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Effect of Hyperbranched Polyesters on HTPB Polyurethane Curing Kinetic

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Effects of hyperbranched polyesters on kinetics of the reaction between hydroxyl-terminated polybutadiene (HTPB) and isophorone diisocyanate (IPDI) were investigated. HTPB and IPDI were in-situ cured in the presence of two different hyperbranched polyesters, stearic acid ester-terminated hyperbranched polyester (SHPE) and acetate-terminated hyperbranched polyester (AHPE). The curing processes were monitored by quantitative Fourier transform infrared (FTIR) spectroscopy. The results showed the stearic acid ester-terminated hyperbranched polyester had catalytic effects on the reaction between HTPB and IPDI, while acetate-terminated hyperbranched polyester did not have an influence on the reaction between HTPB and IPDI.

Keywords: *polyurethane, curing kinetics, hyperbranched polyester, catalysis effect, FTIR, end-group*

1. Introduction

Polyurethane (PU) derived from hydroxyl-terminated polybutadiene (HTPB) possesses excellent adhesive properties, low surface energy, biological compatibility and chemical resistance, as compared with polyether- and polyester-based polyurethanes. Therefore, it has been widely used in various applications, including adhesives, coating, membrane materials, biomedical materials and electronic potting compounds[1-4]. However, one of their major drawbacks is that they have inferior mechanical properties. In recent years a great deal of attention has been given to enhance the mechanical properties of HTPB-derived polyurethane (HTPB-PU)[4-11]. For examples, Wingborg[7] had investigated the impacts of diols as extender and different diisocyanates as cured reagents of HTPB on mechanical properties. They found that the highest tensile strength can be obtained via Desmodur-W (H12MDI) and 1, 4-Butane diol (BDO). Tao[8] studied the modification of HTPB-PU via introducing polytetrahydrofuran glycol (PTMG) into the PU backbone. Chen[4] and Okamoto[10] had investigated mechanical properties of HTPB-PU blend with other polymer. Some researchers[5, 6,11-14] had put their focus on interpenetrating polymer networks (IPNs) technology to enhance mechanical properties of HTPB-PU. So far, most of reported works on HTPB-PU based IPNs had been focused on HTPB-PU, which were interpenetrated with linear one-dimensional polymers, such as Poly-(ethylene oxide)[5], polyethylene glycol[6], poly-methyl methacrylate[12], poly-methacrylic acid B ester[13] and polystyrene[14].

Hyperbranched polymers (HBPs) represent a class of pseudo-globular, highly branched macromolecules with a large number of terminal groups[15-18]. However, to the best of our knowledge, only few studies on HBPs-specially, as a component of IPNs, have been conducted. HPBs are enriched matrices of IPNs, possessing the capacity to tailor their compatibility with other polymers[15,18]. The pseudo-globular structure of HPBs enables decreased viscosity compared with corresponding linear polymer. When it is composing IPNs, the viscosity of the whole mixture will be reduced. In our previous study we presented a novel interpenetrating polymer network based on hyperbranched polyester and HTPB-PU[11]. When HTPB and IPDI are in-situ cured in the presence of stearic acid ester-terminated hyperbranched polyester (SHPE), hyperbranched interpenetrating polymer networks (H-IPNs) will be formed. Tensile tests results indicated the tensile strength and elongation of these H-IPNs were both three times higher than HTPB-PU. H-IPNs exhibit a good synergetic effect. During the research it was also found that the viscosities of these H-IPNs reaction systems increased faster than the neat HTPB-PU during the polymerization. The SHPE had a catalytic effect on the reaction between HTPB and IPDI. In order to investigate the mechanism of this catalysis effect, another hyperbranched polyester was synthesised for comparation. This hyperbranched polyester was acetate-terminated hyperbranched polyester (AHPE). These two hyperbranched polyesters have the same structures, only the termination groups are different. In this work, quantitative Fourier Transform Infrared (FTIR) spectroscopy was used to monitor the reaction systems of H-IPNs and HTPB-PU to obtain the kinetic parameters. The differences in the mechanism of reactions and its kinetics for H-IPNs and HTPB-PU are discussed.

