Thermal properties and micromorphology of polyurethane resins based on liquefied benzylated wood

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Received 09 September 2004; accepted 25 April 2005

Liquefied benzylated wood based Polyurethanes (PUs) are synthesized with excess toluene diisocyanate (TDI), isophorone diisocyanate (IPDI) and hexamethylene diisocyanate (HDI). Four polyethylene glycols (PEG) of molecular weight 400, 600, 1000 and 2000 are mixed with liquefied wood using dibasic ester (DBE) as liquefaction reagent to incorporate different proportions of soft segment into the network prior to crosslinking with TDI. By differential scanning calorimetry, thermogravimetry, wide angle X-ray diffraction and SEM analysis, thermal properties and micromorphology of PU samples are investigated. Results indicated that molecular weight of the PEG had only a minor effect on glass transition temperature ($T_g$) of PU samples, but diisocyanates had major effects. The $T_g$ of HDI-based PU network was –25°C lower than that of TDI (40°C) and IPDI (28.6°C). From SEM analysis, TDI, IPDI-based films have better phase-mixing properties than HDI-based PU. All the films had greater thermal stability than conventional PU films based on polyether or polyester alone.

Keywords: Polyurethane, Liquefied benzylated wood, Glass transition temperature, Phase separation

IPC Code: C02G18/02

Introduction

Much research has been carried out on the synthesis of polymers from renewable resources because of the widely fluctuating cost of petroleum oil. Derivatives of carbohydrates have been particularly utilized as the polyol components of versatile polyurethane (PU) materials. Also, various PU materials have been synthesized from liquefied wood using polyhydric alcohols as liquefaction reagent\textsuperscript{1-3}. These studies show the potential of wood waste as raw materials for PU.

Kurimoto \textit{et al}\textsuperscript{2} observed that polyethylene glycol (PEG) was liquefied reagent and the content of woody component in PU was limited (9.6-29.8 %), but whether wood component could act as filler or reactive polyols was not certain. In other studies\textsuperscript{4,5}, where environmental-friendly dibasic ester (DBE) was first employed as wood liquefaction reagent instead of polyols, authors have successfully synthesized PU with liquefied benzylated wood and different diisocyanate (DI) and investigated the interaction of hydroxyls in wood and toluene diisocyanate (TDI), isophorone diisocyanate (IPDI) and hexamethylene diisocyanate (HDI).

In conventional linear PUs, polyester or polyether of low glass transition temperature form soft segments in PUs, while DI with chain extender comprise the hard segments. Hard block domain formed from hard segments gives the mechanical strength and high thermal properties PU, whereas soft segments give elasticity\textsuperscript{6}. Wood can easily form networks in PU because of its multiple hydroxyls. As a component of PU systems, liquefied wood was found to act both as a network former (due to its comparatively high functionality) and as a part of the hard segment (due to generally stiff nature of the pyranose and lignin aromatic rings in wood). So, systematic studies on the relationship between segment structure and properties become very important.

This paper examines the effect of different segments of PU resins from liquefied wood on thermal properties. Also, the micromorphology of PU samples with different DI are investigated.

Experimental Details

Benzyalted wood meal was prepared according to the method described earlier\textsuperscript{7}. DBE was provided by Tianjin Beacon Paint & Coatings Co. Ltd, China. PEG (mole wt, 400, 600, 1000, 2000) was obtained from Tianjin Tiantai Fine Chemical Product Co. Ltd,

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China. TDI, IPDI and HDI were purchased from Changzhou Tianyi Chemical Co. Ltd, Jiangsu Province, China.

**Liquefaction of Benzylated Wood**

Benzylated wood meal (WPG 75-80 %), catalyst (HCl) and liquefaction reagents (DBEs) in the ratio of 1g/3g/0.1 ml were charged into a reactor with stirrer, condenser and thermometer. The liquefying reaction was conducted at 75-80°C in oil bath for 3 h and the product was filtrated.

**Synthesis of Polyurethane Resins**

Wood solution (32 g) with certain amount of PEG was charged into a reactor used for wood liquefaction and stirred for 30 min at 50°C. Then the mixture of butylacetate (15 g), charged DI and catalyst dibutyltin dilaurate (0.4 wt %) was added. The whole mixture was stirred for 30 min at 50°C, and then heated to 75-80°C for 3 h.

**Differential Scanning Calorimetry (DSC) Analysis**

DSC measurement were carried out on a NETZSCH DSC 204 at a heating rate of 10°C/min, over a temp range of −100-250°C and a sample weight of about 10 mg. It was cooled by liquid N2.

**TG and DTA Analysis**

A thermal gravimetric analyzer (TGA instrument ZRY-ZP) measured the thermal degradation of the PU resins. Samples (~10 mg) were run at a heating rate of 10°C/min from ambient to 600°C in air.

**Wide Angle X-Ray Diffraction (WAXD)**

X-ray diffraction intensity was recorded as a function of diffraction angle, using a Model DMAX-RC with CuKα radiation. PU film powders were packed tightly in the sample holder. X-ray diffraction patterns were recorded in the reflection mode in angular range of 10-30°(2θ) at ambient temperature by a BDX3300 diffractometer, operated at CuKα wavelength (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.

**Scanning Electron Microscopy Observation**

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

**Results and Discussion**

**Effect of Soft Segments on the Thermal Properties of PU samples**

DSC curves of four PUs with various weight molecular PEG 400 (same amount) and TDI have no obvious distinctions (Fig. 1). Glass transitions originated from the PEG phase were not observed. This implies that little or no phase separation of PEG component occurs.

