Synthesis and Properties of Polyurethane Resins Based on Liquefied Wood

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ABSTRACT: Three polyurethane resins were synthesized from liquefied wood and three diisocyanates, i.e., TDI, IPDI, and HDI. The liquefied wood was obtained by the liquefaction of benzylated wood wastes using Dibasic esters (DBE) as solvent with hydrochloric acid as catalyst for 3 h, at 80°C. The thermal stability and microphase morphology of polyurethane films were investigated by TG, DSC, WAXD, and SEM methods. The experimental results indicated that polyurethane resins from liquefied wood had higher thermal stability than traditional ones, and the special structure and the difference of chemical structure of diisocyanates resulted in the crytallinity and microphase separation of obtained polyurethanes. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 351–356, 2004

Key words: DBE; liquefied benzylated wood; microphase morphology

INTRODUCTION

Recently, some efforts have been made to produce the low-cost raw materials for the polyurethane (PU) industry. Liquefaction of renewable biomass resources is one of the effective approaches available currently. This method is based on the fact that the products of liquefied wood can be used as polyols to prepare PU resin, and the resultant PU films have better mechanical properties. So, this technology may solve current resource shortage. In addition, the obtained PU materials can be biodegradable. Therefore, liquefaction of wood waste would have great potential to supply raw materials for the PU industry.

However, most of the recent studies mainly concentrated on polyols as liquefying reagent.[1–3] It is hard to clarify whether wood structure acts as the polyols component or only as the filler in preparation of PU. Although PU adhesives have been successfully synthesized from liquefied wood and polymethylene polyacryl polyisocyanate (PAPI), their mechanical properties were nearly close to the Chinese National Standard, however, toluene was used in this process of liquefaction[4]. This inevitably caused organic solvent pollution in PU industry. In this view, a novel and effective liquefying reagent named dibasic ester (DBE) was employed. As reported in the literature,[5] DBE is an ideal environmentally friendly solvent with lower toxicity and biodegradation, and today it has been extensively used in the coating industry. Furthermore, liquefied benzylated wood (BW) obtained in this way has no residue and the PU resins synthesized from that and three types of diisocyanates have good thermal stabilities and other properties compared to traditional ones. In addition, the microphrase morphology and separation of PU resins were also studied due to their special soft-hard segment structure.

Experimental

Materials and reagents

The BW in this study is prepared according to the method described in our previous paper[6]. Hydrochloric acid (Tianjin Chemical Reagent Co., Ltd, P.R. China), DBE (Tianjin Beacon Paint and Coatings Co., Ltd, P.R. China), and three types of diisocyanate (toluene diisocyanate [TDI], isophorone diisocyanate [IPDI], and hexamethylene diisocyanate [HDI]; all purchased from Changzhou Tianyi Chemical Co., Ltd, Jiangsu Province, P.R. China) were of reagent grade and were used without further purification.

Liquefaction of BW

BW, liquefying reagent, and catalyst were put into a 100-mL three-flask reactor with a stirrer, condenser, and thermometer in the ratio of 1 g : 3 g : 0.1 mL. The reaction was carried out at 75~80°C in the oil bath. After the desired time, about 3 h, the reactant products were filtrated and the filtrate was obtained as materials for the preparation of PU.

Synthesis of PU resins

PU resins were synthesized in the equipment used for liquefaction mentioned above. First, the liquefied wood and plastisizer were put into the reactor and stirred for about 30 min at 50°C. Thus definite amounts of diisocyanate and corresponding butylacetate premixed thoroughly were added gradually and kept the temperature at 50°C. After that, an amount of catalyst was added quickly. The whole mixture was kept stirring for 30 min at this temperature and then raised to 75–80°C. Polymerization proceeded for about 3 h. Finally, the PU resins were obtained. The basic recipes used for the preparation of PU resins are listed in Table I.

FT-IR and ^{13}C-NMR analysis

PU resin samples from liquefied benzylated cellulose were analyzed by using a Fourier transform infrared (FT-IR) spectrometer. IR spectra were recorded on a BIO-RAD EXALIBUR FTS-3000 Fourier transform spectrometer. Transmittance measurements were conducted by using the KBr pellet method.

^{13}C-NMR spectra of PU resins samples from liquefied benzylated cellulose dissolved in deuterated DMSO were recorded using a Varian Unity-Plus 400 spectrometer. Tetramethyl silane was used as an internal standard material. Measurement temperature and frequency were ambient temperature and 400.033 MHz, respectively.

