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Synthesis and Properties of Polyurethane Resins from Liquefied Benzylated Wood

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Abstract: In this paper, polyurethane resins were synthesized from liquefied benzylated wood and TDI (toluene diisocyanate)-TMP (trihydromethylene propane) prepolymer. And the relation between microphase structure and properties of PU samples were also studied. The results indicated that coatings obtained had good mechanical and thermal properties. The amount of the curing agent has great effect on the degree of phase segregation. In addition, with increased the curing agent amount, the thermal stabilities were also improved.

Keywords: Prepolymer, phase segragation, thermal history.

Recently, much attention had been paid on utilizing reproducible resources economically and developing new materials for polyurethane (PU) industry. Many researchers have contributed to preparing PU resins using waste paper and other cellulosic materials as polyols[1-3]. As reported, using wood solution with polyols and phenols as liquefying reagent is one of the methods[4]. These works will be potentially valuable for PU industry.

Compared to the conventional PU, the differences of wood cellulosic materials and polyether in structure inevitably lead to differences of the microphase stucture and other properties of PU. Therefore, systematic studies on the relation between microphase structure and properties of PU with wood cellulosic materials become very important. In this paper, PU samples with benzylated wood solution and TDI (toluene diisocyanate)-TMP (trihydromethylene propane) prepolymer were synthesized, and a novel environmental-friendly reagent-dibasic esters (DBE) without hydroxyl was employed as wood liquefaction reagent. The influence of the curing agent amount on segment structure, phase segregation and thermal stabilities were also systematically studied

Experimental

The benzylated wood and wood solution is prepared according to in our previous work[5]. Dibasic esters (DBE) and TDI-TMP prepolymer all from Tianjin Beacon Paint &

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Coatings Co., Ltd, P.R.China,Butylacete Tianjin Tianhe reagent Co., Ltd, P.R. China.

Synthesis of Polyurethane Resins

40 g wood solution and 0.65 wt% catalyst (dibutyltin dilaurate) were charged into a reactor, stirred for 30 min at 50 ℃. Then the curing agent TDI-TMP prepolymer was added. The whole mixture was stirred for 30 min at 50℃, then cooled to room temperature.

Measurements

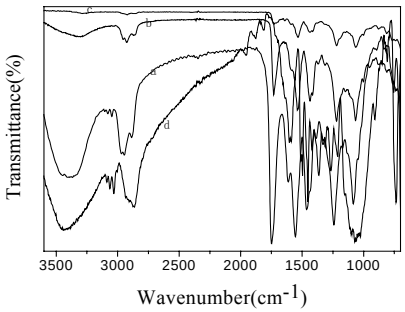
Polyurethane resins samples were analyzed by FT-IR, DSC, TG, DTA and SEM. IR spectra were recorded on a BIO-BAD EXALIBUR FTS-3000 Fourier transform spectrometer using the KBr pellet method for transmittance measurements. DSC were carried out on a NETZSCH DSC 204 at a heating rate of 10℃/min^{-1}, over a temperature range of –100℃~250℃, under N_2 atmosphere. TG and DTA analysis were carried out a thermal gravimetric analyzer (TA instrument ZRY-ZP), and samples with weight of about 10 mg were tested at a programmed rate of 10℃/min from room temperature to 600℃. SEM was conducted by a Philips XL-3 scanning microscope.

Results and Discussion

Influence of curing agent amount on segment structure of PU samples

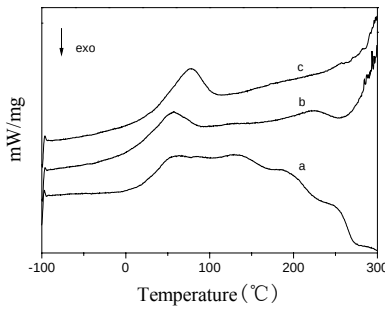
Figure 1 presents FT-IR spectra of benzylated wood and PU samples. As shown in **Figure 1**, as curing agent content was increased, the intensity of hydroxyl characteristic peaks became weak, and finally disappeared. Also, characteristic peaks of NH were detected, γ NH (3352-3298 cm^{-1}) and δ NH (1540-1530 cm^{-1}). It proved that urethane were formed between hydroxyl in benzylated wood power and NCO in prepolymer. In addition, it is interesting to note that the characteristic NH groups of these PU samples absorb at a higher frequency with a higher curing agent content.

