Performance Improvement of Polybenzoxazine by Alloying with Polyimide

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Introduction

Polybenzoxazines are derived from the corresponding benzoxazines that are synthesized from phenols, formaldehyde and primary amines, through Mannich condensation. They have been studied as a novel class of phenol resins due to the similar structures. In addition to the advantages of traditional phenol resins, polybenzoxazines also have many unique properties that overcome the shortcomings of the tranditional phenol resins [1-3]. It is revealed that polybenzoxazines are, however, very brittle with moderate thermal stability, which limit their applications.

Poly(imide-siloxane)s (PISis) are a family of copolymers containing polydimethylsiloxane (PDMS) and polyimide (PI), with an attractive combination of thermal stability and rubbery flexibility, which make them a good candidate for high performance composites [4-8].

In this study, we synthesized PISis with and without hydroxyl functionalities, and introduced them into polybenzoxazine network aiming to obtain polymer alloys with improved thermal and mechanical properties. We expect that the presence of PDMS will improve the toughness as well as the thermal properties of polybenzoxazines. Furthermore, the presence of polyimide copolymerized with PDMS will minimize the phase separation between polybenzoxazine and PDMS as well as enhancing the thermal stability and also the tensile modulus of polybenzoxazine that is anticipated to drop because of PDMS.

Experimental

We used soluble PISis with and without pendent phenolic groups termed as PISi(OH) and

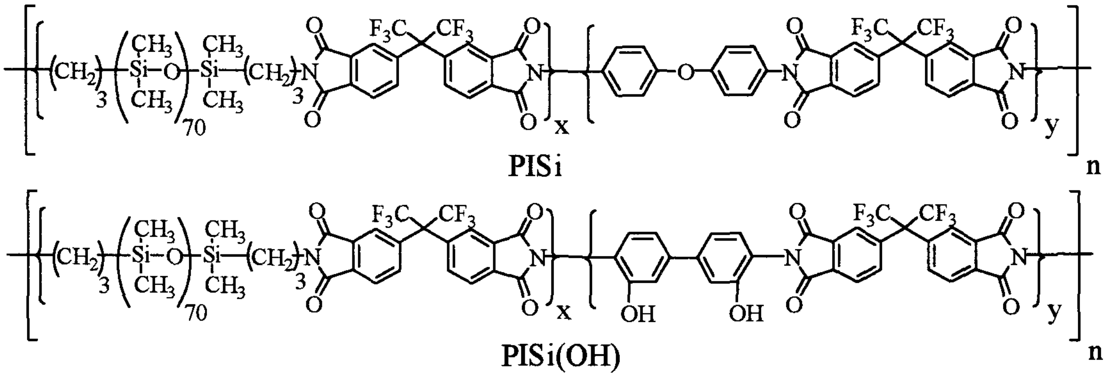


Fig. 1. Structure of PISi and PISi(OH)

PISi, respectively, which were prepared by the copolymerization of 2,2'-bis(3,4-dicarboxylphenyl)hexafluoropropane dianhydride (6FDA), α,ω-bis(aminopropyl)dimethylsiloxane oligomer (MW=5000) and 3,3'-dihydroxybenzidine (with OH group) or 4,4'-diaminodiphenyl ether (without OH group), as shown in **Fig. 1**. All of the PISis were obtained from the imidization of corresponding poly(amide acid) by refluxing in *m*-xylene for 8 h.

A bifunctional benzoxazine monomer, bis(3-phenyl-3,4-dihydro-2H-1,3-benzoxzinyl)isopropane (Ba) as shown in **Fig. 2**, was blended with PISis in various weight ratios using THF/NMP (3:7) solvent mixture at room temperature for 1 hour. Then the solutions were cast on glass plates, dried at 60°C for 6h followed by thermal treatment at 100°C, 150°C, 200°C and 240°C for 1h each. The obtained films were opaque and yellow.

