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Performance enhancement of polybenzoxazine by hybridization with polysiloxane

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ABSTRACT

Polybenzoxazine–polydimethylsiloxane (PBa–PDMS) hybrids were successfully prepared in situ by the ring-opening polymerization of benzoxazine (Ba) and the sol–gel process of diethoxydimethylsilane (DEDMS). The reaction conditions were optimized, and homogeneous opaque hybrid films were obtained up to 13 wt% of PDMS content by using *p*-toluenesulfonic acid as the catalyst for sol–gel process. The domain size of PDMS in the PBa matrix was examined by SEM. The tensile strength and elongation at break of the PBa–PDMS hybrid films were higher than those of pristine PBa, because of the toughening effect of PDMS. Dynamic viscoelastic analysis showed that the glass transition temperature of the hybrid was also higher than that of pristine PBa. Moreover, the decomposition temperatures and weight residue at 850 °C increased with the increase of PDMS content as evidenced by thermogravimetric analysis.

1. Introduction

Polybenzoxazine obtained by the ring-opening polymerization of cyclic benzoxazine monomer has been developed as a new type of phenolic resin [1–3]. Chemical structures of a typical benzoxazine monomer, 6,6′-(1-methylethylidene)-bis-(3,4-dihydro-3-phenyl-2*H*-1,3-benzoxazine) (Ba), and polymer of Ba (PBa) are shown in Scheme 1. Polybenzoxazines have excellent thermal and non-flammable properties like traditional phenolic resins. Polybenzoxazines also have excellent properties that are not found in the traditional phenolic resins, such as molecular design flexibility, low moisture absorption, and no byproduct release upon curing [2–8]. However, PBa has a brittle property, which limits its application. Toughening of brittle PBa has been successfully achieved by adding polymers such as liquid rubber [9], polyurethane [10] and polyimide [11].

Polydimethylsiloxane (PDMS) is an inorganic polymer, which shows not only flexibility but also unique properties such as good thermal and oxidative stability, low surface energy, high hydrophobicity, high gas permeability, and good biocompatibility [12–14]. However, PDMS shows low dispersability in an organic polymer matrix because of its incompatibility with organic polymers. An effective method to improve the compatibility and dispersability of PDMS is copolymerization. Previously, we reported the successful introduction of PDMS component into the PBa matrix by using poly(imide-siloxane) copolymer [15].

In this paper, we report a novel and versatile method for introducing PDMS into PBa expecting the enhancement of both the thermal and mechanical properties of PBa. For the preparation of PBa–PDMS hybrids, we attempted two approaches: blending method and sol–gel method. In the blending method, we used commercial pre-formed PDMS in combination with the in situ ring-opening polymerization of Ba. In the sol–gel method, we utilized diethoxydimethylsilane (DEDMS) as PDMS precursor. The sol–gel process of DEDMS consists of two steps, hydrolysis of DEDMS to generate silanol groups and condensation of the silanol groups, and generally results in cyclic PDMS oligomers [13]. The low molecular weight PDMS is expected to reveal high compatibility with organic polymers. To our knowledge, polymer hybridization using PDMS prepared by sol–gel process has never been reported. In order to obtain homogeneous hybrid films with high PDMS content, the reaction conditions were investigated. Influence of the PDMS content on the mechanical and thermal properties of the hybrids was also examined.

2. Experimental

2.1. Materials

Bisphenol-A, aniline, hydrochloric acid (ca. 36%, HCl), *p*-toluenesulfonic acid (PTS), and aqueous ammonia solution (28%) from Kishida Chemicals (Japan), paraformaldehyde from Merck, DEDMS

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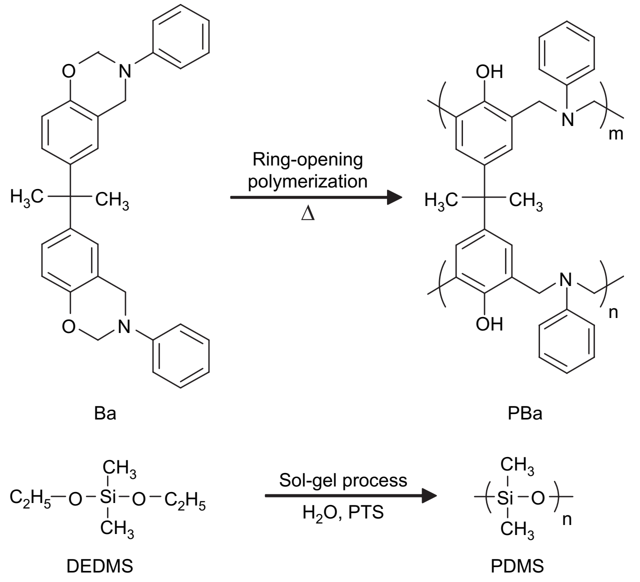

Scheme 1. Synthetic route of polybenzoxazine (PBa, top) and polydimethylsiloxane (PDMS, bottom).

and tetrahydrofuran (THF) from Wako Pure Chemical (Japan) were used as-received. Commercial PDMS (hydroxy terminated, $M_n = 550$) was used as-received from Aldrich. Bifunctional benzoxazine monomer, Ba, was synthesized from bisphenol-A, aniline and paraformaldehyde following the reported method [4]. The crude reaction product was dissolved in ether, washed with 3 N aqueous sodium hydroxide, and dried at room temperature under vacuum to afford Ba as white powder.