2. Experimental

2.1. *Materials*

2-ethyl-2-(hydroxymethyl)-l, 3-propanediol (TMP), stearic acid, acetic anhydride and p-Toluenesulfonic acid (p-TSA) were purchased from Beijing Chemical Factory (China) and used without further purification. A commercial 2, 2-bis (hydroxymethyl) propionic acid (bis-MPA) (purity ≥ 98%) from Beijing Chemical Factory was re-crystallized. Hydroxyl-terminated polybutadiene (HTPB, with the number-average molecular weight of 4050 g/mol

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and the hydroxyl value of 0.515 mmol /g) was supplied by Li Ming Chemical Academy (China). Isophorone diisocyanate (IPDI) was purchased from Fluka (Germany). Triphenyl bismuth (TPB) was supplied by Shanghai Organic Graduate School (China). Potassium bromide (KBr) was purchased from Aldrich (America). The last four materials were used after being dried for 4 hours in a vacuum drier at 80 °C.

2.2. *Sample preparation*

The pseudo-one-step method was adopted to synthesize the hyperbranched polyester to obtain higher degree of branching than possible through the one-step method. The detailed synthesis procedure was described elsewhere[19]. TMP and bis-MPA were employed as core and monomer materials, respectively, and the condensation polymerization procedure was catalyzed by p-TSA. The resultant hydroxyl-terminated hyperbranched polyesters with generations from 1 to 5 are labeled as H_{10}, H_{20}, H_{30}, H_{40} and H_{50}, respectively.

The hyperbranched polyester with hydroxyl-terminated groups exhibited poor miscibility with HTPB-PU because of their high density of hydroxyl groups. In order to improve the thermodynamically miscibility of both polymers, end-group modification was needed to get modified hyperbranched polyester. For comparison purpose, stearic acid and acetic anhydride were used as end-cap modifiers of the hyperbranched polyester. The resultant chemical groups would help to decrease the polymer polarity and yield good affinity to HTPB-PU. The end-caps of the hyperbranched polyester were modified according to the literature[20]. The resultant stearic acid ester-terminated hyperbranched polyesters (SHPE) with generation 1 to 5 are labeled as H_{11}, H_{21}, H_{31}, H_{41}, and H_{51} respectively. The acetate-terminated hyperbranched polyesters (AHPE) with generation 1 to 5 are labeled as H_{12}, H_{22}, H_{32}, H_{42} and H_{52} respectively.

2.3. *Fourier Transform Infrared Spectroscopy (FTIR)*

Infrared spectra were recorded on a Nicolet 8700 infrared Fourier Transform Spectrometer (FTIR) which was equipped with a temperature controlled sample holder that allowed the in-situ analysis of the curing reaction. An isothermal curing process, between 40 °C and 80 °C for 8 hours, was monitored with FTIR.

The mixture of HTPB, IPDI, different generations of SHPE or AHPE and TPB was sandwiched between a pair of KBr plates and then secured in a sample holder preheated to the desired isothermal temperature. All spectra were taken every 30 min for the first five hours and every 1 hour for the last 3 hours by means of 64 scans with a resolution of 4 cm^{-1}.

Using FTIR to investigate reaction kinetics is based on the Beer-Lambert law that the kinetics between -NCO and -OH obeys Beer-Lambert law, as it has been attested by other researchers[21,22]. In this work, the vibration band of the -NCO, which appears as a band at 2260 cm^{-1}, was chosen to measure the reaction rate. The C–H vibration band near 2950-2850 cm^{-1} was chosen as an internal standard due to it being assumed to be unmodified during the polymerization process. The fraction of -NCO groups which had reacted, at a fixed temperature in a certain time, was calculated from the peak areas, A, after testing their direct proportionality with the concentration. Then the conversion of -NCO groups, was calculated according to

$$\alpha = 1 - \frac{A_1 / A_2}{A_1^0 / A_2^0} \qquad (1)$$

where A_1^0 and A_1, are the areas of the -NCO vibration band at the time of beginning and time of curing, A_2^0 and A_2 are counterparts for the reference groups vibration band.

