

## Preparation and Properties of Poly(urethane-benzoxazine)s Based on Monofunctional Benzoxazine Monomer

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**ABSTRACT:** Poly(urethane-benzoxazine) films were prepared by blending a monofunctional benzoxazine monomer, 3-phenyl-3,4-dihydro-2H-1,3-benzoxazine (Pa), and polyurethane (PU) prepolymer that was synthesized from 2,4-tolylene diisocyanate and polyethylene adipate polyol ( $M_w$  ca. 1000) in 2:1 molar ratio, followed by casting as films and thermal curing of the films. The poly(urethane-benzoxazine) films obtained by the thermal cure at 190°C were yellow and transparent. All the films had only one glass transition temperature ( $T_g$ ) from viscoelastic measurements, indicating good miscibility between PU and polybenzoxazine due to the *in-situ* copolymerization of Pa and PU prepolymer. The  $T_g$  shifted increasingly with the increase of Pa content. The films containing less than 50% of Pa had characteristics of elastomer, with elongation at break more than 200%. These elastic films exhibited good resilience with excellent reinstating behavior. The films containing more than 60% of Pa had characteristics of plastics. The poly(urethane-benzoxazine) films showed excellent resistance to the solvents such as tetrahydrofuran, *N,N*-dimethyl formamide, *N*-methyl-2-pyrrolidinone and DMSO.

**KEY WORDS** Polyurethane Prepolymer / Monofunctional Benzoxazine Monomer / Poly(urethane-benzoxazine) Films / *In-Situ* Copolymerization / Elastomer /

Recently developed polybenzoxazines are the new members in the family of phenolic resins, which are derived from the ring opening polymerization of corresponding benzoxazine monomers. These novel types of phenolic resins have not only the characteristics of traditional phenolic resins such as excellent thermal properties, flame retardance and high char yield, but also unique characteristics such as molecular design flexibility, very low moisture absorption, near-zero shrinkage upon polymerization, low melt viscosities, and low dielectric constant.<sup>1–13</sup> Unlike conventional phenolic resins, polybenzoxazines do not need strong acids catalyst for the ring opening polymerization of benzoxazine monomers, and do not produce any harmful by-products during the cure process. Thus, polybenzoxazines overcome the disadvantages of conventional phenolic resins without sacrificing the advantages of those resins, which leads to a novel and promising route for high performance phenolic resins.

Polybenzoxazines based on monofunctional monomers, however, have so low molecular weight, which is caused by the chain transfer during the ring opening polymerization,<sup>1,2</sup> thus their structural applications are limited in quite small fields.<sup>1,14</sup> Therefore, polyfunctional benzoxazine monomers, for example those based on bisphenol A type monomers, are more often employed for obtaining high performance materials.<sup>2–11</sup> These polybenzoxazine thermosetting resins are naturally very brittle, which may cause problems during the processing and the use. Some of their properties like thermal stability and mechanical properties still need to be improved for meeting high performance applications. As a method to improve the performance of polybenzoxazines, we recently reported the preparation of polybenzoxazine-clay nanocomposite. It was achieved that temperature neces-

sary for the ring opening polymerization of benzoxazine monomers lowered, and that the thermal and mechanical properties of polybenzoxazines improved.<sup>15</sup>

Alloying with high performance polymers is another promising method to improve the performance of polybenzoxazines. Polybenzoxazines contain a number of phenolic groups, which are very useful for the combination and copolymerization with various polymers that are reactive with the phenolic groups. For this reason, polybenzoxazines have been widely studied with a number of polymers like epoxy,<sup>16,17</sup> amine-terminated butadiene acrylonitrile (ATBN) or carboxy-terminated butadiene acrylonitrile (CTBN) rubber,<sup>18</sup> and poly(imide-siloxane).<sup>19</sup>

The phenolic hydroxyl groups existing in polybenzoxazines have strong potential for reacting with NCO groups in polyurethane (PU) prepolymer. In the light of this consideration, we have successfully prepared poly(urethane-benzoxazine) films from a bifunctional benzoxazine monomer based on bisphenol A, bis(3-phenyl-3,4-dihydro-2H-1,3-benzoxazinyl)isopropane (Ba) and NCO-terminated PU prepolymer, using the reaction between the phenolic hydroxyl groups in the polybenzoxazine and terminal isocyanate groups of PU prepolymer.<sup>20</sup> The investigation revealed that the reaction undergoes an *in-situ* polymerization, resulting in cross-linked network structures. It was found that the films have the characteristics of plastics or elastomers, depending on the benzoxazine content. The films showed an improvement of thermal stability compared with the pristine PU. Therefore, it is considered to be interesting to find out the characteristics and differences of the poly(urethane-benzoxazine)s based on monofunctional and bifunctional benzoxazine. In this paper, we report the studies on monofunctional benzoxazine based poly-

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(urethane-benzoxazine) films.