2.2. Measurements

IR spectra were obtained using Jasco FT/IR-420 spectrometer. Fluorescent X-ray analyses of hybrid films were performed on a RIGAKU ZSX100e fluorescent X-ray spectrometer. The samples were dried under vacuum at 50 °C for 1 h before measurement. Scanning electron microscopy (SEM) studies were performed using a Hitachi S-4800 scanning electron microscope with the accelerating voltage of 3 kV and emission current of 10 μA. The fracture surfaces of the films were sputter-coated with Pt–Pd under an electric current of 15 mA at 6 Pa for 60 s. Thermogravimetric analysis (TGA) was performed with Rigaku Thermo Plus 2TG-DTA TG8120 at a heating rate of 5 °C/min under argon atmosphere. Differential scanning calorimetry (DSC) was conducted using Rigaku Thermo Plus 2 DSC8230 at a heating rate of 10 °C/min under nitrogen. Dynamic viscoelastic measurements were conducted on Orientec Automatic Dynamic Viscoelastomer Rheovibron model DDV-01FP at 35 Hz at a heating rate of 4 °C/min. Tensile properties were recorded with Imada Seisaku-sho Model SV-3 at a crosshead speed of 1 mm/min using films of about 2 cm long. The tensile properties of each sample were determined from an average of at least 10 tests.

2.3. Preparation of PBa film

Ba (1.5 g, 3.24 mmol) and PTS (0.045 g, 0.24 mmol) were dissolved in THF (8 ml) and kept at room temperature with stirring for 24 h to afford transparent bright yellow solution. The solution was cast on a glass plate and dried at room temperature for 24 h. Further drying was carried out at 60 °C for 12 h followed by thermal curing at 80, 100, 120, 140, 160, and 180 °C for 2 h each in an air-circulating oven. Final curing was carried out at 200 and 220 °C for 1 h each.

2.4. Preparation of PBa–PDMS hybrid by blending method

Ba (1.42 g, 6.23 mmol) was dissolved in THF (8 ml) in a glass bottle equipped with magnetic stirrer at room temperature. The commercial PDMS (0.08 g) was added to the solution. Then, the mixture was cast on a glass plate, and dried at room temperature for 24 h and at 60 °C for 12 h. Gradual thermal curing was conducted at 80, 100, 120, 140, 160, and 180 °C for 2 h each, and then at 200 and 220 °C for 1 h each in an air-circulating oven to give PBa–PDMS hybrid with 5 wt% of PDMS content.

2.5. Preparation of PBa–PDMS hybrids by sol–gel method

The PBa–PDMS hybrids were prepared in situ by combining the ring-opening polymerization of Ba and sol–gel process of DEDMS. A typical experimental procedure for PBa–PDMS (13%) 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 PTS (45 mg, 0.24 mmol) were added successively into the solution, and were stirred for 24 h at room temperature to afford transparent dark yellow solution, which was then cast on a glass plate. The cast

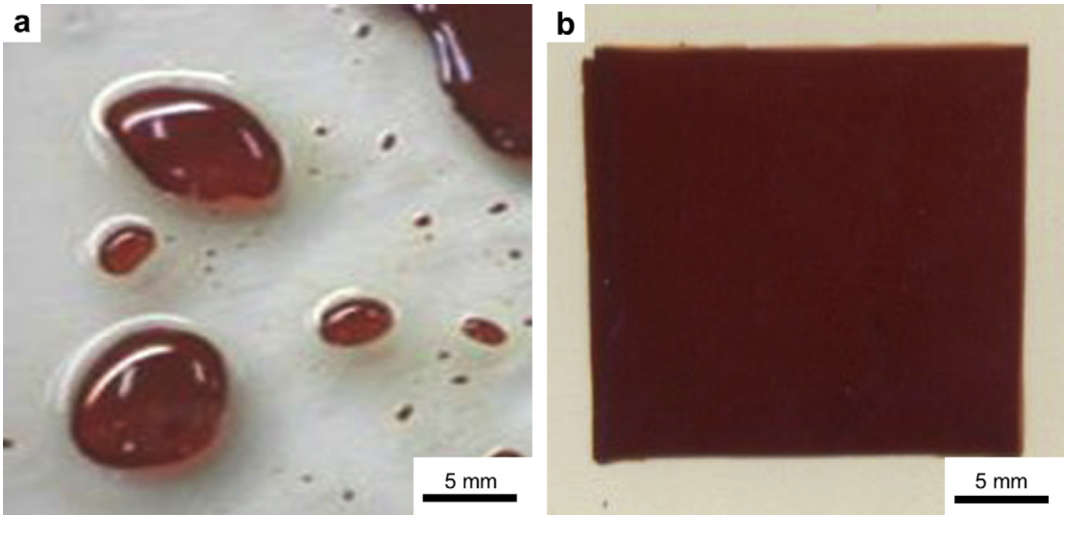

Fig. 1. Photographs of PBa–PDMS hybrids after thermal curing by blending ((a) PDMS: 5 wt%) and sol–gel ((b) PDMS: 7 wt%, thickness: ca. 90 μm) methods.

