

Organic-inorganic hybrids from polybenzoxazine and polysiloxane prepared by sol-gel process: effect of different type of polysiloxane

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[Introduction]

Polybenzoxazine is synthesized by the ring-opening polymerization reaction of cyclic benzoxazine monomer, and is recognized as a new class of phenolic resin. Scheme 1 shows the structure of typical benzoxazine monomer, Ba, which is prepared from bisphenol-A, aniline, and formaldehyde and its thermoset, PBa. The advantages of polybenzoxazine are inexpensive raw materials, ease of polymerization process which does not need strong catalyst and does not generate byproduct, high mechanical properties, and high thermal stability^[1,2].

However, the shortcoming of polybenzoxazine is lack of flexibility. Therefore, various efforts aiming to enhance the toughness of polybenzoxazine have been done^[3,4]. One approach is by mixing with heat resistant and flexible polymer. Polysiloxane is a unique heat resistant and flexible inorganic polymer. Most widely used polysiloxane is polydimethylsiloxane (PDMS). Recently, we succeeded in the performance improvement of polybenzoxazine (PBa) by hybridization with PDMS prepared through sol-gel process^[5]. Herein, we prepared a series of PBa-polysiloxane hybrids using different type of polysiloxanes (PSis), such as PDMS, polymethylphenylsiloxane (PMPS), and polydiphenylsiloxane (PDPS) (Scheme 2). The polysiloxane with phenyl group (PMPS and PDPS) is expected to enhance the compatibility with PBa by phenyl-phenyl interaction between PBa and polysiloxane. The preparation and properties of the hybrids was studied.

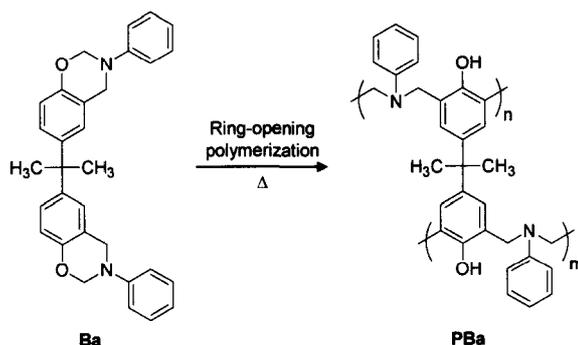
[Experiments]

Preparation of PBa-PSi hybrids by sol-gel method: A typical experimental procedure for PBa-PDMS hybrid is described below. Ba (1.20 g, 5.26 mmol) was dissolved in THF (8 ml). DEDMS (0.60 g, 4.05 mmol), water (0.146 g, 8.1 mmol), and *p*-toluenesulfonic acid (PTS) (0.045 g, 0.24 mmol) were added successively into the solution, and stirred for 24 h at room temperature affording transparent dark yellow solution. The solution was cast on a glass plate. Thermal curing was done at first 60 °C for 12 h, and then step wise from 80 to 220 °C affording opaque brown PBa-PDMS(20%) hybrid film with thickness about 0.2 mm. The content of PDMS was determined by assuming the complete conversion of DEDMS to PDMS. PBa-PMPS, and PBa-PDPS hybrids were prepared in the similar way by using diethoxymethylphenylsilane (DEMPS) and diethoxydiphenylsilane (DEDPS) as polysiloxane monomer, respectively.

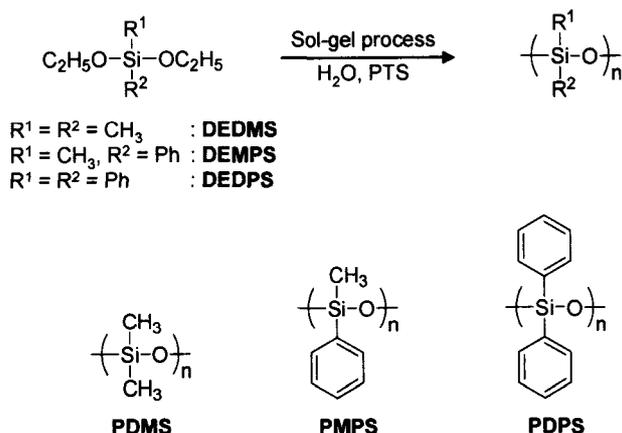
[Results and Discussion]

Preparation of PBa-PSi hybrids

The PBa-PSi hybrids were prepared by the ring-opening polymerization of Ba and the sol-gel process of diethoxysilanes. DEDMS, DEMPS and DEDPS were used as polysiloxane precursors. Ba, polysiloxane precursor, water and PTS catalyst were mixed at various ratios in THF and stirred at room temperature for 24 h affording transparent dark yellow solution. The solution was cast on a glass plate followed by gradual thermal curing up to 220 °C affording PBa-PSi hybrid films.



Scheme 1. Synthesis of PBa



Scheme 2. Synthesis of polysiloxanes by sol-gel process.

