

Preparation and Characterization of Poly(urethane-benzoxazine)s As a Novel Polyurethane/Phenolic Resin

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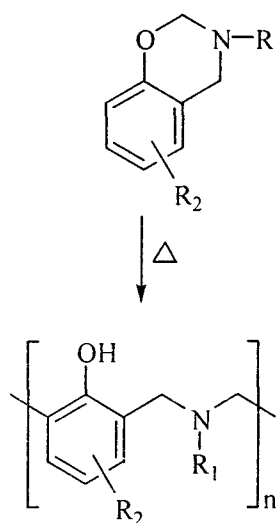
ABSTRACT

Poly(urethane-benzoxazine) films as a novel polyurethane (PU)/phenolic resin were prepared by blending a benzoxazine monomer (**Ba**) and PU prepolymer. DSC of **PU/PBa** blend showed an exotherm with maximum at ca. 246°C due to the ring opening polymerization of **Ba**, giving phenolic OH functionalities that react with isocyanate groups in the PU prepolymer. The poly(urethane-benzoxazine) film was transparent, had only one glass transition temperature (T_g). The T_g increased with the increase of **Ba** content. The films containing 10% and 15% of **Ba** have characteristics of elastomers, while those containing more than 20% of **Ba** have characteristics of plastics. The poly(urethane-benzoxazine) films showed good resistance to organic solvents and enhanced thermal stability.

INTRODUCTION

Polyurethanes (PUs) are extraordinarily versatile materials that can be tailored to meet highly diversified demands due to their widest range of hardness and modulus, which just fill in the gap between plastics and rubbers. It is well known, however, that PU elastomers exhibit very poor thermal stability, which always spoils the excellence of their high mechanical properties, and limits their applications. Since PUs are quite miscible with many synthetic polymers, various kind of PU based composites have been extensively investigated, aiming at improving PUs performance, in particular, the thermal stabilities.

Benzoxazines, 2H-3,4-dihydro-3-substituted-1,3-benzoxazines, are a series of heterocyclic compounds that can be synthesized through Mannich condensation of the corresponding phenol, formaldehyde and primary amine. These compounds can be polymerized simply through thermal ring opening, as shown in scheme 1, affording a new class of thermosetting resins i.e. polybenzoxazines, which are being interested as novel phenolic resins. As a result of the thermal cure of benzoxazine monomers, polybenzoxazines contain a number of phenolic OH groups. These phenolic OH groups can be reacted with NCO-terminated PUs or their prepolymers, giving poly(urethane-benzoxazine). It is expected that the



Scheme 1. Thermal ring-opening
Polymerization of benzoxazine

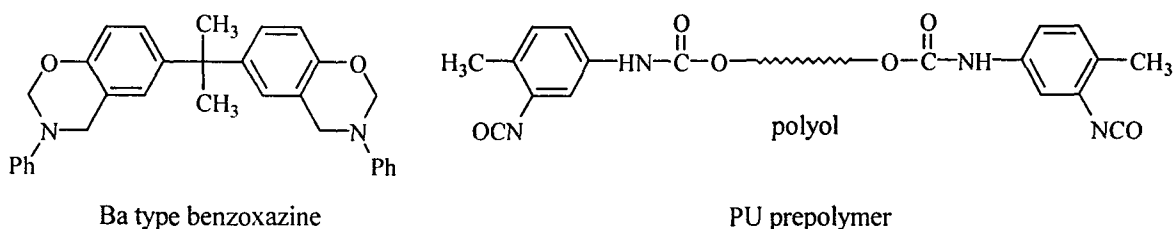


Fig. 1. Structure of Ba and PU prepolymer

combination of PU and polybenzoxazine affords a novel PU/ phenolic resin with enhanced thermal and mechanical properties. This study is an extension of our previous researches on preparation of PU-based elastomers in the film form [1-3]. In this study, we prepared poly(urethane-benzoxazine) by blending PU prepolymer with a bifunctional benzoxazine monomer, Ba.

EXPERIMENTAL

PU prepolymer terminated with NCO groups (Fig. 1) was synthesized from 2,4-tolylene diisocyanate (TDI) and polyethyleneadipate polyol (MW 1,000) in 2:1 molar ratio [1-3].

PU prepolymer was blended with various weight ratios of Ba using THF. The clear homogeneous blend solutions were cast on glass plates, and dried at 50°C for 4 h. The films were then thermally treated as fixed on glass plate at 100°C, 150°C, 170°C, 190°C and 200°C for 1 h each.