Table 1
Formulation for the preparation of PBa–PDMS hybrids

Run	Code	Ba/g (mmol)	DEDMS/g (mmol)	H_2O/g (mmol)	PTS/g (mmol)	Theoretical PDMS content/wt%	PDMS content[a]/wt%
1	PBa	1.50 (3.24)	–	–	–	–	–
2	PBa–PDMS (7%)	1.35 (2.92)	0.3 (2.03)	0.073 (4.06)	0.022 (0.12)	10	6.8
3	PBa–PDMS (13%)	1.20 (2.59)	0.6 (4.05)	0.146 (8.10)	0.045 (0.24)	20	12.8
4	PBa–PDMS (25%)	1.05 (2.27)	0.9 (6.08)	0.219 (12.16)	0.067 (0.35)	30	ca. 25[b]

[a] Determined by fluorescent X-ray analysis.
[b] Macroscopic phase separation occurred.

film was dried at room temperature for 24 h and at 60 °C for 12 h, and then was cured at 80, 100, 120, 140, 160, and 180 °C for 2 h each and at 200 and 220 °C for 1 h each in an air-circulating oven, affording PBa–PDMS (13%) hybrid film. PBa–PDMS hybrids with various PDMS contents were prepared in the similar way.

3. Results and discussion

3.1. Preparation of PBa–PDMS hybrid by blending method

We attempted to prepare PBa–PDMS hybrid at 5 wt% PDMS content using commercial PDMS ($M_n = 550$) by blending method. The hybrid was obtained by casting the THF solution mixture of Ba and the commercial PDMS on a glass plate followed by curing. However, macroscopic phase separation occurred (Fig. 1a), indicating that even the low molecular weight PDMS at low content does not disperse well into the PBa matrix.

Then, we tried to introduce PDMS component into PBa utilizing in situ formation of PDMS by the sol–gel process of diethoxydimethylsilane (DEDMS) which consists of hydrolysis and condensation (Scheme 1) [12,13]. We expected that the homogeneous hybrid films will be obtained when the ring-opening polymerization of Ba and the sol–gel process of DEDMS take place in a synchronized manner.

3.2. Preparation of PBa–PDMS hybrids by sol–gel method

First, we examined the influence of catalyst on the sol–gel process of DEDMS during the curing of Ba. Although the sol–gel reaction did not proceed by using aq. NH_3 as catalyst, the reaction proceeded by using acid catalysts such as aqueous HCl and *p*-toluenesulfonic acid (PTS). Though severe formation of foams was observed by using HCl, hybrid films without foams were obtained by using PTS as a catalyst. Therefore, we used PTS as the sol–gel catalyst for further hybrids preparation. Ba, DEDMS, water and PTS were mixed at various ratios in THF as shown in Table 1, and were stirred at room temperature for 24 h. The solution was cast on a glass plate followed by thermal curing up to 220 °C, affording PBa–PDMS hybrid. It could be possible that DEDMS evaporates during the cure process, resulting in lower content of PDMS in the hybrid films than the theoretical content calculated from the feed content. To estimate the exact content of the PDMS in the hybrid