## EXPERIMENTAL

### Reagents

Polyethyleneadipate polyol with molecular weight of 1000 (OH number in KOH; 113) and 2,4-tolylene diisocyanate (TDI) were kindly provided by Nippon Polyurethanes Industry Co., Ltd. TDI with purity of 99% for 2,4-isomer, solid in winter and liquid in summer, was used as received. Polyethyleneadipate polyol was dried at 80°C for 10 h under vacuum just before use. 3-Phenyl-3,4-dihydro-2H-1,3-benzoxazine monomer, designated as Pa according to the raw materials of phenol and aniline, was kindly supplied by Shikoku Corporation, and used without further purification. A bifunctional monomer, Ba, was also supplied by Shikoku Corporation. All the solvents used in this study were purified according to the standard methods. Tetrahydrofuran (THF) was distilled over calcium hydride before use.

### Preparation of PU Prepolymer

PU prepolymer terminated with NCO groups was synthesized from TDI and polyethyleneadipate polyol in 2:1 molar ratio, according to the method previously described.<sup>21–23</sup>

### Preparation of Poly(urethane-benzoxazine) (PU/Pa) Films

The general procedure for the preparation of PU/Pa films is as follows. To the solution of PU prepolymer (2.70 g, 2.00 mmol) in 5 mL THF in a sample bottle, the desired amount of Pa in the solid state was added in one portion. The solution was stirred for 4 h at room temperature after Pa was dissolved completely. The clear homogeneous solution was cast on glass plates using doctor blade, and dried at 50°C for 6 h. The films were then thermally treated as fixed on glass plates in an air ventilating oven at 100°C, 150°C, 170°C, and then 190°C for 1 h each.

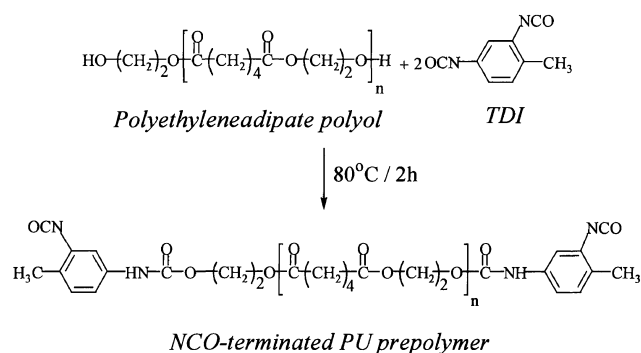
### Measurements

IR spectra were obtained by using a JASCO spectrophotometer model FT/IR-420. Differential scanning calorimetry (DSC) was recorded on Rigaku Thermo Plus 2 DSC8230 at a heating rate of 10°C min<sup>-1</sup> under nitrogen flow. Thermogravimetric analyses (TGA) were determined with Rigaku Thermo Plus 2 TG-DTA TG8120 at a heating rate of 5°C min<sup>-1</sup> under argon flow. The dynamic viscoelastic measurements were conducted on ORIENTEC Automatic Dynamic Viscoelastomer Rheovibron DDV-01 FP with a heating rate of 4°C min<sup>-1</sup> at a frequency of 35 Hz. The tensile properties were measured on Imada Seisaku-sho Model SV-3 at a cross-head speed of 2 mm min<sup>-1</sup> using 20 mm of the film length. The tensile properties of each sample were determined from the average of at least five tests.

## RESULTS AND DISCUSSION

### Preparation of PU/Pa Films

PU prepolymer used in this study was synthesized according to Scheme 1. Pa and PU prepolymer were



