min. The number-average molecular weight of the chain-extended C-BEE at the optimum conditions is 86,716, about 3.5 times of the original P-BEE. The thermal properties and mechanical properties of this chain-extended C-BEE and the original P-BEE were further studied.

Thermal Properties

The thermal properties were studied by DSC and TGA methods. The DSC curves of C-BEE and P-BEE are shown in Figure 4, and the DSC results are summarized in Table V. During the cooling process, there is a crystallization peak on the DSC curve of P-BEE [Figure 4 (b)], while there is only a glass transition on the DSC curve of C-BEE. From the heating curves [Figure 4 (a)] we can see that, both of the two DSC curves represent cold crystallization peaks, and the cold crystallization temperature of P-BEE is much lower than that of C-BEE. The phenomenon indicated that, after chain extension, the crystallization rate of C-BEE decreased largely, because the chain regularity of C-BEE was disturbed after chain extension. The melting point (T_m) and glass transition temperature (T_g) were also affected by the change of the chain regularity of C-BEE and the introduction the rigid benzene group of MDI after chain-extension reaction. It can be seen from Table V that, after chain extension, T_m decreased from 7.25 to 5.39°C and T_g increased from −55.98 to −53.64°C. The increase of T_g may also be attributed to the formation of hydrogen bond between the urethane groups.

The thermal stability of the C-BEE is studied by TGA testing, as shown in Figure 5. After chain extension, the starting decomposition temperature and the maximum decomposition temperature both increased significantly. The increase of molecular weight of the C-BEE and the introduction of MDI are two main factors on the thermal stability of the products.

Mechanical Properties

The mechanical properties of the pure elastomers are usually very weak, thus, the elastomers were always reinforced by nanoclays. To BEE elastomer, the nano-SiO_2 was used as the reinforcing filler in order to see the difference between the P-BEE and the C-BEE. Figure 6 is the stress–strain curves of the P-BEE and C-BEE with or without nano-SiO_2. Before reinforced, the tensile strength shows no obvious difference while the elongation at break of the C-BEE improved significantly. After reinforced with nano-SiO_2, the tensile strength of the C-BEE increased from 11.2 to 14.3 MPa. The mechanical properties of P-BEE and C-BEE are summarized in Table VI. All these are also due to the fact that the reaction of excess MDI with urethane groups, which significantly enhance the tensile strength, because the crosslinking structure enables the polymer to distribute and absorb the stress evenly.

CONCLUSIONS

MDI was proved to be an effective chain extender with the hydroxyl-terminated BEE. The chain-extension reaction was affected by three factors: the molar ratio of NCO/OH, the reaction temperature and the reaction time. When the molar ratio of NCO/OH is 2 : 1, the reaction temperature is 80°C, and the reaction time is 4 min, the number-average molecular weight of the chain-extended BEE could reach 86,716, about 3.5 times of the original BEE ($M_n = 24,785$). After chain extension, the thermal properties and mechanical properties of the sample were both improved. The maximum decomposition temperature was increased from 405 to 410°C and the tensile strength with reinforced nano-SiO_2 was increased from 11.2 to 14.3MPa. It is also worthy to mention that, after chain extension, the crystallization rate of C-BEE became slow, which is favorable for the elastomers. In general, the molecular weight of BEE was greatly increased by using MDI as chain extender, and some of the properties were also improved at the same time, which make the BEE has a wide application in industry.

ACKNOWLEDGMENTS

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