Figure 1 shows the photographs of the cured PBa-PSi hybrids films. Homogeneous PBa-PDMS hybrids were obtained up to 20 wt% of PDMS content and the flexibility increased with increasing of PDMS content (Fig. 1(a)). The films can be bent easily. However, at ca. 30 wt% of PDMS content, severe macroscopic phase separation occurred and the film became brittle.

Homogeneous PBa-PMPS hybrids were obtained up to 40 wt% of PMPS content which is higher than PDMS content and the flexibility increased with increasing PMPS content (Fig. 1(b)). The higher PMPS content at PBa-PMPS than PDMS content at PBa-PDMS hybrid is because of the phenyl-phenyl interaction of PMPS and PBa. Homogeneous PBa-PDPS hybrid films were obtained up to 40 wt% of PDPS content and the flexibility increased with increasing PDPS content (Fig. 1(c)). However, the films were not flexible enough to be bent.

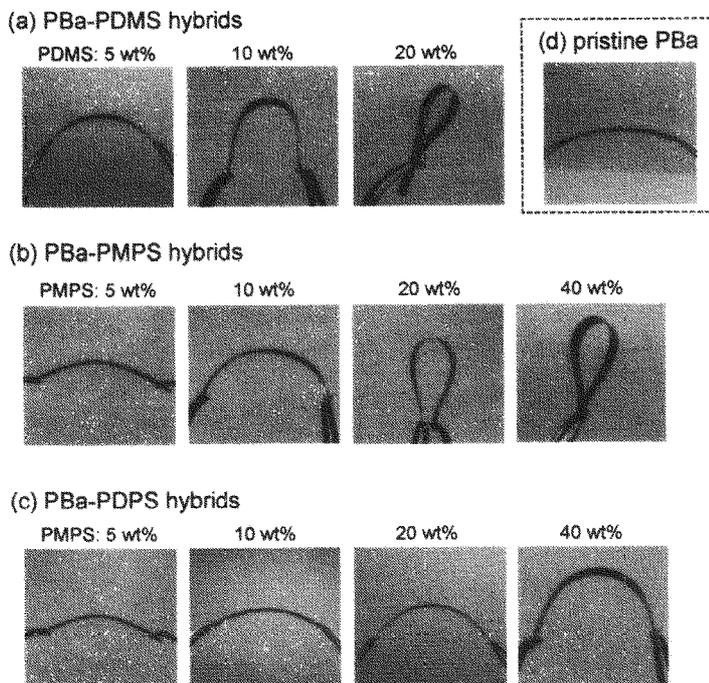


Figure 1. Photographs of PBa-polysiloxane hybrids with different type of polysiloxane at various polysiloxane contents (a-c). The photograph of pristine PBa film is also shown in the dotted square (d). The size of bent film is 4 mm x 50 mm x ca. 200 μ m.

Tensile properties of PBa-PSi hybrids

The tensile properties of the hybrid films were examined and the results are summarized in Table 1. Pristine PBa reveals high modulus, but low elongation at break. All the PBa-PSi hybrids revealed lower modulus, but higher tensile strength and higher elongation at break than PBa because of the toughening effect of the in-situ formed PSis. PBa-PDMS revealed higher tensile strength and elongation at break than PBa because of PDMS that acts as a toughener. PBa-PMPS has even higher tensile strength than PBa-PDMS because of high toughening effect of PMPS and phenyl-phenyl interaction. PBa-PDPS has higher tensile strength and elongation at break than PBa, however, lower than PBa-PMPS because of lower toughening effect of rigid PDPS. PBa-PMPS hybrid reveals the optimum enhancement of tensile properties.

Viscoelastic properties of PBa-PSi hybrids

Viscoelastic properties of PBa-PSi hybrids were examined by DMA (Fig. 3). Pristine PBa reveals high glass transition temperature (T_g) at 159 $^{\circ}$ C from E'' . The PBa-PDMS hybrid film revealed two T_g 's corresponding to the PDMS at low temperature and PBa at high temperature suggesting phase separation in the hybrid. Interestingly, the T_g of PBa shifts to higher temperature in the presence of in-situ formed PDMS. It is considered that crosslink density of PBa was increased because of the plasticizing effect of PDMS during polymerization of Ba. PBa-PMPS also revealed two T_g corresponding to the PMPS at low temperature and PBa at high temperature. The T_g of PBa in the PBa-PMPS is even higher than T_g of PBa in the PBa-PDMS because of high plasticizing effect of PMPS and

Table 1. Tensile properties of PBa-PSi hybrids

Code	Modulus (GPa)	Strength (MPa)	Elongation (%)
PBa	3.3	35	1.5
PBa-PDMS(5%)	2.8	38	2.6
PBa-PDMS(10%)	2.6	42	3.5
PBa-PDMS(20%)	2.2	48	4.4
PBa-PMPS(5%)	3.0	40	2.0
PBa-PMPS(10%)	2.8	46	3.1
PBa-PMPS(20%)	2.7	50	4.2
PBa-PMPS(40%)	2.2	55	5.7
PBa-PDPS(5%)	3.0	37	2.1
PBa-PDPS(10%)	2.8	42	2.2
PBa-PDPS(20%)	2.7	44	2.3
PBa-PDPS(40%)	2.5	52	3

phenyl-phenyl interaction. PBa-PDPS revealed one T_g at high temperature corresponding to PBa. The T_g of PBa in the PBa-PDPS was higher than pristine PBa, but lower than PBa-PMPS because of lower plasticizer effect of rigid PDPS than PMPS during polymerization of PBa.