Differential scanning calorimetry (DSC)

DSC measurements were carried out on a NETZSCH DSC 204 at a heating rate of 10°C/min$^{-1,}$ over a temperature range of –100°C~250°C and with sample weight about 10 mg under N_2 atmosphere.
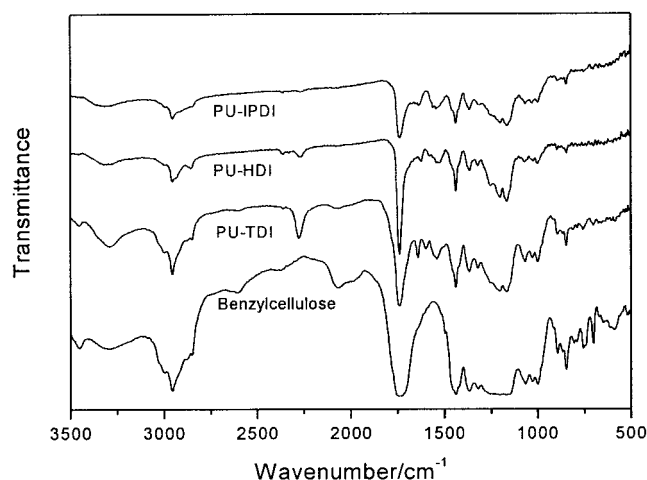
Wide angle X-ray diffraction (waxd)

The x-ray diffraction intensity was recorded as a function of diffraction angle, using a Model DMAX-RC diffraction with Cu K_α radiation. The PU films were

Figure 1 The IR spectra of liquefied benzylcellose and PU resins.

ground to powders and then packed tightly in the sample holder. X-ray diffraction patterns were recorded in the reflection mode in angular range 10–30° (2θ) at the ambient temperature by a BDX3300 diffractometer, operated at the CuK$_\alpha$ wavelength of 1.542 Å. The radiation from the anode, operating at 36 KV and 20 mA, was monochromized with a 15-μm nickel foil. The diffractometer was equipped with 1° divergence slit, a 16-mm beam bask, a 0.2-mm receiving slit, and a 1° scatter slit. Radiation was detected with a proportional detector.

Thermal gravimetric (TG) and differential thermal DTA analysis

A TG analyzer (TA instrument ZRY-ZP) was used to measure the thermal degradation of the PU resins. Samples with weight of about 10 mg were tested at a programmed rate of 10°C/min from room temperature to 600°C.

Scanning electron microscopy (SEM) observation

Observation of the films' morphology was conducted by using a Philips XL-3 scanning microscope. The samples were suspended in ethanol by ultrasonic and a suspension drop was mounted on the glass plates, dried to remove the ethanol, and then coated with a thin layer of gold in a vacuum.

RESULTS AND DISCUSSION

FT-IR and ^{13}C-NMR analysis

The FT-IR spectra of liquefied benzylated cellulose and the PU resin samples from it and three diisocyanates are shown in Figure 1. Due to the complexity of wood structure, including cellulose, semicellulose,
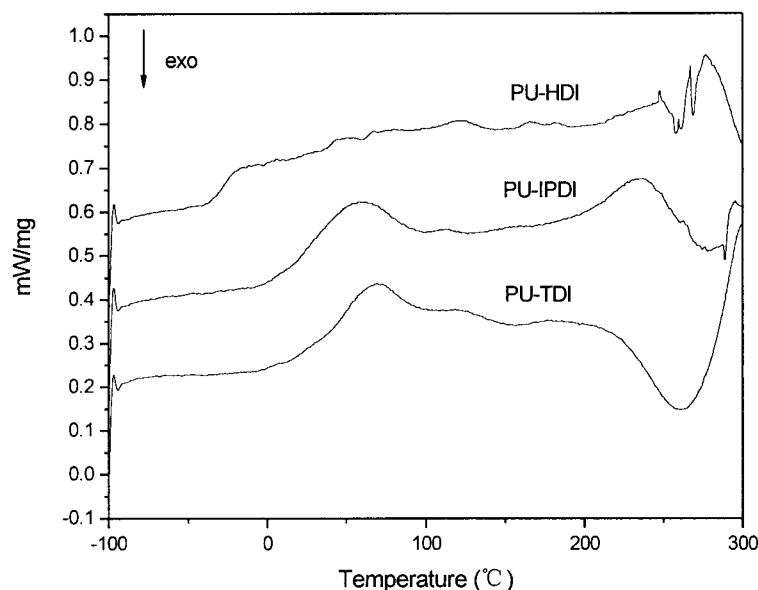
TABLE I
Basic Recipe Used for the Preparation of Polyurethane Resins