RESULTS AND DISCUSSION

Preparation of poly(urethane-benzoxazine) films

The curing behavior of the blend of Ba and PU prepolymer was investigated by DSC. Fig. 2 shows the DSC profiles for PU/Ba-90/10 (molar ratio; 76/24) after each cure cycle. The amount of exotherm was 6.2, 3.8, 1.9 and 0.3 cal/g after thermal treatment at 100, 150, 180 and 190°C for 1 h each, respectively. It is clearly observed that the curing of Ba monomer was not completed after 150°C/1h, and a little was remained after 190°C/1h cure cycle. However, there is no exotherm existing after 200°C/1h cure, suggesting that Ba polymerized through ring opening polymerization as shown in scheme 1.

Since the temperature necessary for the ring opening of Ba and the temperature for the degradation of PU are relatively close, the final cure temperature for the poly(urethane-benzoxazine)s was set differently; 190°C/1h for the PU/PBa films containing more than 85% of

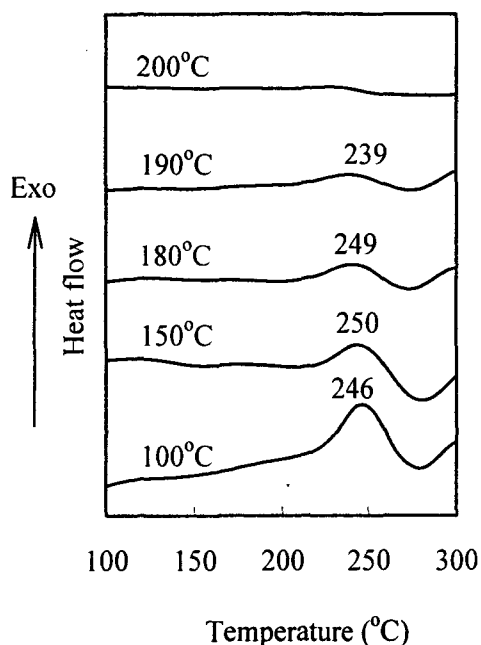


Fig. 2. DSC of PU/Ba-90/10 after different curing stage.

Table 1. Physical properties of cured PU/PBa films

Sample Code	Curing Condition	T _g ^a (°C)	E (MPa)	σ (MPa)	Elongation (%)	Solubility ^b		
						NMP	DMF	THF
PU/Ba-90/10	190°C/1h	-13	2.1	3.3	244	Δ	Δ	Δ
PU/Ba-85/15	190°C/1h	-7	6.0	6.7	182	×	×	×
PU/Ba-80/20	200°C/1h	0	213	20	36	×	×	×
PU/Ba-70/30	200°C/1h	7	283	153	28	×	×	×
PU/Ba-50/50	200°C/1h	38	550	179	14	×	×	×
PU/Ba-30/70	200°C/1h	63	1326	212	4	×	×	×
PU/Ba-0/100	240°C/1h	151	--	--	--	×	×	×

a. determined by viscoelastic properties.

b. immersed for at least one week, Δ; swelling, and ×; insoluble.

PU, 200°C/1h for those less than 80% of PU. All the cured films were transparent, having yellow to pale wine color with the increase of Ba content.

Properties of poly(urethane-benzoxazine) films

The PU/PBa films containing more than 20% of Ba are characteristics of plastics, while the films of PU/PBa-85/15 and PU/PBa-90/10 are evidently characteristics of elastomers. The tensile properties of PU/PBa films are shown in Table 1, and the stress-strain curves of the elastomer films in Fig. 3. These data indicate that the tensile properties change dramatically with the content of Ba. As the content of Ba increases, both the tensile modulus and tensile strength increase, while the elongation at break decreases. Consequently, the film characteristics were either plastics or elastomers depending on the Ba content.

Viscoelastic properties of elastomer films are shown in Fig 4. It is clearly seen that there are rubbery flat zones in E' curves between room temperature to over 150°C. All the PU/Ba films showed only one T_g from the max of E'', which increased with the increase of Ba content (Fig. 5). Both PU prepolymer and Ba are actually the precursors for PUs and PBa, respectively. Thus, this is quite understandable that the final products are obtained through *in-situ* copolymerization of PU prepolymer and Ba in a homogeneous phase affording PU/PBa network structure.

