Polymer 50 (2009) 5959–5969

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Effect of pendant group of polysiloxanes on the thermal and mechanical properties of polybenzoxazine hybrids

Hosta Ardhyananta [a], Takehiro Kawauchi [a], Hanafi Ismail [b], Tsutomu Takeichi [a,*]

[a] Department of Materials Science, Toyohashi University of Technology, Tempaku-cho, Toyohashi, 441-8580, Japan
[b] School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, Seri Ampangan, 14300 Nibong Tebal, Pulau Pinang, Malaysia

ARTICLE INFO

Article history:
Received 8 July 2009
Received in revised form
1 October 2009
Accepted 3 October 2009
Available online 9 October 2009

Keywords:
Polybenzoxazine
Polysiloxane
Sol–gel process

ABSTRACT

Polybenzoxazine (PBa) was successfully hybridized with polysiloxanes by synchronizing two reactions; ring-opening polymerization of benzoxazine (Ba) and sol–gel process of diethoxysilanes. Diethoxydimethylsilane, diethoxymethylphenylsilane, and diethoxydiphenylsilane were used as precursors for the formation of polydimethylsiloxane (PDMS), polymethylphenylsiloxane (PMPS), and polydiphenylsiloxane (PDPS), respectively. The effect of pendant group of polysiloxane on the optical, mechanical, and thermal properties of PBa–polysiloxane hybrids was studied. The progress of sol–gel process was confirmed by IR, ^{1}H NMR and size exclusion chromatography. Opaque PBa–PDMS hybrid films were obtained up to 15 wt% of PDMS content, corresponding to the phase separation with 1–2 μm domain size of PDMS as observed from the scanning electron microscope. Meanwhile, transparent PBa–polysiloxane hybrid films were obtained up to 29 wt% for PMPS and 36 wt% for PDPS, which revealed no apparent domain of PMPS and PDPS, indicating high compatibility of the polysiloxanes with PBa. Dynamic viscoelastic analysis (DMA) of the PBa–PDMS hybrid revealed two glass transition temperatures corresponding to PDMS and PBa components, while the DMA of the PBa–PMPS and PBa–PDPS hybrids revealed only one glass transition temperature. The tensile strength and elongation at break of the hybrid films increased with increasing polysiloxane content. Thermogravimetric analysis revealed high weight residue at 850 °C for PBa–polysiloxanes with phenyl group.

1. Introduction

Polybenzoxazine, synthesized by the ring-opening polymerization reaction of cyclic benzoxazine monomer, is recognized as an interesting new class of phenolic resin. Polybenzoxazine has a Mannich base bridge (–CH_2–N(R)–CH_2–), meanwhile, traditional phenolic has a methylene bridge (–CH_2–) for connecting the phenolic moieties [1,2]. Scheme 1 shows the structure of typical benzoxazine monomer, Ba, which is prepared by reacting bisphenol-A, aniline, and formaldehyde and its thermoset, PBa. The advantages of polybenzoxazine are molecular-design flexibility, inexpensive raw materials, ease of polymerization process which does not need strong catalyst and does not generate byproducts, excellent dimensional stability during polymerization, high thermomechanical properties, high resistance against chemical solvents, and low dielectric properties [1–5].

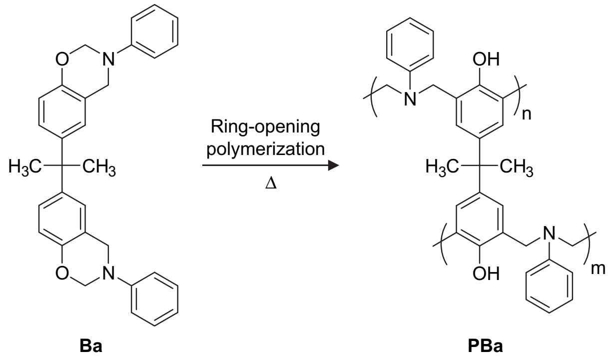
The shortcoming of polybenzoxazine is lack of flexibility. Therefore, various efforts have been done to enhance the toughness of polybenzoxazine. Generally, the toughness enhancement of polybenzoxazine can be classified into two approaches. First approach is molecular design of the benzoxazine monomer such as linear aliphatic diamine-based benzoxazine [6] and high molecular weight polybenzoxazine precursors [7]. Second approach is alloying with flexible polymers such as liquid rubber [8,9], polyurethane [10,11], poly(ε-caprolactone) [12], polyimide [13], and poly(imide-siloxane)s [14]. The alloying is a versatile approach to enhance the toughness of polybenzoxazine by simply mixing with an available flexible polymer. Polydimethylsiloxane (PDMS) is a unique inorganic polymer which has considerable high thermal stability [15–17], high oxidative stability [15,18], and high flexibility [19–22]. However, PDMS shows phase separation when blended with organic polymers such as epoxy [20] and polyimide [23] because of its incompatibility with organic polymers.