3. Results and Discussion

In the preparation of the H-IPNs, two hyperbranched polyesters were previously synthesized. HTPB and IPDI were reacted in the presence of one of these hyperbranched polyesters to get the H-IPN system. HTPB and IPDI were also reacted without hyperbranched polyester to obtain a control system. The kinetics were investigated to determine the effects of the presence of the hyperbranched polyesters on the reaction between the -OH groups in HTPB and the -NCO groups in IPDI. The content of -NCO was reduced during the curing reactions, with the amount identified by the FTIR spectra (Figure 1). The band intensity of the -NCO was decreased with the reaction time increase.

Calculating from the peak areas of -NCO and $-CH_3$, the relationship between conversion and reaction time was obtained. Figure 2 indicates this relationship for H-IPNs with 20 wt % of different generations of SHPE and pure HTPB-PU. Figure 3 shows the conversion-time curves of H-IPNs with different proportions of H_{41} and pure HTPB-PU.

From Figures 2 and 3, we can see the degree of conversion increased with time sharply at the beginning of curing and then reaching a pseudo-plateau. The conversion of the H-IPN systems increased faster than the control system. It means the reaction rate was enhanced when SHPE is introduced. Moreover, there was no significant dependence of conversion on the amount and generation or content of SHPE added into HTPB-PU.

For comparison purpose, H-IPNs with different generations and contents of AHPE were also investigated. Figure 4 shows the conversion-time relationships for the control sample and H-IPNs with 20 wt% different generations of AHPE. And Figure 5 gives the conversion-time relationships for the control sample and H-IPNs with different contents of AHPE. Figures 4 and 5 suggest that the existence of AHPE did not affect the reaction rate between -OH and -NCO.

Thus, the existence of SHPE had some catalyzing effect on the reactions between -OH and -NCO, in contrast, AHPE did not have this effect. In order to calculate the polymerization activation energies of the control system and

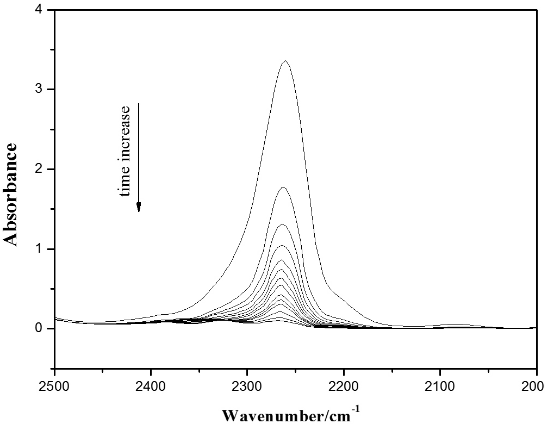


Figure 1. Changes of the FTIR spectra for the -NCO group during the curing process.

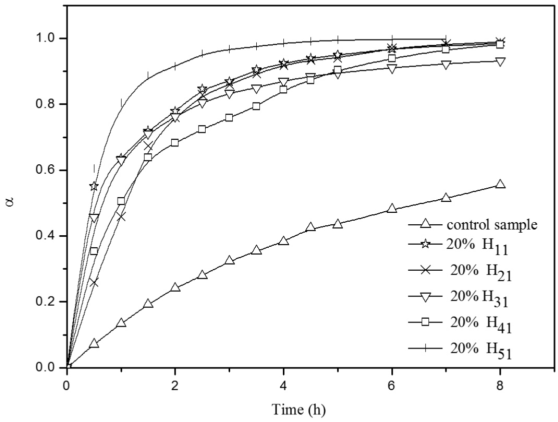


Figure 2. Conversion-time curves for the control sample and H-IPNs with 20 wt% different generation of SHPE.