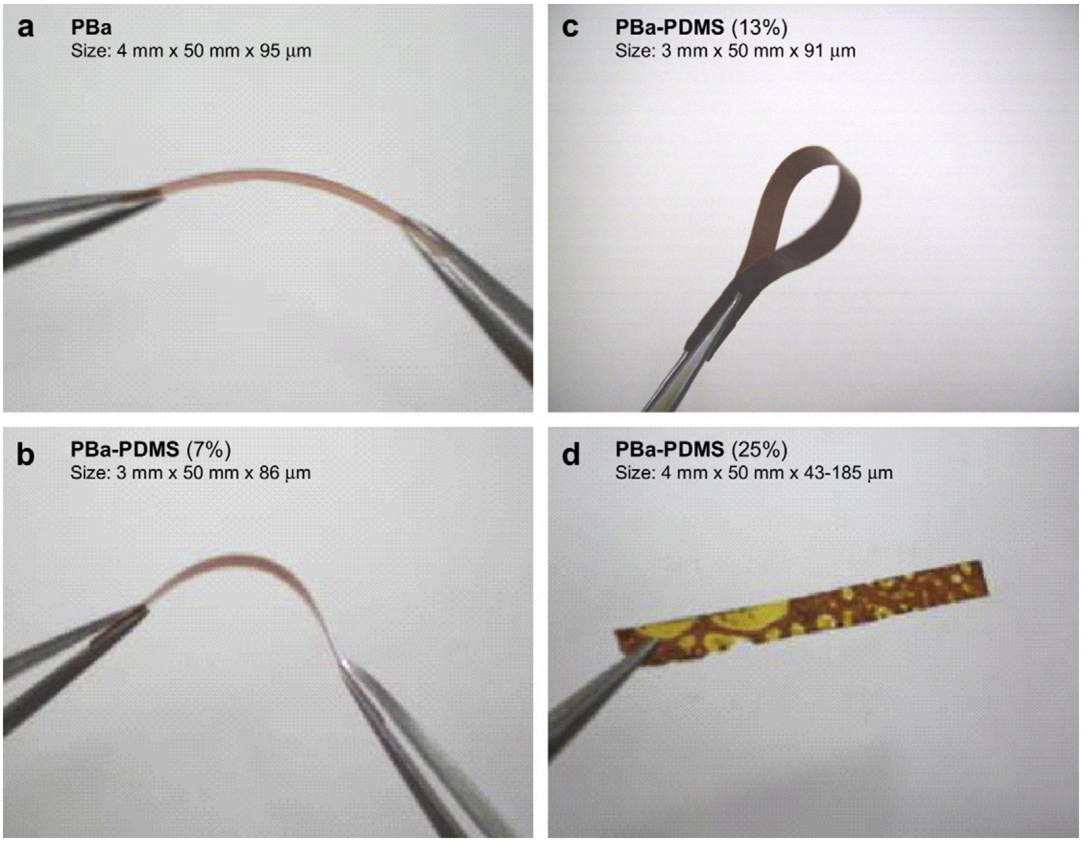

Fig. 2. Photographs of pristine PBa (a) and PBa–PDMS hybrids prepared by sol–gel method at 7 (b), 13 (c) and 25 wt% (d) PDMS contents.

film, fluorescent X-ray analyses were performed. As a result, the PDMS content calculated based on the C/Si ratio was found to be lower than that of the theoretical value, as shown in Table 1. Interestingly, hybrid with 7 wt% PDMS was obtained without apparent phase separation (Fig. 1b and run 2 in Table 1). Furthermore, homogeneous hybrid films were obtained up to 13 wt% PDMS content and the flexibility increased with the increase of PDMS content (Fig. 2). However, at ca. 25 wt% PDMS content, macroscopic phase separation occurred and the film became brittle. The sample codes are abbreviated in Table 1 using the PDMS content such as PBa–PDMS (7%).

It is known that the ring-opening polymerization of benzoxazine is catalyzed by acidic compounds [2,3]. Since PTS was used as the sol–gel catalyst, the influence of PTS on the ring-opening polymerization of Ba during cure was monitored by DSC (Fig. 3). The DSC curves of PBa and PBa–PDMS (13%) hybrid after the removal of solvent at 60 °C for 24 h showed broad exothermic peak started at ca. 198 °C with peak maximum at 234 °C and 9 cal/g as exothermic heat corresponding to the ring-opening polymerization of Ba influenced by sol–gel process of DEDMS (Fig. 3a). It should be noted that the exotherm of Ba in the presence of PTS started at 165 °C, with peak maximum at 212 °C and 21 cal/g as exothermic heat, lower temperature range than that of pristine Ba without PTS that shows a sharp exothermic peak at ca. 250 °C [16]. The decrease of peak maximum indicates that PTS used as the catalyst of sol–gel process also acts as the catalyst for the polymerization of Ba. Furthermore, the decrease of exothermic heat by adding of PTS also indicates that the polymerization proceeded even at 60 °C due to the catalytic effect of PTS. The exothermic amount gradually decreased with the increase of heat treatment temperature and disappeared after heat treatment at 220 °C