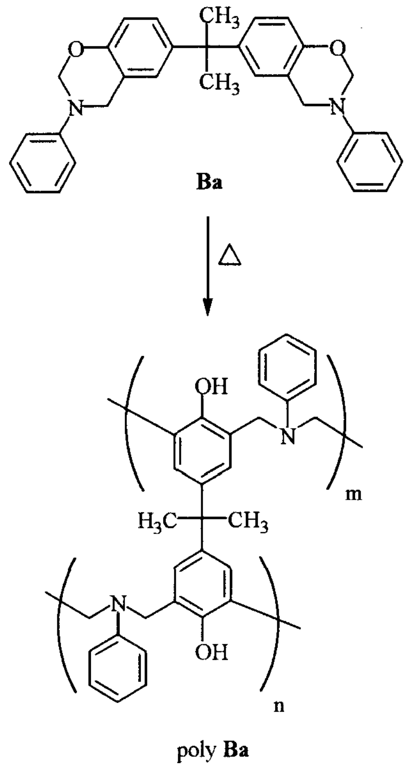
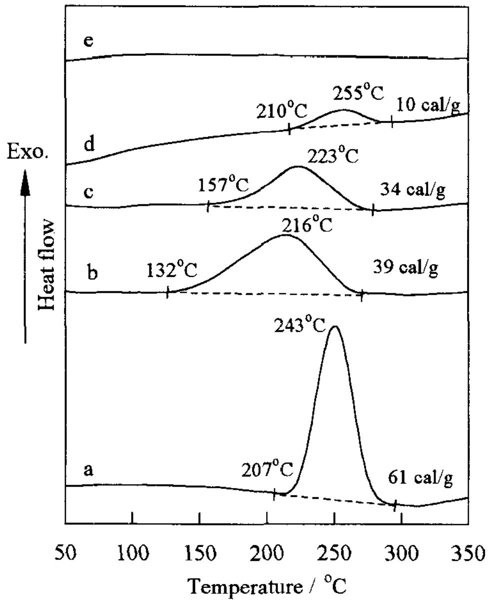


Fig. 2. Ring-opening polymerization of Ba.

Results and discussion

1. Preparation of polymer alloys from Ba/PISi and Ba/PISi(OH)

The blend solutions of Ba/PISi were apparently different from those of Ba/PISi(OH), the former were translucent, and the later transparent. This is probably due to the interaction



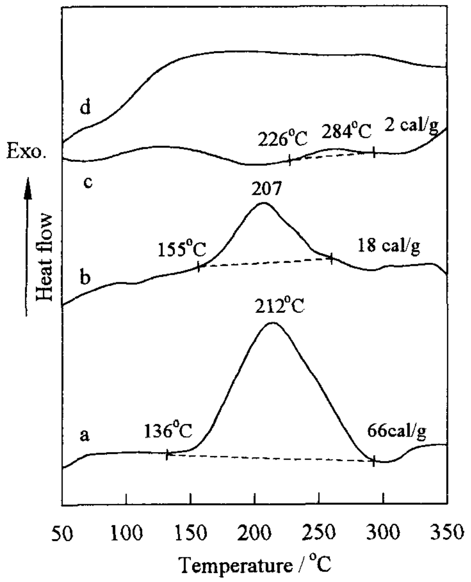
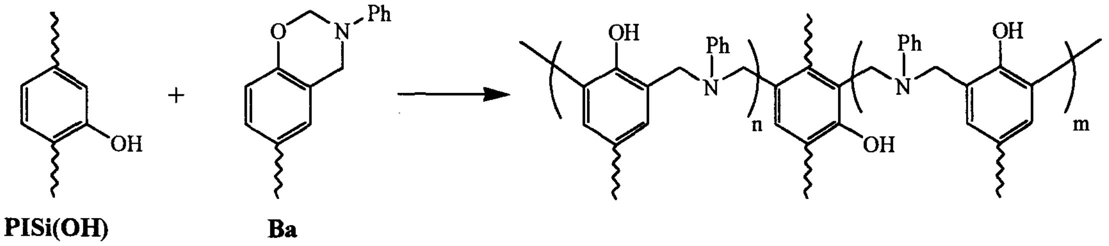


Fig. 3. DSC of (a) Ba, Ba/PISi-80/20 blend of (b) before cure and cured at (c) 150°C/1h, (d) 200°C/1h, and (e) 240°C/1h.