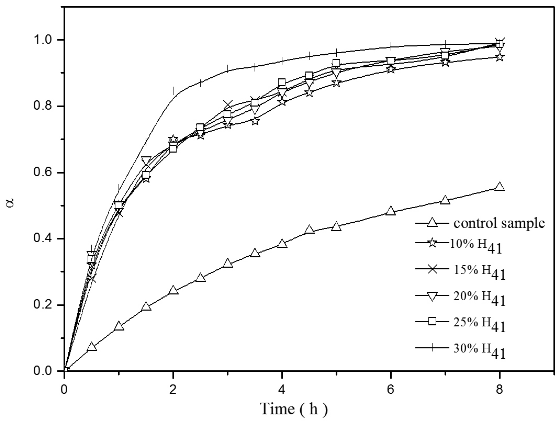


Figure 3. Conversion-time curves for the control sample and H-IPNs with different content of H_{41}.

H-IPNs with the SHPE system, it was needed to obtain the conversion-time relationships of these systems at different temperatures. Figures 6 and 7 depict the evolution of the conversion versus curing time for different isothermal curing temperatures of the control systems and the H-IPNs systems respectively. As the temperature was increased, higher values of the plateaus were achieved and were reached more rapidly. The conversion of -NCO strongly depended on the reaction temperature in all cases we investigated.

The kinetic order of the -NCO and -OH reaction was determined according to the relationship between $(1-\alpha)^{-(n-1)}$ and t[21]. When depicting $\alpha/(1-\alpha)$ as a function of reaction time t, a series of lines (with good agreement $R \geq 0.99$) were obtained all passing through zero (Figures 8 and 9). This suggests that the reactions all followed a second-order kinetics mechanism, whether the SHPE was added or not. Thus SHPE only enhanced the reaction rate without changing its order.

According to the Arrhenius equation, $\ln k = \ln A - E_a/RT$, where A is a factor of frequency, R is the universal gas constant (8.314 J/mol K) and E_a is the activation energy. As discussed above, the values of k can be obtained from the slopes of the lines in Figures 8 and 9. The obtained k values are plotted in Figure 10 as lnk against 1000/T for all the systems. Two linear fits are shown, the higher k values corresponding to the H-IPNs systems with SHPE and the lower for the control systems.

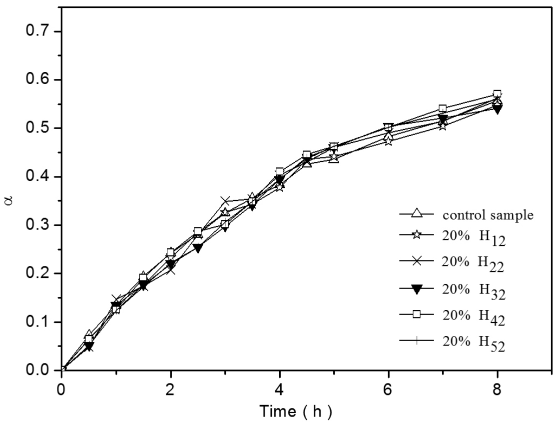


Figure 4. Conversion-time curves for the control sample and H-IPNs with 20 wt% of different generations of AHPE.

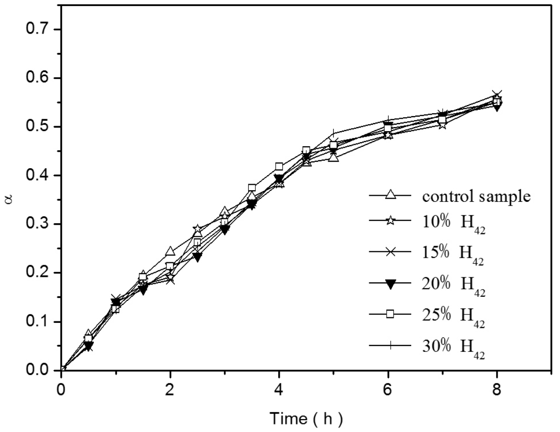
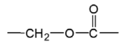


Figure 5. Conversion-time curves for the control sample and H-IPNs with different contents of H_{42}.

