

Synthesis and Characterization of Polyurethane/Poly (Urethane Modified Bismaleimide-Bismaleimide) IPNs

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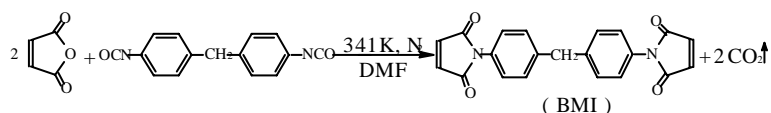
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Abstract: PU/P(UBMI-BMI) IPNs with excellent thermal stability and mechanical properties were synthesized and characterized. The interpenetrating occurs in the hard segment domains of PU, which leads to enhancement of hydrogen bonding of N-H, and narrow-distributed small size of the dispersed phase.

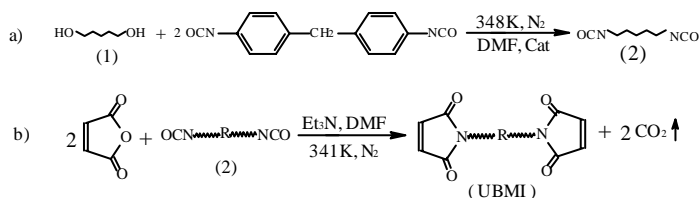
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The method of blending by interpenetrating polymer networks (IPNs) is often used to obtain elastomers with properties in excess of those exhibited by traditional blending ways¹. In this paper, a series of novel polyurethane/poly (urethane modified bismaleimide-bismaleimide) (PU/P(UBMI-BMI)) IPNs were synthesized and characterized by ¹HNMR, FTIR, TEM, and TGA analysis.

BMI was synthesized as follows:



UBMI was introduced to modify the compatibility of the two networks, which was synthesized as follows:



Where (1) is hydroxyl-terminated poly (diethylene adipate) glycol ($M_n=1440$, $I_a=0.38$) and (2) is isocyanate-terminated prepolymer.

FTIR spectra of monomers show that the absorption at 2270cm^{-1} ($\nu(\text{NCO})$) and at 1840cm^{-1} ($\nu(\text{C}=\text{O})$ in maleic anhydride) disappeared, and strong absorption at 1780cm^{-1} ($\nu(\text{C}=\text{O})$ in maleimide) and 1170cm^{-1} ($\nu(\text{C}-\text{N}-\text{C})$ in maleimide) were observed^{2,3}.

¹HNMR results of BMI and UBMI show that the experimental proton chemical shifts and its peak areas are fundamentally consistent with the calculated values⁴.

PU/P(UBMI-BMI) IPNs were synthesized *via* two steps. First, BMI and UBMI in DMF pre-polymerized at 120°C until the viscosity was obviously increased before gel formation, dicumyl peroxide was used as initiator. Then, 2,4-TDI, 1,4-butanediol, trimethylol propane and poly(diethylene adipate) glycol was added. The mixture was cast into a PTFE mold. The solvent was evaporated in a vacuum at 60°C and then maintained at 120°C for 15 hours and postcured at 180°C for 1 hour, demolded after cooling. The weight fraction of P(UBMI-BMI) in PU/P(UBMI-BMI) IPNs is 20 wt.%.

FTIR spectra of PU/P(UBMI-BMI) IPNs show that $\nu(\text{C-N-C})$ in maleimide shifts to 1172 cm^{-1} , different from that in the net bismaleimide resins (at 1187 cm^{-1}). Another interesting observation is that the relative intensity of hydrogen-bonded N-H stretching was increased dramatically and the frequency was observed at 3325 cm^{-1} for PU/P(UBMI-BMI) IPNs with UBMI/BMI=40/60, which at 3337 cm^{-1} for net crosslinked PU, suggesting the hydrogen bonding of N-H was enhanced^{2,3}.

TEM photographs show that interpenetrating occurs in the hard segment domains of PU, causing narrow-distributed and small size of the disperse phase. The average dispersed phase domains of PU/P(UBMI-BMI) IPNs with UBMI/BMI=60/40 is only 31 nm, far smaller than that of net PU (1174 nm).

Bismaleimide resins are crosslinked polymers with excellent thermal stability and mechanical strength⁵. Due to the synergistic deformation and thermal response, relative small fraction of P(UBMI-BMI) dramatically improves the thermal stability and mechanical properties. The pyrolysis of PU/P(UBMI-BMI) IPNs with UBMI/BMI=40/60 starts at 262.4°C, 30°C higher than that of net crosslinked PU (230.7°C). The tensile strength and toughness are also largely improved by interlocking of P(UBMI-BMI) networks and hard segment of PU. This will be reported in a future paper.

References

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