Sample	Ingredients[a]			
	Wood solution (g)	Plastisizer (g)	Diisocyanate (g)	Butylacetate (g)
PU-TDI	32	8	18.32	15
PU-IPDI	32	8	23.28	15
PU-HDI	32	8	18.90	15

[a] According to the measurement results of hydroxy number of liquefied wood in the previous method.[4]

Figure 2 The DSC of PU films with three different diisocyanates.

and lignin, it is hardly possible or impossible to conclude which type of hydroxyl can easily react with diisocyanate to format the urethane bonds. For ease in conducting the research, we selected cellulose as the object and liquefied and then copolymerized it with three diisocyanates.

As shown in Figure 1, the band at 1,733–1,739 cm^{-1} can be attributed to the stretching vibration of carbonyl groups, which may be from the N–H and C=O groups of urethane linkages or free C=O present in liquefying reagent DBE. The absorption bands at 1,539.710, 1,522.588, and 1,541.058cm^{-1} (δNH) show the characteristic linkages that were formed through the copolymerization of liquefied benzylated cellulose and diisocyanates. A band at 2,270 cm^{-1} was observed in all FT-IR spectra of three samples of different diisocyanates. This is the characteristic absorption band of the excess –NCO group. And the excess of –NCO directly resulted in the formation of allophanate or biuret crosslinkages. The bands at 1,640.228, 1,622.946, and 1,636.081 cm^{-1} can be attributed to the stretching vibration of carbonyl groups of allophanates corresponding to PU-TDI, PU-HDI, and PU-IPDI respectively.

In addition, the peaks near 154 ppm detected in the ^{13}C-NMR spectrum of three different PU resins from liquefied cellulose showed the formation of urethane linkages between the hydroxyl in cellulose and isocyanate. This further proved that cellulose could be used as polyols to prepare PU.

DSC analysis of pu films

The DSC scans of PU films prepared from liquefied BW and three diisocyanates are shown in Figure 3. It is expected that microphase separation of PU materials be first reflected in the thermal transition points. This may be based on the fact that two phases constituting the PU remain their seperate segment structure, so the glass transition temperature (T_g) or melting temperature (T_m) of their own can be detected in the DSC curves of segmented PU block copolymer. Therefore, DSC analysis plays an important role in the study of morphology of PU block polymer and has been employed extensively in investigating the extent of microphase compatibility of segments. But in our research system, wood component isn't the veritable soft segment comparing to the conventional polyols. For its special structure, it is hard to clarify the soft and hard segment in this system, therefore, by measuring the T_g of PU samples, can we estimate their microphase separation.

We could see from the Figure 2 that there were obvious changes in the DSC curves due to the different chemical structure of the three diisocyanates. The T_g of PU-TDI is about 28.6°C higher than other two, and no hard segment endotherm was observed in the DSC curves. These results indicated that the higher compatibility between wood component and diisocyanate and the lowest degree of crystallinity of hard segment for PU-TDI. But longer soft segments in HDI result in the lowest T_g, only –34.5°C. It indicates the highest degree of phase segregation for PU-HDI, i.e., the amount of solubilized hard segment in the soft segment phase would be small. In addition, due to the same reactivity of two NCO, the hard segment easily formed the hydrogen bonds to crystalline, and a hard segment endotherm appeared at 276.8°C. As for PU-IPDI, its higher degree asymmetric structure resulted in only microcrystalline or no crystalline. In summary
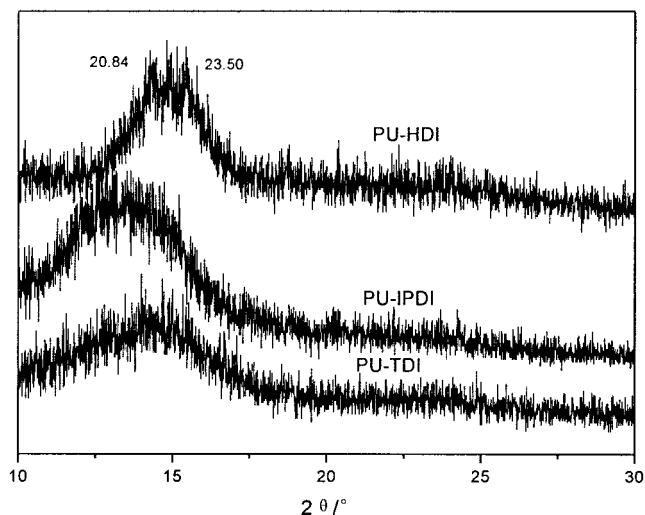
Figure 3 The X-ray diffraction spectra of three PU resins.