Fig. 4. DSC of Ba/PISi(OH)-80/20 blend of (a) before cure, and cured at (b) 150°C/1h, (c) 200°C/1h, and (d) 240°C/1h



Scheme 1. The formation of AB-crosslink copolymer from PISi(OH) and Ba.

between the ether linkage of Ba and the OH group in PISi(OH). We used DSC analyses to investigate the cure of Ba/PISi and Ba/PISi(OH), and some examples are shown in **Figs 3** and **4**, respectively. Interestingly, exotherm for curing Ba in both cases shifted significantly to lower temperature range, the onset was lowered by ca.60°C and the max. by 30°C. This may be considered to result, in both systems, from the catalytic effect of remained carboxyl group due to the incomplete imidization. The exothermic amount in case of Ba/PISi blend was in accordance with content of Ba, which suggests that PISi is not involved in the ring-opening polymerization of Ba. Therefore, the polymer alloys from Ba/PISi lead to the formation of seim-IPN structures. In case of Ba/PISi(OH), on the other hand, the exothermic amount at every cure cycle was higher than that in case of Ba/PISi. This may imply that PISi(OH) is associated with the curing reaction of Ba. Thus, it is considered that the phenolic groups in PISi(OH) helps the ring-opening reaction of Ba through copolymerization with Ba following **Scheme 1**, affording AB crosslinked polymer [9-11].

The ring-opening polymerization of Ba in both cases was also confirmed by IR changes from the disappearance of the absorptions at 1233 cm^{-1} (oxazine ring), 950 cm^{-1} and 1500 cm^{-1} (trisubstituted benzene ring) after 240°C thermal treatment. Meanwhile, new absorptions at 1480 cm^{-1} assigned to tetrasubstituted benzene ring appeared, indicating the ring-opening polymerization of Ba.

2. Dynamic Mechanical properties (DMA) of the polymer alloys

The results of DMA of Ba/PISi and Ba/PISi(OH) are shown in **Figs 5** and **6**, respectively. HomopolyBa after cured at 240°C has Tg at 152°C from the maximum of E" or at 171°C from the maximum of tanδ, respectively. For the polymer alloys from both Ba/PISi and Ba/PISi(OH), a Tg due to the dimethylsiloxane unit was found at -55°C from the maximum of tanδ. For the Tg in high-temperature range, two Tgs were observed from the maxima of tanδ in case of Ba/PISi (**Fig. 5**), indicating phase separation between polyBa and polyimide.

In case of PISi(OH), however, only one broad Tg in high-temperature range was found from both tanδ and the E" as shown in **Fig. 6** between the Tgs of polyBa and of PI. This shows that there is no phase separation between polyBa and PI in PISi(OH). This is in support with the co-polymerization of the Ba mainly with the vacant *ortho* or *para* positions

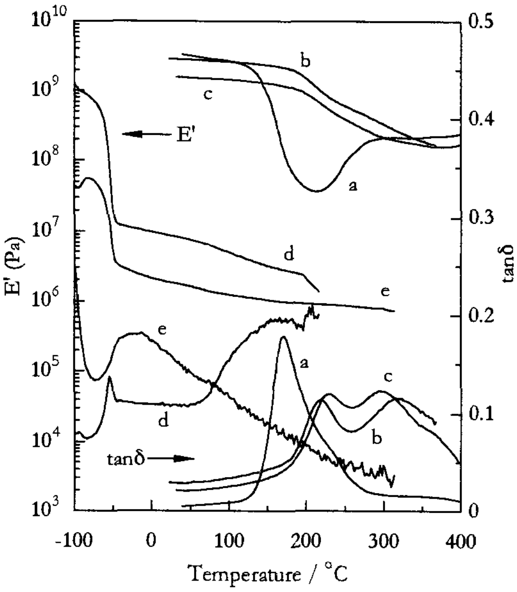


Fig. 5. DMA of (a) polyBa and polymer alloys from Ba/PISi with ratio of (b) 95/5, (c) 85/15, (d) 50/50 and (e) 0/100.