**Scheme 1.** Preparation of NCO-terminated PU prepolymer.

**Table I.** Formulation of PU and Pa

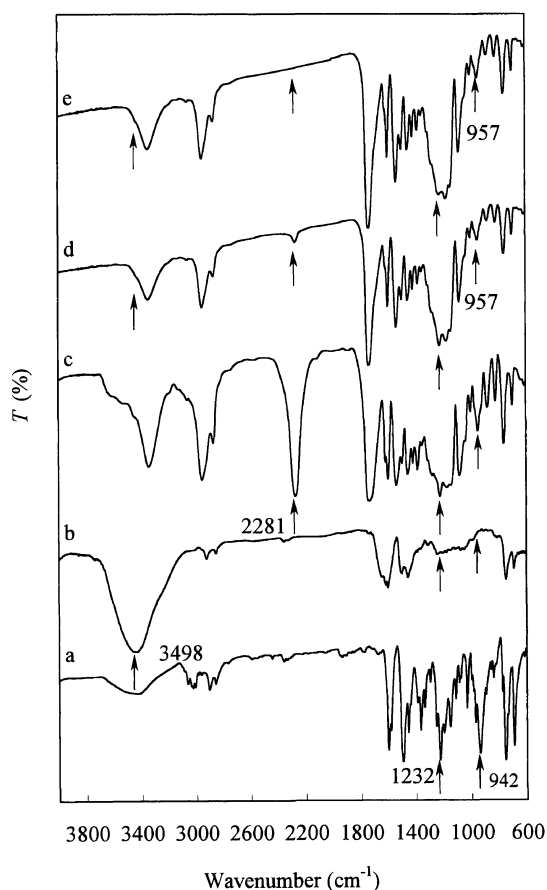
Sample code	PU <sup>a</sup>		Pa		PU/Pa ratio/%	
	g	mmol	g	mmol	wt.	mol
PU/Pa-20/80	1.55	1.15	6.20	29.39	20/80	4/96
PU/Pa-40/60	2.67	1.98	4.00	18.96	40/60	10/90
PU/Pa-50/50	2.71	2.01	2.71	12.83	50/50	14/86
PU/Pa-60/40	2.73	2.02	1.82	8.61	60/40	19/81
PU/Pa-70/30	2.70	2.00	1.16	5.48	70/30	27/73
PU/Pa-86/14	2.74	2.03	0.45	2.11	86/14	50/50

<sup>a</sup> PU prepolymer terminated with TDI.

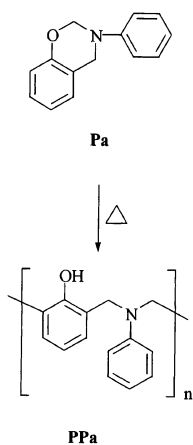
blended in various weight ratios as summarized in Table I.

The reaction between Pa and NCO terminated PU prepolymer was examined by IR. Figure 1 shows an example of the IR spectra in the case of PU/Pa-70/30. Characteristic absorptions of Pa were found at 942 and 1232 cm<sup>-1</sup> both assigned to C–O–C stretching mode of benzoxazine ring (Figure 1a). Those absorptions disappeared after the thermal treatment at 190°C for 1 h (Figure 1b). Instead, a broad intensive absorption appeared at 3498 cm<sup>-1</sup>, which is assigned to the phenolic hydroxyl group. These indicate that Pa thermally polymerized through its ring opening to give PPa as shown in Scheme 2. It was confirmed by IR that the blend of Pa and PU prepolymer (Figure 1c) contains both benzoxazine and isocyanate characteristics absorptions, such as 942 and 1232 cm<sup>-1</sup> assigned to benzoxazine structure, and 2281 cm<sup>-1</sup> to NCO group of PU prepolymer. After being cured at 150°C for 1 h, however, the absorption at 942 cm<sup>-1</sup> shifted to 957 cm<sup>-1</sup> (trisubstituted benzene ring) and the absorption at 2281 cm<sup>-1</sup> (NCO group) greatly decreased (Figure 1d). Furthermore, the absorption at 3498 cm<sup>-1</sup> (phenolic hydroxyl groups) did not appear, which existed in PPa. This means that the ring opening polymerization of Pa occurred at 150°C and the phenolic hydroxyl groups reacted with the NCO groups simultaneously. After cure at 190°C for 1 h, the absorptions due to NCO (2281 cm<sup>-1</sup>) and benzoxazine (942 cm<sup>-1</sup> and 1232 cm<sup>-1</sup>) disappeared completely (Figure 1e), suggesting the formation of PU/Pa network.

Since the benzoxazine monomer Pa has both open *ortho*- and *para*- position to the oxygen in the oxazine ring, cross-linking through these reactive *ortho*- and also *para*- position could happen.<sup>1</sup> However, PPa showed a good solubility in THF, DMSO, DMAc, and NMP as will be described later, which suggests linear structure for



**Figure 1.** IR spectra of the compounds: (a) Pa, (b) PPa, (c) blend of Pa, and PU prepolymer, (d) PU/Pa treated at 150°C for 1 h and (e) 190°C for 1 h.



