

PROPERTIES OF BLOCKED POLYURETHANE/PHENOLIC INTERPENETRATING POLYMER NETWORK COMPOSITES

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Introduction

Interpenetrating polymer network (IPN) are a special class of polymer blends in which the polymers are crosslinked [1]. These materials are characterized by the presence of two networks strongly entangled ideally only by topological constraints [2]. Interpenetrating polymerization is a mode of blending two polymers to produce a mixture in which phase separation is not as extensive as it would be otherwise [3]. IPN synthesized so far exhibit various degrees of phase separation depending mainly on the miscibility of polymers [4]. It is often important to know the morphology of multicomponent polymer systems, and the factors influencing it, since phase domain size and shape, interfacial bonding and phase connectivity determine the physical, mechanical and thermal properties of such materials [5]. With highly incompatible polymers, the thermodynamic driving force phase separation is so powerful that gross phase separation occurs before gelation.

In this study, the simultaneous polymerization (SIN) method was used to synthesize the IPN of blocked polyurethane (BPU) and phenolic (PF). The BPU prepolymer with m-xylylenediamine (MXDA) as a chain extender and PF prepolymer using p-toluene sulfonic acid (PTSA) as a catalyst are mixed at room temperature, and reacted at elevated temperature. The paper is focused on the synthesized, morphology and mechanical properties of BPU/PF IPN system.

Experimental

Materials

A BPU prepolymer was prepared from toluene di-isocyanate (TDI-80, 80/20 blend of 2,4 and 2,6 isomers) and branched polyester at the NCO/OH equivalent ratio of 2/1, and then was blocked by ϵ -caprolactam, which supplied by the Bayer Co., Germany. It has a viscosity of 31000 mPa.s at 25°C, a weight-average molecular weight of 4230, and an equivalent weight of 1410. The chain extender of BPU used was m-Xylylenediamine (MXDA), supplied by the Epocone Chemical Co. Ltd., USA. It has a weight-average molecular weight of 136. The PF prepolymer used was resole PF 650 and was supplied by the ChangChun Plastics Co. Ltd., Taiwan. It has a viscosity of 200 mPa.s at 25°C, and a solid content of 60-64%. The catalyst of PF used was p-Toluene sulfonic acid (PTSA), which supplied by the ChangChun Plastics Co. Ltd., Taiwan. It has a specific gravity of 1.2.

Preparation of BPU/PF IPN samples

- (1) One equivalent of BPU prepolymer was heated to 50°C and then mixed with one equivalent of MXDA homogeneously. Then, the mixture was blended with PF prepolymer at 50°C and mixed with various BPU mixtures, and then mixed completely using a high torque stirrer.
- (2) The mixtures was molded in an ASTM standard stainless steel mold, the surfaces of the stainless steel mold have been treated by chrome plating.
- (3) The mixture of mold was cured in an oven for 3 hour and the temperature was maintained at 140°C.
- (4) Finally, the samples were removed from the mold and kept in a desiccator where the relative humidity was maintained at 50% for at least 2 days before they were tested.

Results and Discussion

Synthesis of BPU/PF IPN

Fig.1 shows the FTIR spectra of the reaction system of BPU and PF at various reaction times of 140°C. From the Fig.1, there was no absorption peak intensity of NCO at 2270 cm⁻¹ and having absorption peak intensity of OH at 1000 cm⁻¹ when the reaction started. After heating at 140°C for 3 min, the absorption peak of NCO of BPU at 2270 cm⁻¹ appeared. After heating at 140°C for 16 h, the absorption peak of NCO of BPU at 2270 cm⁻¹ and OH of PF at 1000 cm⁻¹ disappeared during the same time.

It was found that in the BPU/MXDA system, the absorption peak of NCO disappeared within 4 h. However, in BPU/PF system, it required 16 h for the absorption peak of NCO to disappear. Results indicated that the NCO group of BPU reacts slowly with the OH group of PF compared with the reaction between NCO group of BPU and NH₂ group of MXDA.

From the above FTIR spectrum analysis, it was also confirmed that in the BPU/MXDA/PF system, the major reactions are the polymerization of BPU/MXDA and the self-polymerization of PF.

Morphology

Fig.2 showed the scanning electron micrographs (SEM) of fracture surface of the pure PF and BPU and BPU/PF IPN at various BPU contents, respectively. From the figure (a), the pure PF expressed the smooth and glossy microstructure due to it was brittle materials. From the figure (f), the BPU exhibited the rough microstructure because it was ductile materials. From the figures (b) to (e), as the BPU content increased, the microstructure of

IPN became rougher. As the BPU content was above 50 wt%, the microstructure is very similar to that of the pure BPU component. It was found that the BPU was partially dissolved in the PF of the BPU/PF IPN. As the BPU content was above 50 wt% in the BPU/PF IPN, the microstructure was dominated by BPU network. It was obviously found that the BPU network and the PF network penetrated each other, there is an interpenetrating effect existing in the BPU/PF IPN. The compatibility of the both networks was improved. The morphology study showed that the IPN system was heterogeneous and more than one phase existed in the networks.