of these DSC data, we may draw the following order of degree of hard segment crystallinity: PU-HDI > PU-IPDI > PU-TDI. This result can be verified by the later X-ray diffraction analysis.

WAXD analysis

Figure 3 represents WAXD curves of PU films from liquefied BW and three different diisocyanates. All of the samples showed a rather broad center around a diffraction angle of about 20°. The WAXD curve of the PU-TDI sample, as shown in Figure 3, is very similar to that of PU-IPDI, which indicates that no crystallinity occurs or the amount of segment crystallinity is too small to produce the peaks in WAXD under the experimental conditions. But for the PU-HDI sample, a small extent of soft segment crystallinity is observed, as shown in Figure 3, and two small peaks at diffraction angles of 20.84 and 23.50 appear. The first is considered spurious, while the other is a crystallinity peak. This behavior is also reflected in the SEM photograph.

Thermal degradation of PU samples

The thermal stability of BW and PU samples is estimated from TG and DTA curves. Figures 4 and 5 are the plots of TG curves of BW and different PU samples. As shown in Figure 4, the thermal degradation of BW proceed in three steps, which is corresponding to the individual thermal degradation of wood constitution, with hemicellulose breaking down first at 163~209°C and the weight decrease by 23.62%, cellulose next at 274~324°C and the weight decrease by 42.23%, and then lignin at 441~461°C and the weight decrease by 9.73%. Comparing the three curves of PU samples, it is obvious that the three samples have the

similar weight loss tendency. As reflected in Figure 6, approximately two distinct regions of weight loss were observed for every DTA plot of PU sample. The first part of the degradation correlates with the diisocyanate component, while the second peak correlated with the degradation of cellulose in wood and plasticizer. However, the rates of change of other fragments that originated from hemicellulose and lignin were not clear since their weight loss region overlapped with that of other products in PU.

The temperature range in the initial stage appeared at from 280 to 320°C, as shown in Figure 5; among the starting degradation temperature of PU samples, the highest is PU-HDI with a starting degradation temperature of 294°C, PU-IPDI is 310°C, and PU-TDI is 289°C. These were higher than that of the BW, which is about 283.0°C. For example, the starting degradation temperature of PU-TDI is obviously higher than the traditional one, which is only about 245°C. This can be explained from two aspects, the diisocyanate mixing into liquefied wood and the crosslinkages thus formed between wood component and diiocyanate together caused the raise of the starting degradation temperature of wood; on the other hand, it is a general rule that the more easily formed urethanes are less stable, i.e., more easily dissociated than are the more difficult ones. In other words, the more reactive isocyanate is, the less stable urethanes are from it.[7] In terms of the reactivity, TDI is first, HDI is next, and IPDI is last. So it is obvious that the thermal stability of hard segments of these polyurethanes are the following order PU-IPDI > PU-HDI > PU-TDI. The second region (440~530°C), mainly attributed to the degradation of cellulose and other difficultly breaking parts, and also the isocyanurate generated by excess of isocyanate. In conclusion, owing to the special structure
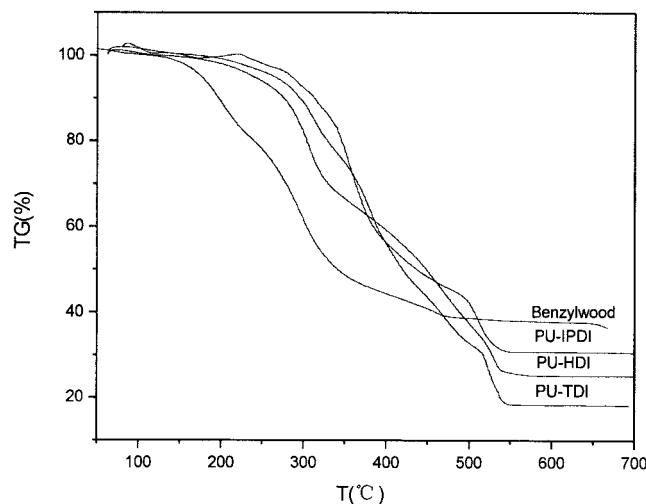