There are approx three temperature stages in every DSC curve (Fig. 1, Table 1). The endotherm of region-I around 45-75°C may be resulted from the break-up of short-range order of the hard segments induced by room temperature annealing. The endotherm around 80-150°C (region-II) corresponded to the disruption of long-range order of hard segment. The endotherm around 175-250°C (region-III) corresponded to the melting of microcrystalline hard segments. Also, at this temperature range, either decomposition of unstable biurets and allophanates could occur or the H-bond of hard segment bonded near the multifunctional liquefied component and...
urethanes may be broken. These results suggest that molecular weight of soft segment-PEG had no pronounced effect on thermal properties of PU samples.

**Effect of Hard Segments on the Thermal Properties of PU samples**

In the plots of nonisothermal DSC scanning curves for PU-TDI, PU-IPDI and PU-HDI under air atmosphere (Fig. 2), there were obvious changes in the appearance of the DSC curves around the glass transition. All the three PU samples were prepared from the same amount of soft segments (PEG 400). $T_g$ of HDI-based films is –25°C lower than that of TDI (40°C) and IPDI (28.6°C). These results indicated that the extents of soft and hard segments phase mixing of TDI and IPDI based films were better than that of HDI, which has lowest $T_g$ in the three films because of the segmental hexamethylene contribution. Compared with the conventional PU made from linear polyether, the incorporation of liquefied wood with multiple hydroxyls into PU directly resulted in more cross link points. Also, this can be supported by $^{13}$C-NMR Spectrum of PU resins made with three DIs and benzylated lignocellulose. Therefore, more energy may be required to initiate chain movements. Moreover, the cross links may immobilize the chains to some extent and either prevent or reduce the aggregation of the hard segments into domains. Also, the cross links can make hard segments disperse in the continuous soft segments.

Two peaks appeared in the curve of benzylated wood (Fig. 3, Table 2), the first part of the degradation correlates with the breaking of semi cellulose, cellulose and added benzyl groups, while the second peak correlates with lignin. The decomposition of PU samples occurred approx in two steps (Figs 3 & 4), the peaks around 280-320°C might correspond to volatile compounds in liquefied wood (such as liquefaction reagent dibasic ester-DBE). The disruption of the urethane bonds causing decomposition of hard segments may contribute to this part. If the onset degradation temperature ($T_{1on}$)
was taken as the criterion of stability, three PU films have greater thermal stabilities (degrading at above 280°C) than conventional ones (<250°C), and IPDI- and HDI-based films had better stability than that of TDI (Table 2). The incorporation of multifunctional liquefied wood component into PU resulted in formation of crosslink networks, and a higher stability than most of the PU based on the polyether or polyester alone.

The peaks around 500-550°C could be attributed to the decomposition of soft segments of PU samples. The onset decomposition temperatures of these peaks ($T_{2on}$) were all higher than conventional ones (300-400°C). The decomposition of PEG could contribute to the part, and liquefaction reagent-DBE can interact with PEG by transesterification. Also, the formation of alcohol-D-glycosides between the liquefied wood components and PEG also caused the high decomposition temperature of soft segment. The formation of crosslink networks between hard segments and soft segments may greatly restrict the movement of soft segments.

**WAXD Analysis**

WAXD curves of PU films made from liquefied benzylated wood, PEG-400 and three different DIs showed a rather broad centered around a diffraction angle of about 20°C (Fig. 5). The WAXD curve of PU-TDI sample was very similar to that of PU-IPDI, which indicated either no crystallinity occurred or the amount of segment crystallinity was too small to produce the peaks in WAXD under the experimental condition. But for PU-HDI sample, a small extent of soft segment crystallinity was observed; two small peaks at diffraction angles of 20.84 and 23.50 appear, the first was considered semicrystallinity peak, while the other was microcrystallinity peak. This phenomenon was also reflected in the SEM photographs (Fig. 6).

**SEM Analysis**

TDI-based films has more homogeneous surface than HDI (Fig. 6). Some micro-particles were found at the surface of HDI-based film, and in zoomed photo part of areas were predominated by amorphous domains. It was obvious that microphase separation occurred in this system. These phenomena were in consistent with the results of DSC and WAXD analyses. This may be attributed to the incompatibility between liquefied wood and HDI due to their different structure. TDI-based films had higher reactivity than other two, because the steric presence of -CH$_3$ side chain on the benzene ring hindered the formation of hard segment intermolecular hydrogen bond. Also, TDI-based films have good mechanical properties as per the results of Tianjin Beacon Paint & Coatings Co. Ltd, China. Impact resistance of the films is not less than 50 kg·cm, adhesion rating is II; pencil hardness is 2H, resistance to different liquids.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{1on}$ °C</th>
<th>$T_{1max}$ °C</th>
<th>$T_{2on}$ °C</th>
<th>$T_{2max}$ °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzyl-wood</td>
<td>283.0</td>
<td>296.0</td>
<td>423.0</td>
<td>460.0</td>
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<tr>
<td>PU-TDI</td>
<td>289.0</td>
<td>314.0</td>
<td>502.0</td>
<td>529.0</td>
</tr>
<tr>
<td>PU-IPDI</td>
<td>310.0</td>
<td>316.0</td>
<td>494.0</td>
<td>508.0</td>
</tr>
<tr>
<td>PU-HDI</td>
<td>294.0</td>
<td>317.0</td>
<td>515.0</td>
<td>523.0</td>
</tr>
</tbody>
</table>
Conclusions

The incorporation of multifunctional liquefied wood endowed three PU films with better thermal stability (280°C) than the conventional ones (<250°C). The types of DI can affect thermal properties of PU films. Glass transition temperatures of TDI and IPDI-based films were higher than HDI. But molecular weight selected of soft segment-PEG had no pronounced effect on thermal properties. SEM showed that TDI and IPDI-based films had a more homogeneous surface than HDI-based PU. WAXD showed that small amount of microcrystalline existed in hard microdomain of HDI-based film.

References