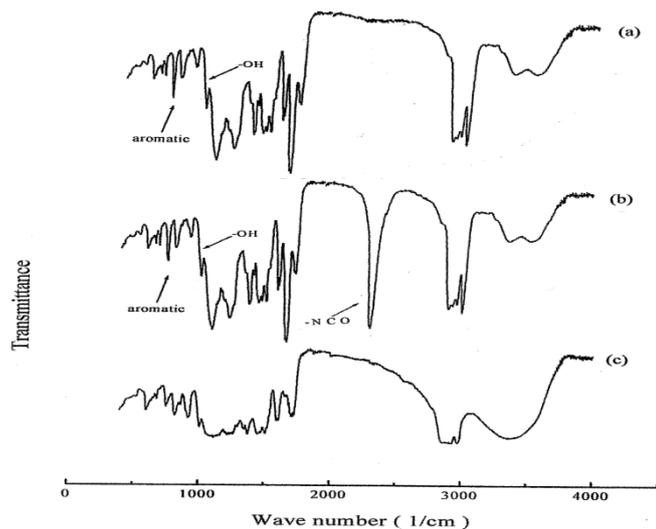


Fig.1 FTIR spectra of BPU/PF at (a) $t = 0$, (b) $t = 3$ min, (c) $t = 16$ h at a temperature of 140°C .

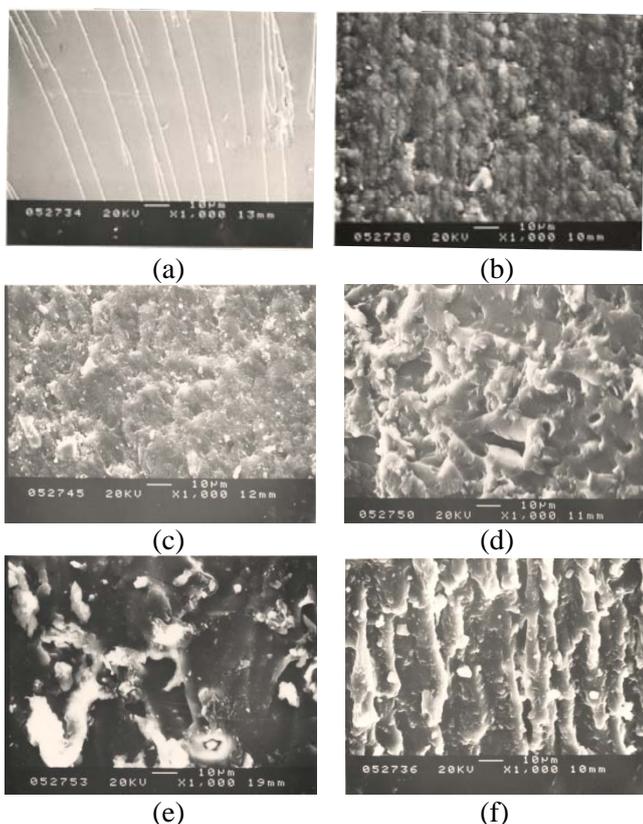


Fig.2 SEM fracture surface of the BPU/PF IPN compositions at (a) 0/100, (b) 15/85, (c) 25/75, (d) 50/50, (e) 75/25, (f) 100/0.

Mechanical properties

Fig.3 illustrated the tensile strength versus BPU content for unfilled and 10 phr filled (kaolin) of BPU/PF IPN. From this figure, it can be seen that the tensile strength decreased with increasing of BPU content. As expected, this can be explained that the hard segments of PF appeared to have higher strength and modulus properties, and the soft segments of BPU appeared to have lower strength and modulus properties; hence, the higher the BPU content, the lower the tensile properties of IPN.

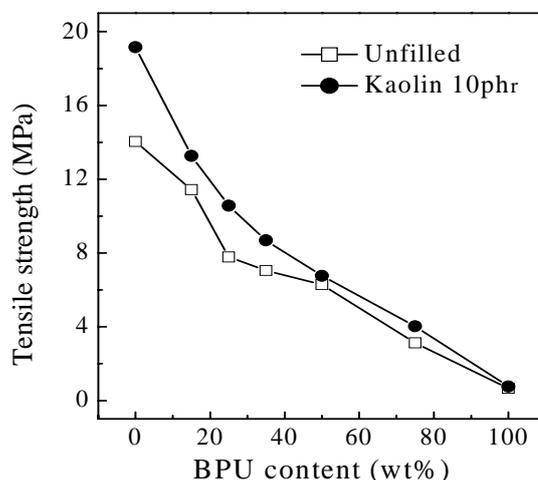


Fig.3 Tensile strength versus BPU content for unfilled and 10 phr filled (kaolin) of BPU/PF IPN.

Conclusion

From FTIR spectra analysis, it was found that the major reactions were polymerization of BPU/MXDA and the self-polymerization of PF in the BPU/PF IPN system. It was confirmed from scanning electron micrography (SEM) that the BPU/PF IPN compatibility of the both networks was improved, and the system was heterogeneous and more than one phase existed in the interpenetrating polymer network. The tensile strength of the BPU/PF IPN decreased with increasing of BPU contents.

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