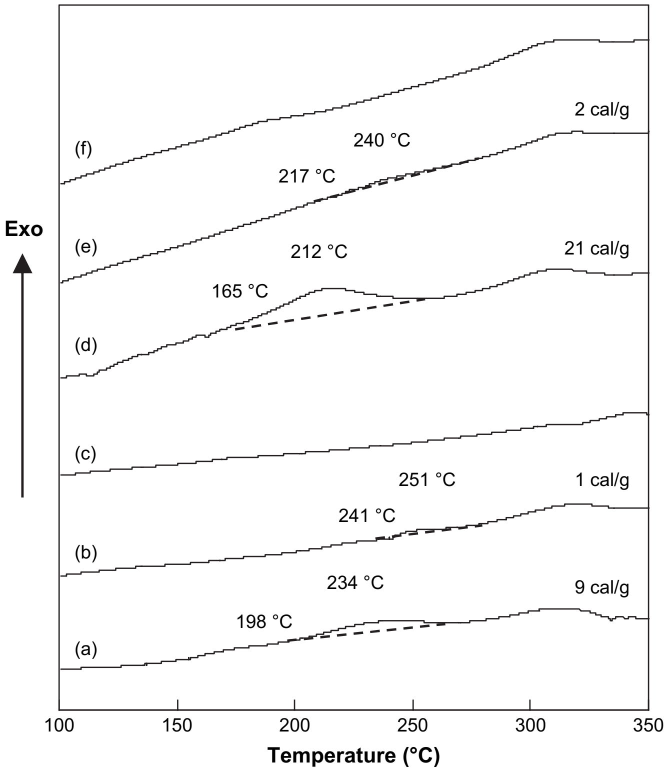

Fig. 3. DSC thermograms of PBa–PDMS (13%) hybrid after thermal treatment at 60 (a), 180 (b), 220 °C (c), and PBa with PTS after thermal treatment at 60 (d), 180 (e) and 220 °C (f).

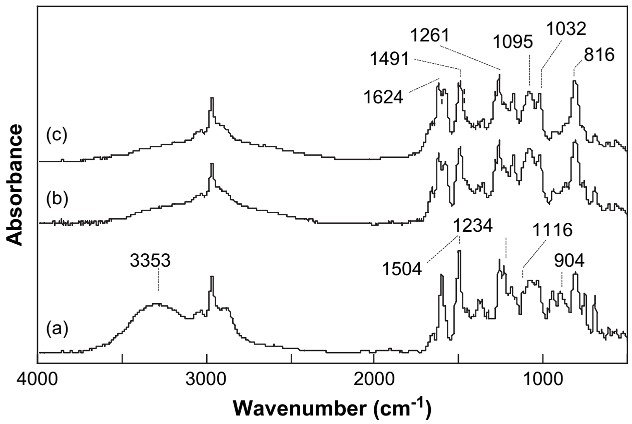

Fig. 4. IR spectra of PBa–PDMS (13%) hybrid after thermal treatment at 60 (a), 180 (b) and 220 °C (c).

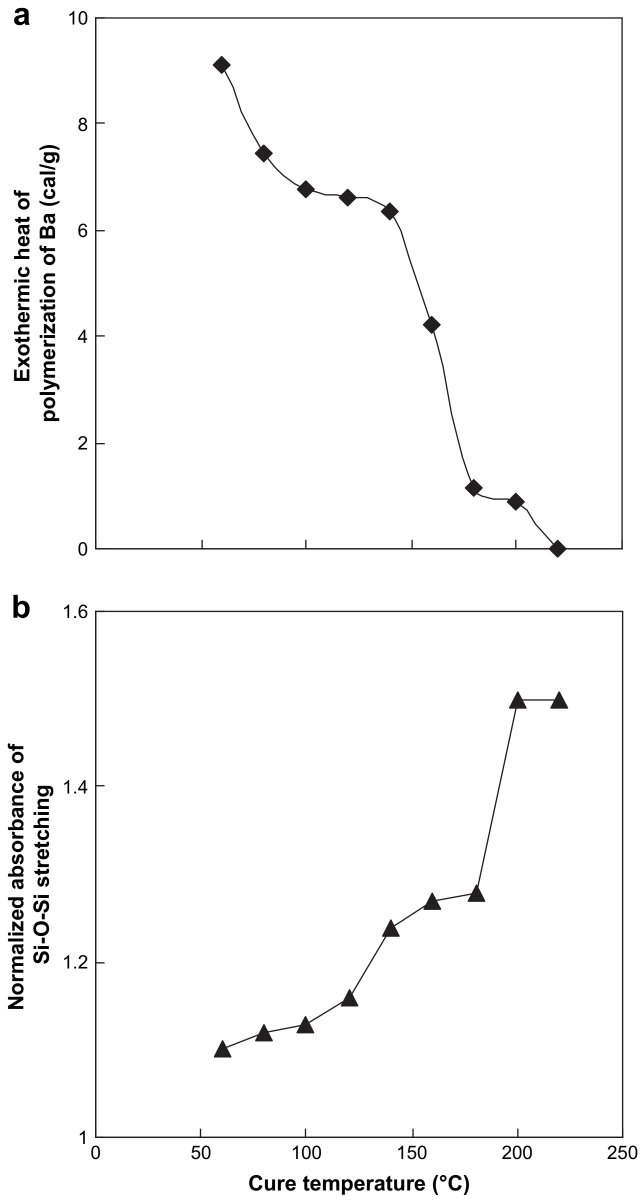

Fig. 5. Progress of ring-opening polymerization of Ba and sol–gel reaction of DEDMS in PBa–PDMS (13%) hybrid. Changes in the exothermic heat determined by DSC (a) and in the normalized absorbance of Si–O–Si stretching from IR spectra (b) with curing temperature.

(Fig. 3c and f), indicating that the reaction of Ba completed even at the cure as low as 220 °C.