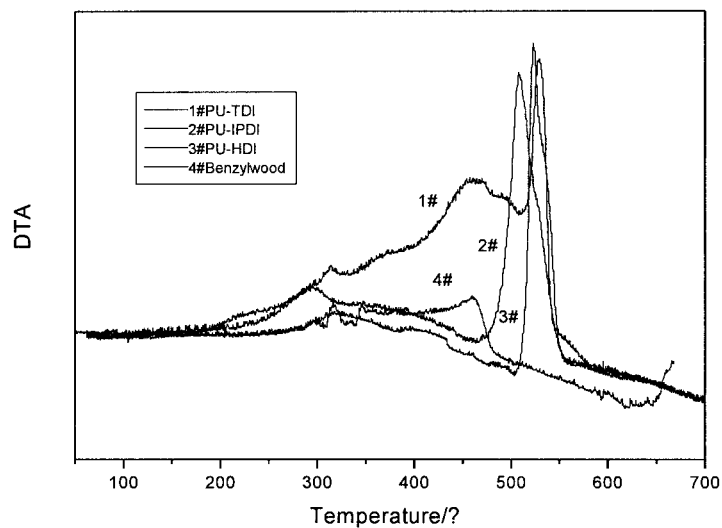**Figure 4** TG curves of BW and PU from diisocyanate and liquefied wood.

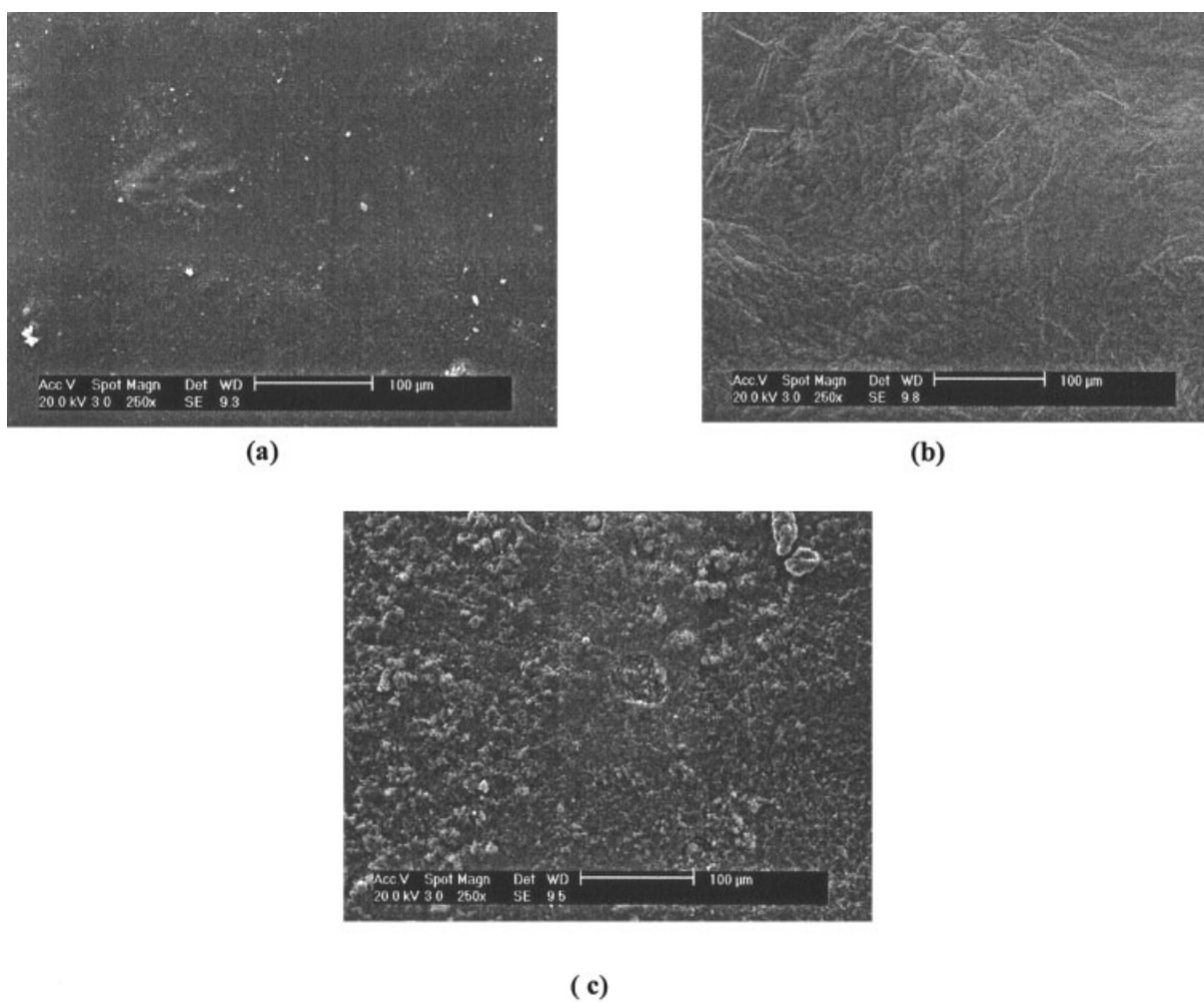**Figure 5** Plots of DTA curves for PU samples.