From the slopes of the lines in Figure 10, we can get experimental values of the activation energy, 28.3 kJ /mol and18.3 kJ/mol, corresponding to the control system and H-IPNs with 20 wt% H_{41}. The activation energy decreased when the SHPE was added, indicating that SHPE had catalytic effect on the reaction between HTPB and IPDI.

The two hyperbranched polyesters, SHPE and AHPE have the same structures, only the terminal groups were different. However, SHPE had a catalytic effect on the reaction between HTPB and IPDI, where AHPE did not. This catalysis could be due to the difference in the end-groups. SHPE has long alkyl chains, which make it possess an amphiphilic structure. This structure could compatibilize HTPB and IPDI. By contrast AHPE did not have amphiphilic structure, so the existence of AHPE did not have any effect on the reaction between HTPB and IPDI.

The structure of SHPE can be divided into two distinct parts which have different structures and solubility parameters. One, called the "core", has the basic repeat unit  $-CH_2-O-\overset{\overset{O}{\|}}{C}-$ (calculated solubility parameter is 23.5 $(J/cm^3)^{1/2}$); The other called the "shell", consists of the end-

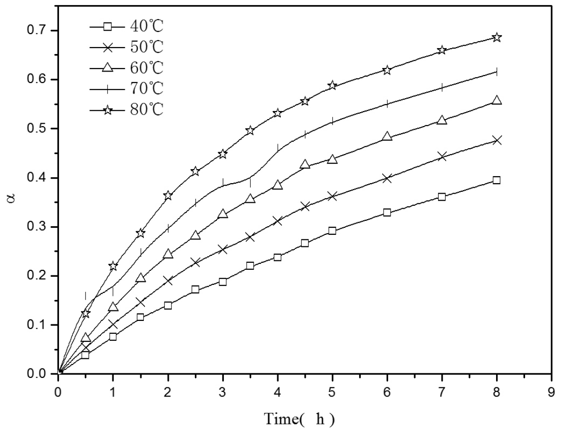


Figure 6. Conversion-time curves of the control sample at different temperatures.

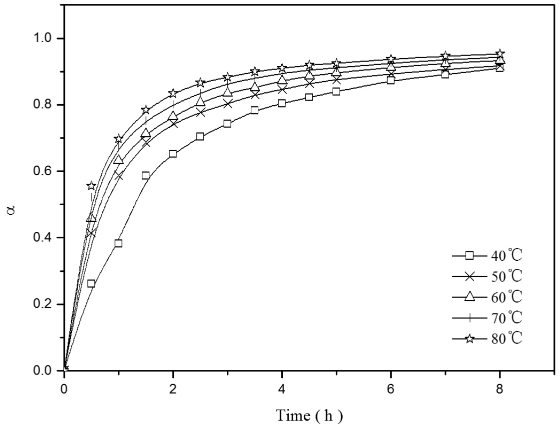


Figure 7. Conversion-time curves of the H-IPNs systems with 20 wt % H_{41} at different temperatures.

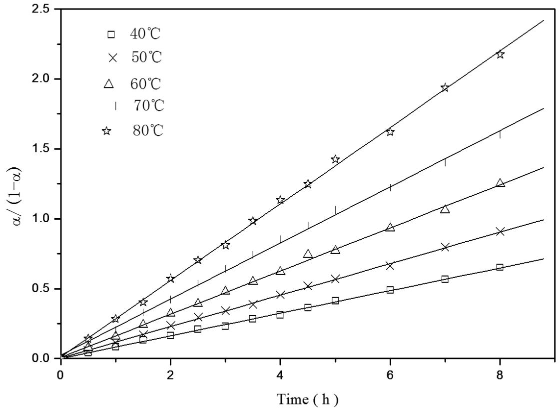


Figure 8. Plots of α/(1- α) - t for control sample at different temperatures.