The curing phenomena of the hybrid films were also monitored by IR. Fig. 4 shows the IR spectra of PBa–PDMS (13%) hybrid after various cure stages. The absorptions corresponding to Ba were observed at 1234 (C–O–C stretching mode of oxazine ring) and 1504 cm^{-1} (trisubstituted benzene ring) (Fig. 4a). These absorptions decreased with the progress of cure and almost disappeared after the cure at 180 °C, while the absorptions corresponding to PBa appeared at 1491 (tetrasubstituted of benzene ring) indicating that the ring-opening polymerization of Ba proceeded. These IR changes with temperature are in accord with the DSC changes with temperature. Introduction of PDMS into the hybrid was confirmed by the absorptions of Si–CH_3 (816 and 1261 cm^{-1}) and Si–O–Si (1032 and 1095 cm^{-1}) stretching. Interestingly, the Si–O–Si absorption increased with the progress of cure, while absorptions of Si–OH (904 cm^{-1}) and Si–OC (1116 cm^{-1}) decreased. These results suggest that the condensation of DEDMS that increase the molecular weight of PDMS occurred during the cure. The decrease of absorption corresponding to O–H stretching of PDMS chain end (3353 cm^{-1}) with the increase of cure temperature also supports the progress of condensation during the cure.

In Fig. 5a is shown the decrease of the exothermic amount from DSC that shows progress of ring-opening polymerization of Ba, and in (b) is shown the increase of the normalized absorbance of Si–O–Si stretching from IR that shows progress of sol–gel reaction of DEDMS with curing temperature. The plots clearly show that both reactions proceeded at the same time during the cure. It is probably due to the synchronized reactions of the ring-opening polymerization of Ba and the sol–gel process of DEDMS that we could get homogeneous hybrid films without macroscopic phase separation, even though the interaction between PBa and PDMS is very weak.

3.3. Morphology of PDMS in the PBa–PDMS hybrids

The PBa–PDMS hybrid films were opaque and homogeneous without macroscopic phase separation. We investigated the morphology of the in situ formed PDMS in the hybrid films by SEM. The SEM images of fracture surface of hybrid films are shown in Fig. 6. Hemispheres and holes were observed on the continuous matrix of PBa. The average diameter of spherical phases increased with the increase of PDMS content from 1.25 to 1.90 μm for the hybrids with 7 and 13% PDMS content, respectively, suggesting that