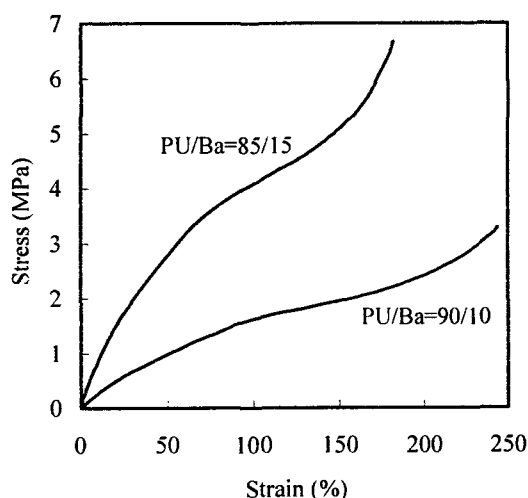


Fig. 3. Strain-stress curves of PU/Ba elastomer films

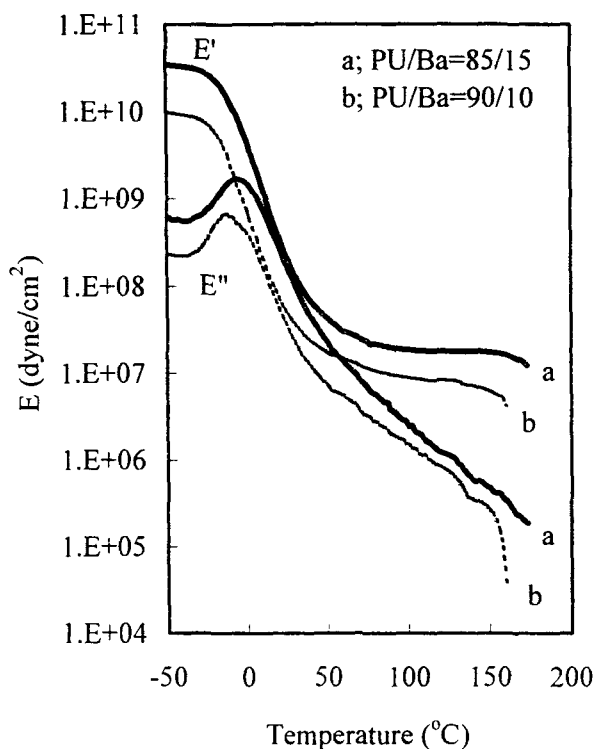


Fig. 4. Viscoelastic properties of PU/Ba elastomer films

The thermal properties were investigated from thermogravimetric analysis (TGA). Fig. 6 illustrated the effect of Ba content on the thermal stabilities of PU/PBa films determined by the 5 and 10% weight loss temperatures. The results show that the initial decomposition temperatures (5% and 10% weight loss) of PU/PBa films are higher than that of pristine PU. It can be seen that increasing Ba content led to a higher decomposition temperature and even small amount of Ba is effective to enhance thermal stability of PUs.

REFERENCES

1. Zuo, M. and Takeichi, T. 1997, *J. Polym. Sci. Part A: Polym. Chem.*, **35**, 3745.
2. Zuo, M., Xiang, Q., and Takeichi, T. 1998, *Polymer*, **39**, 6883.
3. Zuo, M. and Takeichi, T. 1999, *Polymer*, **40**, 5153.
4. Takeichi, T., Zuo, M., and Ito, A. 1999, *High Perform. Polym.*, **11**, 1.
5. Takeichi, T., Yamazaki, Y., Ito, A., and Zuo, M. 1999, *J Photopolym. Sci. & Technol.*, **12**, 203.

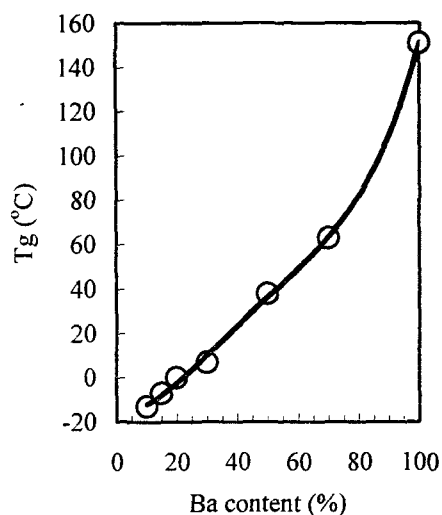


Fig. 5. Shift of Tg depending on the Ba content

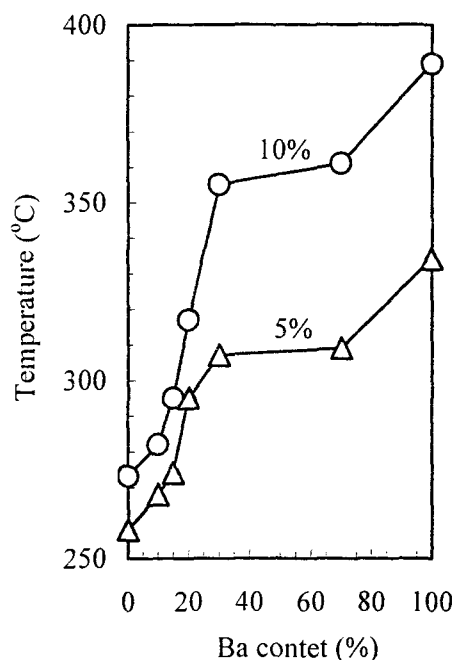


Fig. 6. Effect of Ba content on the thermal stability of PU/PBa films