Thermal stabilities of PBa-PSi hybrids

The thermal stability of PBa-PSi hybrids was examined by TGA (Fig. 4). Pristine PBa reveals high thermal stability and char yield. PBa-PSi hybrids reveal higher thermal stability and char yield than PBa because of high thermal stability and flame retardancy of PSis. PBa-PMPS has lower thermal stability, but higher char yield than PBa-PDMS because of higher content of rigid aromatics. PBa-PDPS has higher thermal stability and char yield than PBa-PMPS because of high rigid aromatic content.

[Conclusion]

PBa-polysiloxane hybrids with different type of polysiloxanes were successfully prepared by the ring-opening polymerization of Ba and sol-gel process of diethoxysilanes. Phenyl group enhanced the compatibility of polysiloxane with PBa. PMPS revealed the optimum enhancement of toughness and T_g of PBa. PDPS revealed the optimum flame retardancy of PBa.

[References]

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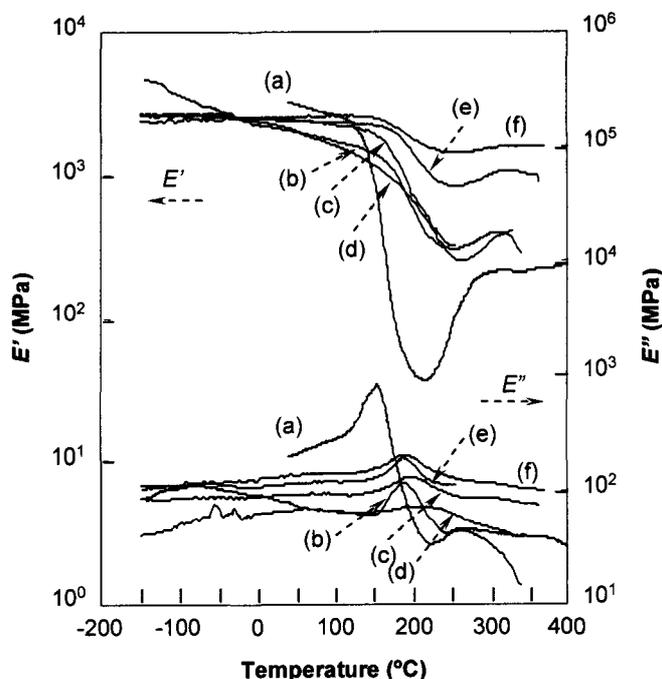


Figure 3. DMA results of pristine PBa (a), PBa-PDMS(20%) (b), PBa-PMPS(20%) (c), PBa-PMPS(40%) (d), PBa-PDPS(20%) (e) and PBa-PDPS(40%) (f) hybrid.

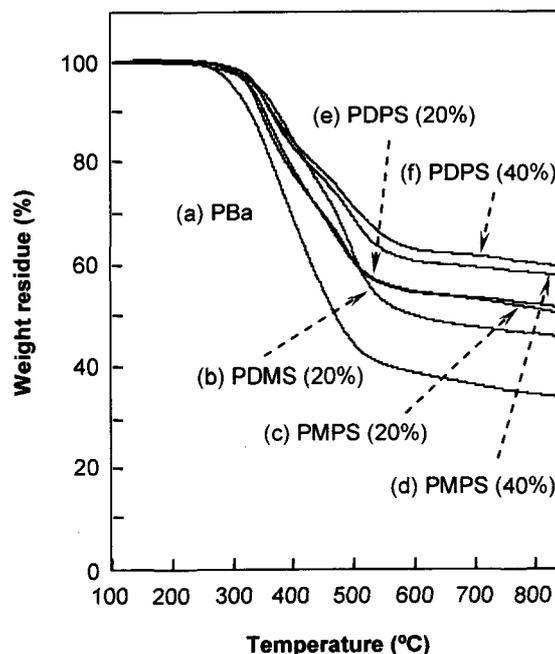


Figure 4. TGA curves of pristine PBa (a), PBa-PDMS(20%) (b), PBa-PMPS(20%) (c), PBa-PMPS(40%) (d), PBa-PDPS(20%) (e), and PBa-PDPS(40%) (f).