Figure 1 FT-IR spectra of benzylated wood and polyurethane samples with different curing agent content



(a) 23.8 %; (b) 53.5 %; (c) 69.9 %
(d) benzylated wood powder

Figure 2 DSC of polyurethane with different curing agent content



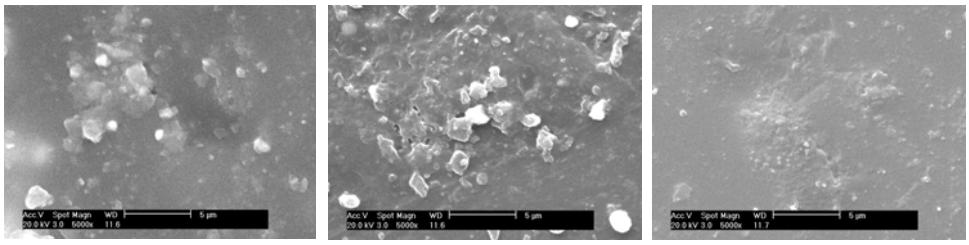
(a) 23.8 %; (b) 53.5 %; (c) 69.9 %

Influence of the content of curing agent on the glass temperature transition (T_g) of polyurethane

Figure 2 shows the DSC curves of PU samples with different curing agent content. As shown in **Figure 2**, no obvious glass transition for each soft and hard segment in PU were detected. This proved that phase mixing in this system was good. Therefore, we considered the transition with a temperature range of 0-100℃ as glass transition of PU system and defined top temperature of these peaks as glass transition temperature. Also from **Figure 2**, it is obvious that, with the curing agent content increased from 23.8 % to 69.9 %, the glass transition temperature increased from 53.5 ℃ to 77 ℃. And the PU sample (69.9 %) has the best mechanical properties as tested among the three[6].

Influence of the content of curing agent on microphase structure of PU samples

Figure 3 SEM photos of polyurethane films with different content of curing agent



(a) (b) (c)

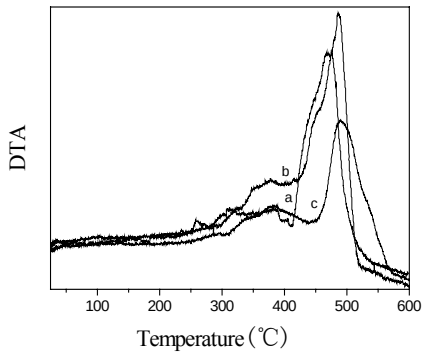
(a) 23.8 %; (b) 53.5 %; (c) 69.9 %

Figure 3 shows SEM photos of PU films with different content of the curing agent. **Figure 3** showed that increase of the amount of curing agent from 23.8 % to 53.5 %, the degree of phase segregation increased accordingly. But when the content of curing agent increased to 69.9 %, no obvious phase segregation was detected. In this process, PU continuous phase transition occurred from soft segments to hard segments. Also, after phase transition, the mechanical properties were greatly improved.

Thermal stabilities of PU samples

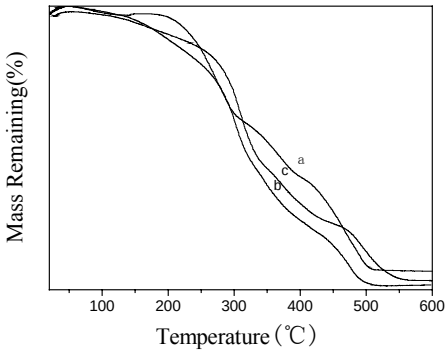
As shown in **Figure 4**, the decomposition of PU samples proceeds in about two stages. The first part of the degradation correlates with the hard segment, while the second peak correlates with the soft one. **Figure 4** and **Figure 5** showed that the onset degradation temperatures of PU samples synthesized from wood solution are all higher than 250 ℃. These results indicated that PU from wood solution has better thermal stabilities than the conventional ones. With the increase of the content of curing agent, the onset degradation temperature of PU samples also increases.

Figure 4 DTA of polyurethane with different content of cuing agent



(a) 23.8 %; (b) 53.5 %; (c) 69.9 %

Figure 5 TG of polyurethane with different content of curing agent



(a) 23.8 %; (b) 53.5 %; (c) 69.9 %

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References and Notes

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6. PU sample (69.9%) have the best properties according to the results of Tianjin Beacon Paint & Coatings Co., Ltd, China. The film' s technological index as following, impact resistance is no less than 50kg·cm; adhesion is rating Ⅰ; Pencil hardness is 3H, and resistance to different liquids (including 10% NaOH, 10%H_2SO_4, 10% NH_4OH) in 24 h.

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