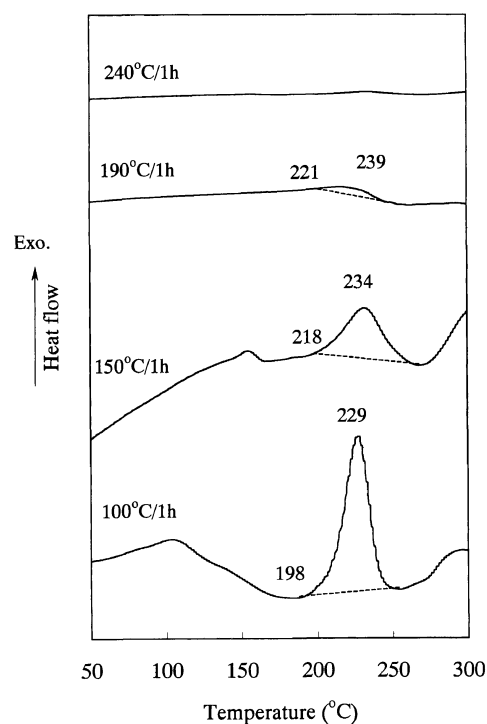
**Scheme 2.** Ring opening polymerization of Pa.

this polybenzoxazine. Also, there is no any characteristic absorption (*i.e.*, at 1490  $\text{cm}^{-1}$  due to tetra-substituted benzene ring<sup>2,11,20</sup>) of cross-linked structure in the IR spectra of PPa. Therefore, the polymerization of Pa is supposed to proceed as shown in Scheme 2, affording a linear polybenzoxazine containing phenolic hydroxyl groups. The reaction between the phenolic hydroxyl groups and NCO groups gives a network structure.

The curing behavior of both pristine Pa and PU/Pa were followed by DSC and the results are summarized in Table II. Figure 2 illustrated examples in the case of PU/

**Table II.** DSC of PU/Pa

Sample code	Curing condition	Exothermic band		
		onset/ $^{\circ}\text{C}$	max./ $^{\circ}\text{C}$	quan./ $\text{cal g}^{-1}$
PU/Pa-40/60	100 $^{\circ}\text{C}/1\text{ h}$	228	245	22.8
	150 $^{\circ}\text{C}/1\text{ h}$	219	237	9.7
	190 $^{\circ}\text{C}/1\text{ h}$	230	249	0.2
PU/Pa-50/50	100 $^{\circ}\text{C}/1\text{ h}$	219	246	19.7
	150 $^{\circ}\text{C}/1\text{ h}$	223	252	8.9
	190 $^{\circ}\text{C}/1\text{ h}$	231	253	0.3
PU/Pa-60/40	240 $^{\circ}\text{C}/1\text{ h}$	—	—	0.0
	100 $^{\circ}\text{C}/1\text{ h}$	224	242	17.9
	150 $^{\circ}\text{C}/1\text{ h}$	221	232	9.0
PU/Pa-70/30	190 $^{\circ}\text{C}/1\text{ h}$	238	253	0.1
	100 $^{\circ}\text{C}/1\text{ h}$	198	229	11.4
	150 $^{\circ}\text{C}/1\text{ h}$	218	234	6.8
PU/Pa-86/14	190 $^{\circ}\text{C}/1\text{ h}$	221	239	0.1
	240 $^{\circ}\text{C}/1\text{ h}$	—	—	0.0
	100 $^{\circ}\text{C}/1\text{ h}$	227	238	10.9
Pristine Pa	170 $^{\circ}\text{C}/1\text{ h}$	229	240	5.1
	190 $^{\circ}\text{C}/1\text{ h}$	230	248	0.1
	189	235	32.6	
	150 $^{\circ}\text{C}/1\text{ h}$	166	218	17.6
	190 $^{\circ}\text{C}/1\text{ h}$	201	232	1.8
200 $^{\circ}\text{C}/1\text{ h}$	217	245	0.4	
240 $^{\circ}\text{C}/1\text{ h}$	—	—	0.0	



**Figure 2.** DSC thermograms of PU/Pa-70/30 treated at various temperatures.

Pa-70/30. Previous studies revealed that ring opening polymerization of monofunctional and bifunctional benzoxazines occurs above 150 $^{\circ}\text{C}$ .<sup>1,2</sup> From Figure 2, exothermic peak due to the ring opening of Pa is clearly seen. The exothermic quantity upon curing is 11.4  $\text{cal g}^{-1}$  for the mixture before curing, and decreased gradually to 6.8  $\text{cal g}^{-1}$  after the treatments at 150 $^{\circ}\text{C}$  for 1 h, suggesting that the partial ring opening of Pa occurred by the treatment at 150 $^{\circ}\text{C}$ . After the treatments at 190 $^{\circ}\text{C}$  for 1 h, the exothermic amount was as low as 0.09  $\text{cal g}^{-1}$ . The exotherm was disappeared at 240 $^{\circ}\text{C}$ , as shown in

Figure 2.

Similar DSC behavior was observed for PU/Pa films with different ratios. After the cure at 150°C for 1 h, the exothermic amount decreased by *ca.* 50%. After the cure at 190°C for 1 h, the exothermic peak almost disappeared. After the cure at 240°C for 1 h, the exothermic peak disappeared completely. Compared with pristine Pa, the overall amount of exotherm decreased for the PU/Pa films, in proportion to the weight ratio of Pa.