Figure 6 The SEM photograph of PU films from liquefied BW and different diiocyanates: (a) TDI; (b) IPDI; (c) HDI.

and plasticity of BW, PU resins from liquefied BW have higher stability than traditional ones.

SEM analysis

SEM analysis of PU films from liquefied BW showed the extent of film homogeneity and microphrase separation. From Figure 6, it is very clear that PU film from TDI as the isocyanate component has a more homogeneous surface then IPDI; the worst is HDI. And some microparticles were found on the surface of PU film from HDI. It is obvious that microphase separation occurred in this system. Comparing the chemical structure of these three diiscyanates, we may conclude that the results of DSC and WAXD analyses were reasonable. Among the three diisocyanates, HDI has a chemical structure of higher degree symmetry and, considering the system studied in which liquefied BW as polyols, didn't actually act as soft segment due to its special structure. On the contrary, HDI has six methylenes in moleculars; in this system it can serve as a traditional soft segment in PU. It is the structure of HDI that leads to formation of higher degree of intermolecular hydrogen bond and a higher degree of hard-soft segment phase separation. IPDI has a hexamethylene structure with higher degree asymmetry, and multiisomers exist. This results in better compability with the wood component. So, PU film surfaces from it were uniform. As for TDI, first, it has higher reactivity than other two, then, the presence of a –CH$_3$ side chain on the benzene ring seriously sterically hindered the formation of hard segment intermolecular hydrogen bonds. Thus, PU films from it have the lowest degree of hard segment crystallinity and the highest degree of soft and hard segment phase mixing. As seen from the Figure 6(a), the film was completely homogenous; the little spots may be caused by ambient pollution. All other properties were better than PU-IPDI and PU-HDI.

CONCLUSION

In the present work, a novel and effective liquefying reagent was employed for the liquefaction of BW wastes. And three PUs, i.e., PU-TDI, PU-IPDI, and PU-HDI, were synthesized from wood waste solutions and three diisocyanates, i.e., TDI, IPDI, and HDI, respectively. The TG and DTA analysis indicated that PUs prepared from liquefied wood wastes had higher thermal stability than conventional ones, and, owing to the different chemical structure of three diisocyanates, PU-IPDI synthesized from alicyclic isocyanate, PU-HDI from aliphatic isocyanate, and PU-TDI from aryl isocyanate, their thermal stability follows an order of PU-IPDI > PU-HDI > PU-TDI. The DSC, WAXD, and SEM data revealed that PU-HDI had the highest degree of hard segment crystallinity and lowest hard and soft segment interphase mixing, while PU-TDI had the lowest degree of hard segment crystallinity but the highest degree of hard and soft segment interphase mixing. In terms of these, PU-IPDI was located between PU-TDI and PU-HDI. Considering the mechanical and surface properties of PU films obtained above and requirements for the painting industry, in the process of utilizing the wood wastes to produce PU materials, TDI was selected first, then IPDI, while HDI is not suitable for this system.

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