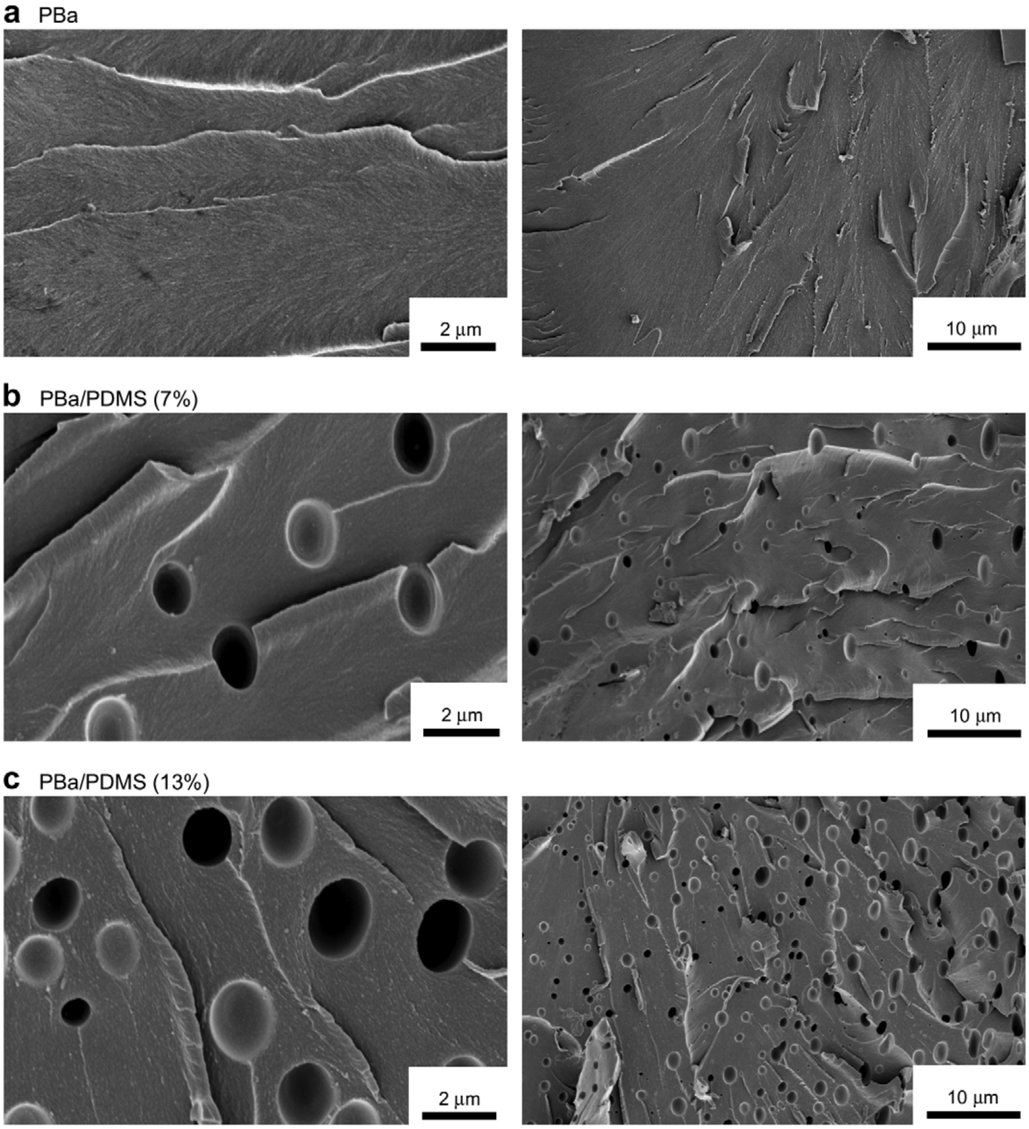

Fig. 6. SEM images of pristine PBa (a) and PBa–PDMS hybrids at 7 (b) and 13 wt% (c) PDMS contents.

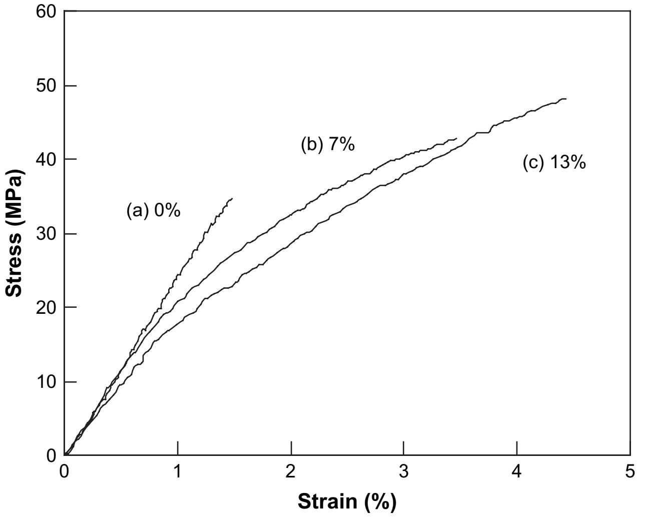

Fig. 7. Stress–strain curves of pristine PBa, and PBa–PDMS hybrids at 7 (b) and 13 wt% of PDMS content.

Table 2
Tensile properties of PBa and PBa–PDMS hybrids

Code	PDMS content (wt%)	Modulus (GPa)	Strength (MPa)	Elongation (%)
PBa	0	3.3 ± 0.16	35 ± 2.12	1.5 ± 0.33
PBa–PDMS (7%)	7	2.6 ± 0.15	42 ± 1.58	3.5 ± 0.23
PBa–PDMS (13%)	13	2.2 ± 0.13	48 ± 1.62	4.4 ± 0.17

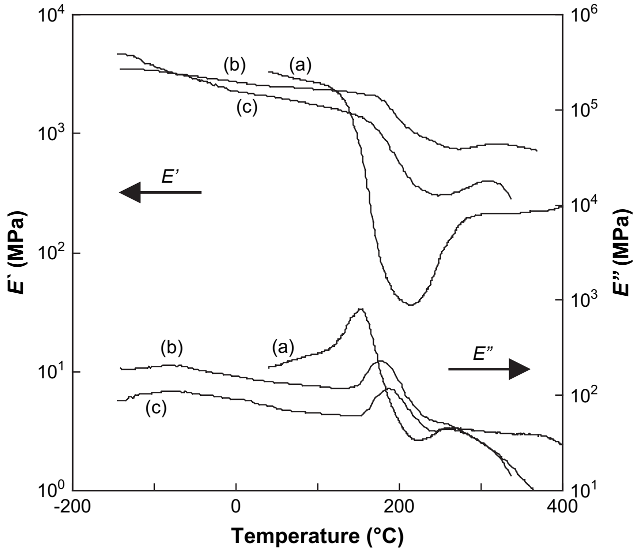

Fig. 8. DMA of pristine PBa, and PBa–PDMS hybrids at 7 (b) and 13 wt% of PDMS content.

the spherical phases correspond to PDMS. This result indicates that phase separation at micrometer-scale occurred in the hybrid.

Moreover, the fracture morphology of pristine PBa showed smooth surface due to the lack of plastic deformation. The fracture morphology of the hybrids showed rough surface and some amounts of deformation lines correspond to the increasing plastic deformation. The plastic deformation reduces the crack growth rate, thus, increases the toughness.