All the cured films were transparent and yellow after the treatment at 190°C for 1 h, while the films containing more than 50% of PU were dark brown with less transparency after the cure at 200°C for 1 h. Partial thermal decomposition may have happened by the 200°C treatment. Thus, in order to avoid any thermal degradation of PU component, the final cure condition for the formation of poly(urethane-benzoxazine) was set at 190°C for 1 h for PU/Pa films.

#### Tensile Properties of PU/Pa Films

The tensile properties of PU/Pa films are summarized in Table III and stress-strain curves for the elastomer films are shown in Figure 3. As the content of PU increases, the elongation at break increases, while both the modulus and tensile strength decreases. Subsequently, the film changed from plastic to elastomer. The films containing 50% or more of PU have the character-

istics of elastomer, with more than 200% elongation at break. While those containing less than 40% of PU have characteristics of plastic. The elastomer films were also tested simply by hand tensing, showing reinstating very well upon releasing from tensing.

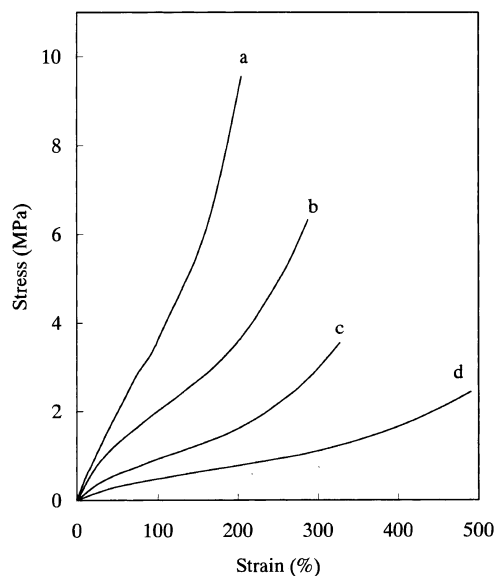
It was shown from the tensile properties of the PU/Pa-50/50 films after the cure at 200°C for 1 h that the higher temperature cure made the films plastic. Both the tensile strength and elongation at break decreased, and the films were dark brown, and less transparent, which may suggest thermal degradation.

Compared with recently reported PU/Ba elastic films<sup>20</sup> with similar benzoxazine content after the same cure, the strength and modulus of PU/Pa films are inferior, but the elongation at break is superior. For example, the tensile strength of PU/Pa-86/14 film is *ca.* one third of PU/Ba-85/15, but the elongation is almost three times larger than that of PU/Ba-85/15. In the case of Pa, PU/Pa films still exhibit more than 200% elongation with 50% of Pa content, while in the case of Ba, only in the case of 15% or less of Ba, PU/Ba films become elastomer. This may be due to the lower cross-link density of PU/Pa films, because Pa type polybenzoxazine has linear structure, while Ba type polybenzoxazine has network structure. The detailed cross-link density calculation will be given below from the dynamic mechanical analysis.

**Table III.** Tensile properties of PU/Pa films after curing

Sample code	Curing condition	E	$\sigma$	Elongation	Remark
		MPa	MPa	%	
PU/Pa-20/80	190°C/1 h	117	34	4	P <sup>a</sup>
PU/Pa-40/60	190°C/1 h	31	22	21	P
PU/Pa-50/50	200°C/1 h	13	8.9	86	P
∕	190°C/1 h	9.8	9.6	204	E <sup>b</sup>
PU/Pa-60/40	190°C/1 h	7.3	6.3	287	E
PU/Pa-70/30	190°C/1 h	5.8	3.4	327	E
PU/Pa-86/14	190°C/1 h	3.2	2.4	491	E

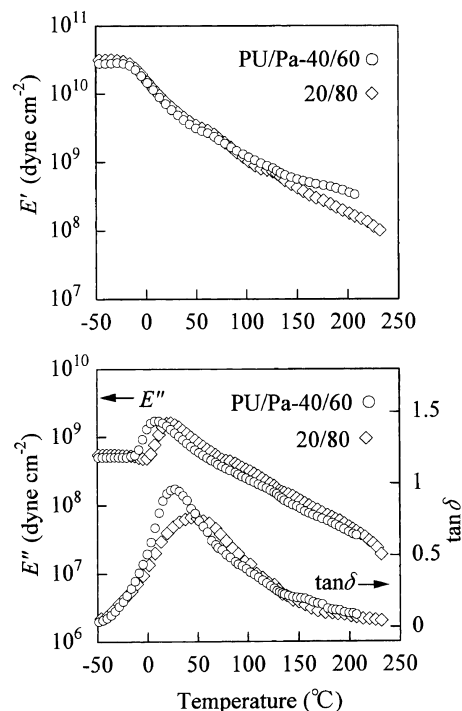
<sup>a</sup> Plastic films. <sup>b</sup> Elastic films.