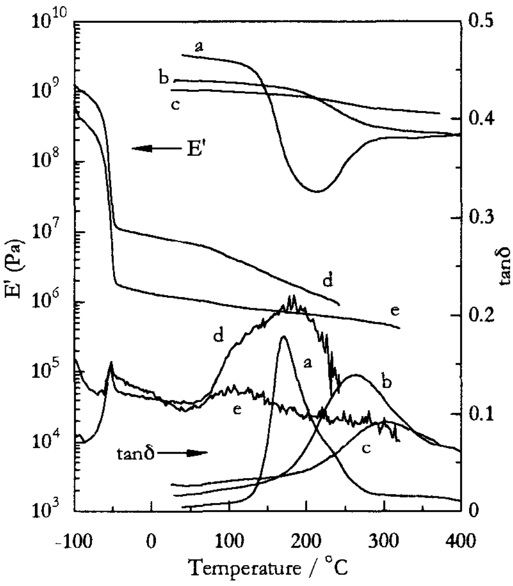


Fig. 6. DMA of (a) polyBa and polymer alloys from Ba/PISi(OH) with ratio of (b)90/10, (c) 80/20, (d) 50/50 and (e) 0/100.

of the hydroxyl functionalities on PISi(OH), affording a network structure of AB crosslinked polymer. The broadening of the tanδ peak indicates the increase in the number of modes of branching resulting in wider distribution of structures.

Fig. 7 shows the shift of the high-temperature Tg depending on the content of poly(imide-siloxane)s. In case of the polymer alloys with PISi that leads to semi-IPN, the Tg values from the maximum of tanδ increased for more than 60°C by the introduction of only 10% of PISi. In case of the polymer alloys with PISi(OH) that leads to AB-crosslinked structure, Tg values further increased for more than 80°C by the introduction of only 10% of PISi(OH).

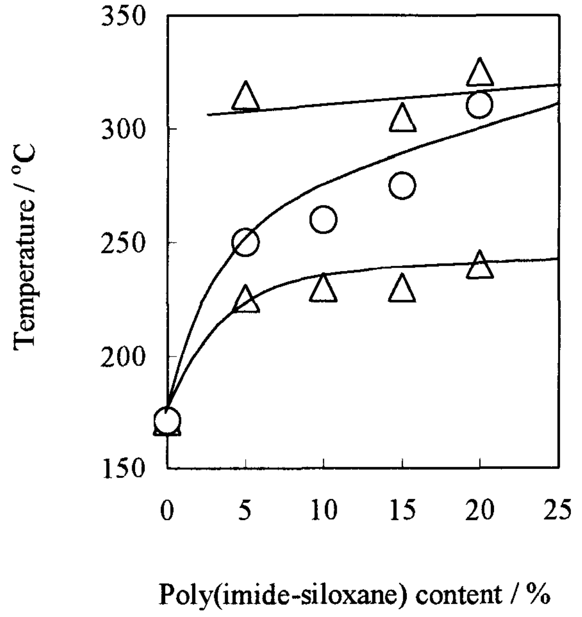


Fig. 7. Effect of PISi (Δ) or PISi(OH) (O) on the shift of Tg.

3. Tensile properties of the polymer alloys

The tensile properties of the polymer alloys from both Ba/PISi and Ba/PISi(OH) were

Table 1. Tensile properties of polymer alloys of Ba/PISi and Ba/PISi(OH)

Sample Code	Modulus (GPa)	Strength (MPa)	Elongation (%)
polyBa	3.3	42	1.3
PBa/PISi-90/10	2.2	64	4.2
80/20	1.9	38	2.5
50/50	0.009	1.1	17
PISi	0.0005	0.34	168
PBa/PISi(OH)-90/10	2.1	23	1.5
50/50	0.17	2.7	4.1
30/70	0.013	0.81	11.7
PISi(OH)	0.013	1.3	74

examined, and the results are summarized in **Table 1**. It is noteworthy that as the content of PISi or PISi(OH) increased, the tensile modulus and strength decreased, and the elongation at break increased. The polymer alloys of Ba/PISi(OH), however, gave higher modulus and lower elongation than those of Ba/PISi in case of the same ratio, which is probably attributed to the difference between AB-crosslinked polymer and semi-IPN. Therefore, it is conclusive that the introduction of poly(imide-siloxane) enhance toughness of polyBa, and the effect is more pronounced with PISi probably because of the formation of semi-IPN.