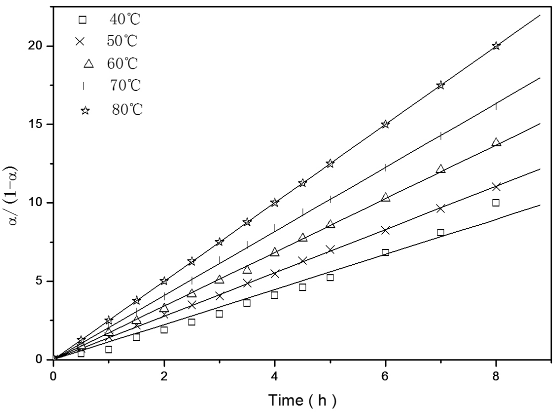


Figure 9. Plots of α/(1- α) - t for H-IPNs with 20 wt % H_{41} at different temperatures.

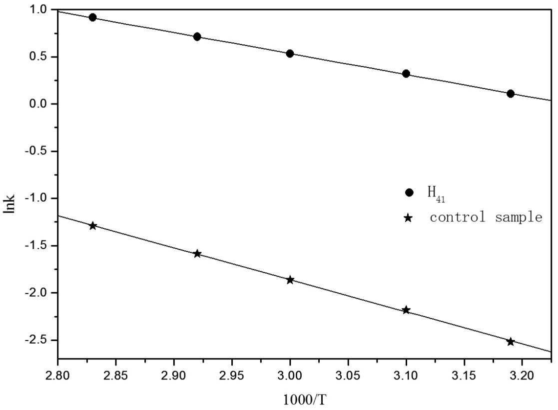


Figure 10. Plots of lnk - 1000/ T for the H-IPNs systems and the control sample.

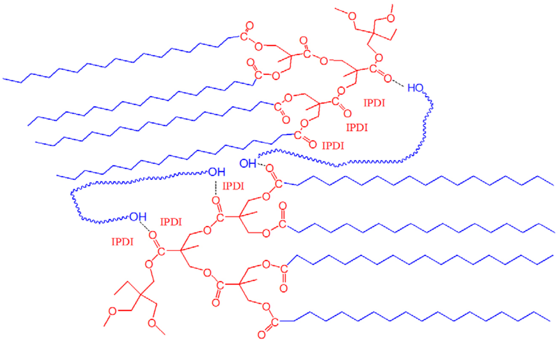


Figure 11. The compatibility between SHPE, HTPB and IPDI (In which 〰 stand for main chain of HTPB).

capping part caused by the stearic acid. The basic repeat unit of the shell is —CH_2— (calculated solubility parameter is 17.5 $(J/cm^3)^{1/2}$). The calculated solubility parameters of IPDI (21.8 $(J/cm^3)^{1/2}$) and HTPB (17.6 $(J/cm^3)^{1/2}$) are separately, close to the "core" and "shell" respectively. As a result the "core" and "shell" part would rich in IPDI and HTPB respectively. At the same time the end-groups of HTPB consist of hydroxyl groups, so inter-molecular H-bonds will easily be developed between hydroxyls in HTPB and carbonyls in the "core" part of SBPE. Hence the "core" is also rich in the -OH groups of HTPB. As Figure 11 shows, the "core" part of SHPE supplied reaction points between -OH and -NCO, and the local concentrations of -NCO and -OH were higher than other places, so the reaction rate increased. By contrast, AHPE does not possess this kind of core-shell structure, and thus it did not catalyze the reaction between IPDI and HTPB.

4. Conclusions

The curing kinetics of pure HTPB-PU and various H-IPNs were determined by FTIR. The results indicated that the existence of AHPE in H-IPNs did not influence the reaction between HTPB and IPDI, however, the existence of SHPE in H-IPNs had a catalytic effect on the reaction between HTPB and IPDI. The neat HTPB-PU and H-IPNs with SHPE are all followed a second-order kinetic mechanism. Their activation energies were 28.2 kJ/mol and 18.5 kJ/mol, respectively. The decrease of activation energy may be due to the SHPE having an amphiphilic structure which could compatibilize the HTPB and IPDI.

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