**Figure 3.** Stress-strain curves of PU/Pa elastic films: (a) PU/Pa-50/50, (b) PU/Pa-60/40, (c) PU/Pa-70/30, (d) PU/Pa-86/14.

#### Dynamic Mechanical Analysis of PU/Pa Films

The dynamic mechanical properties of the PU/Pa plastic films are illustrated in Figure 4. It was shown that the PU/Pa films containing less than 40% of PU component have characteristics of plastic, which is in an agreement with the results from the tensile properties. From both  $E''$  and  $\tan \delta$ , only one  $T_g$  was observed for those PU/Pa plastic films, and the  $T_g$ s shifted from 8°C



**Figure 4.** Viscoelastic properties of PU/Pa plastic films.

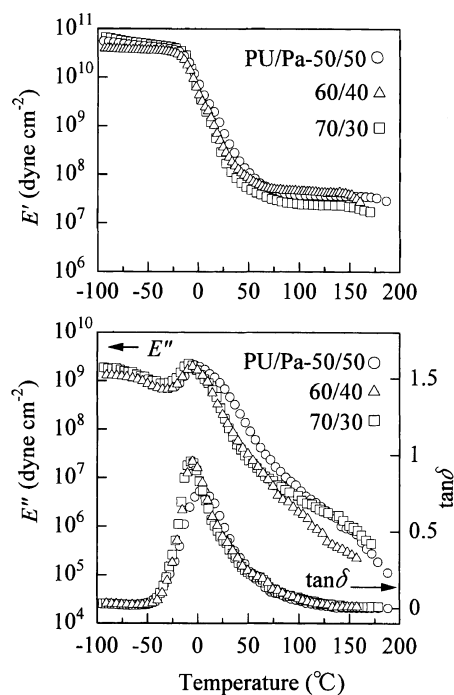


Figure 5. Viscoelastic properties of PU/Pa elastomer films.

to 27°C as Pa content increased from 60% to 80%. These may indicate that there is no phase separation happened to PU/Pa plastic films. The dynamic mechanical properties of the PU/Pa elastic films are shown in Figure 5. The cured PU/Pa films containing more than 50% of PU show elastic characteristics with a good reinstating behavior. It is evidently observed that a rubbery plateau region appeared in the storage modulus from room temperature to *ca.* 180°C for every elastic film. The dissociation of urethane linkage at *ca.* 200°C limited the use temperature of these films up to *ca.* 200°C. These results are similar to those of PU/Ba films.<sup>20</sup>

According to the statistical theory of rubber elasticity, the cross-link density of rubbery materials can be estimated in an equation as follow.<sup>24</sup>

$$G_e = \Phi \nu RT = \Phi(\rho / Mc)RT$$

where  $G_e$  is the equilibrium modulus in the rubbery region,  $\Phi$  is a front factor that is unity for ideal rubber,  $\nu$  is the cross-link density that means the mole number of network chains per unit volume of the polymer,  $R$  is the gas constant,  $T$  is absolute temperature,  $\rho$  is the density of the polymer, and  $Mc$  is the molecular weight between the cross-linkage. Cross-link densities of the PU/Pa elastic films were evaluated, though they are not ideal rubbers. For PU/Pa elastic films, the measured values of  $\rho$  were 1.094, 1.098, 1.113, and 1.201 g cm<sup>-3</sup> for PU/Pa-50/50, PU/Pa-60/40, PU/Pa-70/30, and PU/Pa-84/16, respectively. By assuming  $\Phi=1$ , the values of  $\nu$  were calculated from the values of  $G_e$  shown in Figure 5, to be 1352, 1176, 949, and 308 mol m<sup>-3</sup> for PU/Pa-50/50, PU/Pa-60/40, PU/Pa-70/30, and PU/Pa-84/16, respectively. Consequently, the values of  $Mc$  were calculated to be 8716, 9248, 11527, and 63795 for PU/Pa-50/50, PU/Pa-60/40, PU/Pa-70/30, and PU/Pa-84/16, respectively. Compared with the PU/Ba films,<sup>20</sup> PU/Pa type