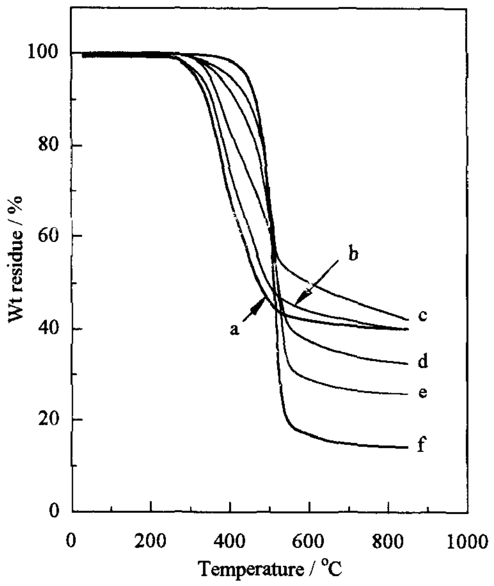


Fig. 8. TGA of (a) polyBa and polymer alloys from Ba/PISi with ratios of (b) 90/10, (c) 80/20, (d) 50/50, (e) 30/70 and (f) 0/100.

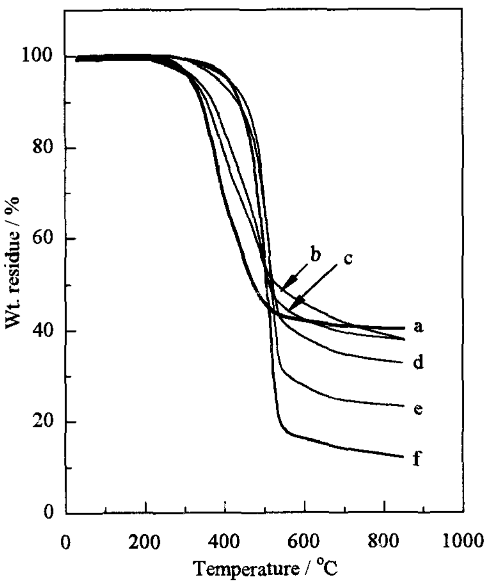


Fig. 9. TGA of (a) polyBa and polymer alloys from Ba/PISi(OH) with ratios of (b) 90/10, (c) 80/20, (d) 50/50, (e) 30/70 and (f) 0/100.

4. Thermal stability of the polymer alloys

Thermal stability of the polymer alloys from both Ba/PISi and Ba/PISi(OH) was examined by TGA, and the TGA profiles are shown in **Figs. 8** and **9**, respectively. The decomposition temperature (defined as 5% weight loss temperature) of polyBa was clearly improved by alloying with both types of poly(imide-siloxane). **Fig. 10** shows the tendency of this improvement. The inclusion of poly(imide-siloxane)s in polyBa was found very effective to enhance the thermal stability, although effect of poly(imide-siloxane)s on the thermal stability is somewhat different from type to type. In both cases, small amount (10- 20%) of poly(imide-siloxane) was very effective on the improvement of the thermal stability (by 30-50°C for decomposition temperature).

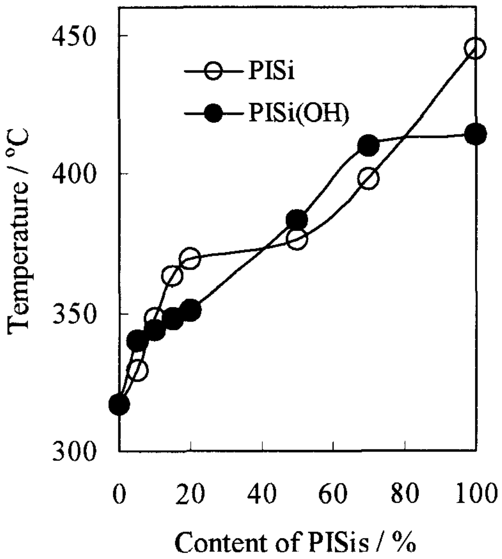


Fig. 10. Effect of PISis content on the initial decomposition temperature of the polymer alloys from Ba/PISi and Ba/PISi(OH).

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