3.4. *Tensile properties of PBa–PDMS hybrids*

The tensile properties of the hybrid films were examined. Fig. 7 shows stress–strain curves of various PBa–PDMS hybrid films and the results are summarized in Table 2. Pristine PBa possesses high modulus, but low elongation at break, corresponding to the brittleness of the film. As the content of PDMS increases, tensile modulus slightly decreases but tensile strength and elongation at break increase, clearly showing that the in situ formed PDMS acts as a toughener.

3.5. *Viscoelastic properties of PBa–PDMS hybrids*

Viscoelastic properties of PBa–PDMS hybrids were investigated by DMA. The storage modulus (E') and loss modulus (E'') are plotted in Fig. 8 and the results are summarized in Table 3. The E' value at room temperature decreased by the addition of PDMS. The tendency is in good agreement with the results from the tensile test mentioned above. The glass transition temperatures (T_gs) were determined from the maxima of E'' and $\tan\delta$. The hybrid films revealed two T_gs, lower T_g (−63 to −72 °C from E'') and higher T_g (176–185 °C from E'') corresponding to the PDMS and PBa components, respectively, suggesting that phase separation at micrometer-scale occurred in the hybrid as was shown by SEM. Surprisingly, in spite of the addition of PDMS that has low T_g, T_g of Ba component shifts to higher temperature with the increase of PDMS content. The decrease of E' above T_g was also suppressed. These results suggest that crosslink density of PBa increased by the addition of PDMS, demonstrating that the in situ formed PDMS also behaves as a plasticizer during the polymerization of Ba.

3.6. *Thermal stabilities of PBa–PDMS hybrids*

Thermogravimetric analysis (TGA) of the hybrids was examined (Fig. 9 and Table 3). The 5 and 10% weight loss temperatures increased with increasing PDMS content. In fact, it was reported that properly prepared PDMS possesses excellent thermal stability and can be used at 450 °C for 2 h as a high temperature liquid phase for gas chromatography [17]. Therefore, the introduction of PDMS resulted in the improvement of thermal stability of the hybrid. Moreover, the weight residue at 850 °C of hybrids increased with the increase of the PDMS content, indicating that the flame retardancy is also improved.

Table 3
Thermal properties of PBa and PBa–PDMS hybrids

Code	PDMS content (wt%)	DMA[a]					TGA		
		E' at 30 °C (GPa)	T_g from E'' (°C)		T_g from $\tan\delta$ (°C)		T_5 (°C)	T_{10} (°C)	Weight residue at 850 °C (%)
			Lower	Higher	Lower	Higher			
PBa	0	3.2	–	159	–	174	302	327	31
PBa–PDMS (7%)	7	2.5	−63	176	−55	189	325	352	40
PBa–PDMS (13%)	13	2.1	−72	185	−61	210	339	368	46

[a] DMA data were collected at a resolution of 2 °C.

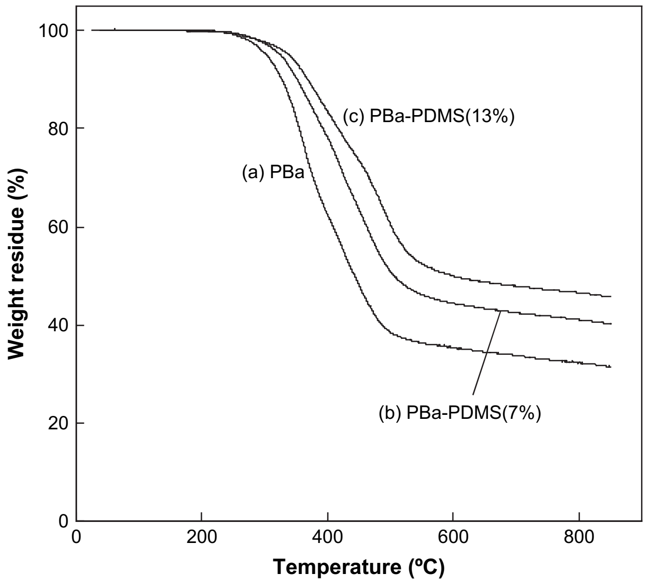

Fig. 9. TGA curves of pristine PBa (a), PBa–PDMS hybrids with 7 (b) and 13 wt% (c) of PDMS content under argon atmosphere at a heating rate 5 °C/min.

4. Conclusions

We have successfully prepared the hybrids of PBa and PDMS by synchronizing two types of reactions: the ring-opening polymerization of Ba and the sol–gel process of DEDMS. By using this method, it became possible to introduce PDMS as fine particles into network polymers affording homogeneous and tough hybrid films. Because of the toughening effect of PDMS, the hybrid revealed better tensile strength and elongation at break than pristine PBa. PDMS also acted as a plasticizer, and the crosslink density of PBa increased, affording hybrids having higher T_g. Moreover, the decomposition temperature and weight residue at 850 °C increased with increasing PDMS content. Thus, introduction of PDMS into PBa leads to the improvement of not only mechanical properties but also thermal properties.

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