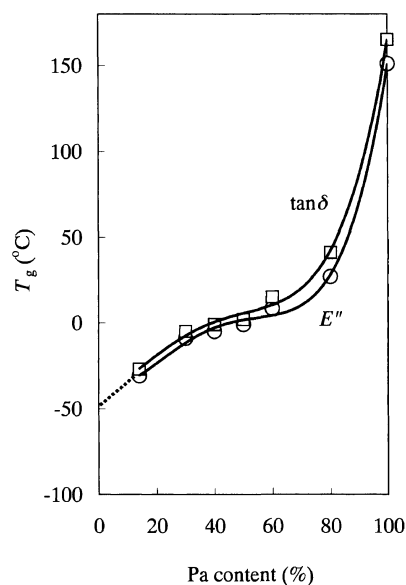


Figure 6. Shift of  $T_g$  of PU/Pa films with Pa content. PU/Pa films were cured at 190°C for 1 h, and Pa was cured at 240°C for 1 h.

elastic films were found to have lower cross-link density, and higher molecular weight between cross-linkage. For instance, the calculated values of  $\nu$  and  $Mc$  of PU/Ba-85/15 were 944 mol m<sup>-3</sup> and 12305, respectively, which equal to *ca.* three times and one fifth of those of PU/Pa-84/16.

All of the PU/Pa elastic films showed only one glass transition temperature ( $T_g$ ) from  $E''$  max, regardless the Pa content.  $T_g$ s of PU/Pa films obtained from  $E''$  max shifted from -26°C to -1°C, as PU content decreased from 86% to 50%. Similar tendency was observed with  $\tan \delta$  max. Figure 6 shows the change of  $T_g$  that was observed from  $E''$  and  $\tan \delta$  max with the Pa content, among which  $T_g$  of PU is cited by a common polyester-based PU,<sup>25</sup> and  $T_g$  of PPA was observed from the viscoelastic properties of the PPA cured at 240°C because the PPA treated at 190°C was too brittle to prepare a measurable film. It is seen that as Pa content increases, the  $T_g$  increases in an invert S-shaped curve. Since PU prepolymer and Pa are actually the precursors for PU and polybenzoxazine, respectively, the ring opening polymerization of Pa and the reaction between the phenolic OH of the resulting polybenzoxazine and the NCO of PU prepolymer occur simultaneously, in other words, these poly(urethane-benzoxazine)s are obtained through *in-situ* copolymerization. Thus, the resulting PU/Pa films do not show phase separation. This also supports the abovementioned formation of PU/Pa network structures.

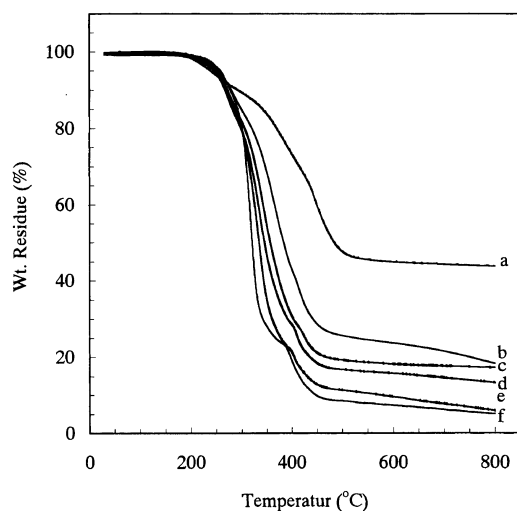
#### Solubility of PU/Ba Films

The solubility properties of PU/Pa films are summarized in Table IV. Both pristine PU and Pa polymer are soluble in the examined solvent, but all the PU/Pa films are not soluble, although they swelled in the strong polar solvent like DMSO, DMF, and NMP. This is also considered to be attributed to the network structure of the poly(urethane-benzoxazine)s. This clearly demonstrates that poly(urethane-benzoxazine)s contain covalent

**Table IV.** Solubility of PU/Pa films<sup>a</sup>

Sample code	Solubility				
	CHCl <sub>3</sub>	THF	DMSO	DMF	NMP
PU/Pa-0/100	×	○	○	○	○
PU/Pa-20/80	×	×	×	×	×
PU/Pa-40/60	×	×	△	△	△
PU/Pa-50/50	×	×	△	△	△
PU/Pa-60/40	×	×	△	△	△
PU/Pa-70/30	×	×	△	△	△
PU/Pa-86/14	×	×	△	△	△
PU/Pa-100/0	△	○	○	○	○

<sup>a</sup> Films cured at 190°C for 1 h were immersed in the solvents for 2 weeks. ×; Insoluble, △; Swelling, ○; Soluble.



**Figure 7.** TGA of PU/Pa films: (a) PU/Pa-0/100, (b) PU/Pa-50/50, (c) PU/Pa-60/40, (d) PU/Pa-70/30, (e) PU/Pa-86/14, (f) PU/Pa-100/0.

bonds between PU and PPa, and are not polymer blends.

In the case of PU/Ba elastic films, for example PU/Ba-85/15, the film was neither soluble nor swelling after 2 weeks immersed in the solvents.<sup>20</sup> This shows that the solvent resistance of PU/Pa films is not so good as PU/Ba films due to their lower crosslink density.

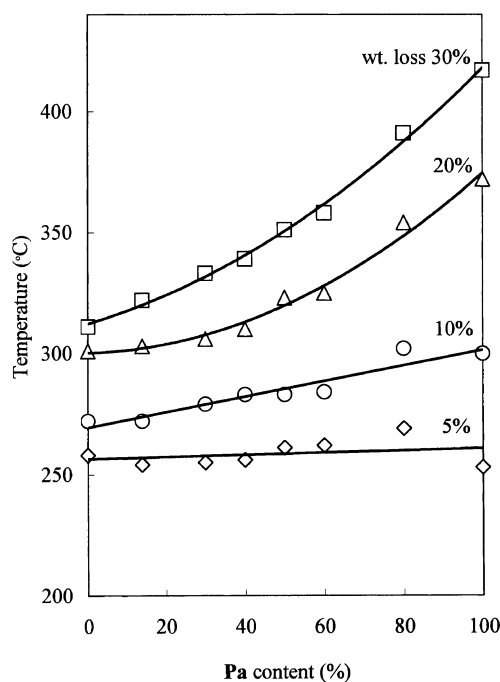
#### Thermal Properties of PU/Ba Films

Thermal properties were investigated from thermogravimetric analysis (TGA). Figure 7 shows TGA profiles of PU/Pa, and Table V summarizes the results of PU/Pa. The initial decomposition temperatures of pristine PU defined at 5% weight loss were not improved by the incorporating Pa type polybenzoxazines. This is due to the moderate thermal stability of Pa based polybenzoxazine that was derived from the same treatment as PU/Pa, and the thermally weak bondages between PU and Pa component, as well as lower crosslink density. On the other hand, the temperatures at 10%, 20%, and 30% weight loss increased with the Pa content. Figure 8 shows these trends. Therefore, it is considered that the heat resistance of PU is improved by incorporation of Pa. In the case of PU/Ba, the thermal properties of PU were greatly improved by incorporation of even a small amount of Ba, in both initial decomposition temperatures and weight loss temperatures. This is also contributed by the network structure of PBa. Many kinds of

**Table V.** Thermal properties of PU/Pa after curing

Sample code	Curing condition	$T_g^a$	Temperature (°C) at <sup>b</sup>	
		°C	5% wt. loss	10% wt. loss
PU/Pa-0/100	190°C/1 h	—	253	300
PU/Pa-20/80	190°C/1 h	27	268	302
PU/Pa-40/60	190°C/1 h	8	258	281
PU/Pa-50/50	190°C/1 h	-1	259	283
PU/Pa-50/50	200°C/1 h	—	260	283
PU/Pa-60/40	190°C/1 h	-5	256	279
PU/Pa-70/30	190°C/1 h	-9	253	271
PU/Pa-86/14	190°C/1 h	-31	256	272
PU/Pa-100/0	190°C/1 h	—	258	273

<sup>a</sup> Data from  $E''$  max on viscoelastic properties. <sup>b</sup> Data from TGA analyses.



**Figure 8.** Effect of Pa content on the thermal stability of PU/Pa.

benzoxazine monomers are available. So if those with excellent thermal stability are used for the modification of PU, the decomposition temperature of PU will be improved very well like that of Ba.<sup>20</sup>

## CONCLUSIONS

We successfully prepared a series of new poly(urethane-benzoxazine) films from Pa and PU prepolymer. Network structures were formed in PU/Pa due to the urethane bondage between NCO of PU prepolymer and phenolic OH from ring-opening polymerization of Pa. The cured PU/Pa films were yellow and transparent, suggesting good compatibility between PU and Pa components due to *in-situ* polymerization. All the PU/Pa films have only one  $T_g$  from their viscoelastic properties, indicating no phase separation in poly(urethane-benzoxazine). The films were insoluble but swelled in polar organic solvents such as DMSO, DMF, and NMP. In the case of the combination with PU, significant difference is found between monofunctional benzoxazine monomer, Pa, and bifunctional monomer, Ba, in many

characteristics. The elastic films can be prepared with up to 50% Pa content in the case of PU/Pa. While the elastic films were prepared with only less than 15% of Ba in the case of PU/Ba. The structures of PU/Pa are bound by two linear polymers with low cross-link density, while PU/Bas are connected by two cross-linked ones with high cross-link density. Because many types of benzoxazine monomers are available, poly(urethane-benzoxazine) can be tailor-made into a wide range of performance by choosing a proper monomer for a specific application.

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