Previously, by utilizing sol–gel process for the formation of PDMS [24,25], we successfully prepared polybenzoxazine–polydimethylsiloxane (PBa–PDMS) hybrids which revealed enhancement of not only toughness but also thermal properties with the increase of PDMS content [26]. However, the introduction of PDMS into PBa for more than 30 wt% showed severe macroscopic phase separation because of incompatibility between PDMS and PBa.

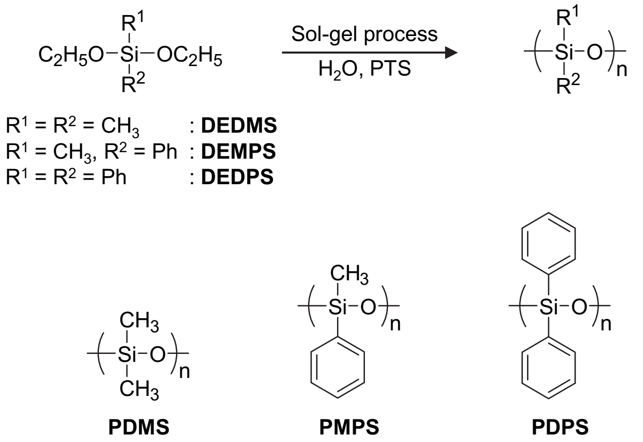
---

* Corresponding author. Tel.: +81 532 44 6815; fax: +81 532 48 5833.
E-mail address: takeichi@tutms.tut.ac.jp (T. Takeichi).

0032-3861/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2009.10.001



Scheme 1. Synthesis of PBa.



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

Hence, the PDMS content in the hybrids was limited. Polysiloxane having phenyl group as the pendant is expected to enhance the compatibility between PBa and polysiloxane because of the π–π interaction between the phenyl groups of the two components, and high polysiloxane content in the PBa–polysiloxane hybrids can be achieved. Herein, we report a series of PBa–polysiloxane hybrids using different type of polysiloxanes containing phenyl groups such as polymethylphenylsiloxane (PMPS) and polydiphenylsiloxane (PDPS), and compared the properties of the hybrids with that of PBa–PDMS hybrid. The polysiloxanes were prepared by sol–gel process (Scheme 2).

2. Experimental

2.1. Materials

Bisphenol-A, aniline, and *p*-toluenesulfonic acid (PTS) from Kishida Chemicals (Japan), paraformaldehyde from Merck, diethoxydimethylsilane (DEDMS), diethoxymethylphenylsilane (DEMPS), diethoxydiphenylsilane (DEDPS) and tetrahydrofuran (THF) from Wako Pure Chemical (Japan) were used as received. Bifunctional benzoxazine monomer, Ba, was synthesized from bisphenol-A, aniline and paraformaldehyde following the reported method [2].

2.2. Measurements

^{1}H NMR spectra were recorded on a Varian Mercury 300 (300 MHz) instrument. Size exclusion chromatography (SEC) was measured with JASCO instrument with refractive index detection. THF was used as an eluent at a flow rate of 1.0 ml/min at 40 °C. Two polystyrene gel columns (Shodex KF806LX2) were used. A calibration curve was made with polystyrene (PSt) standard to determine molecular weights and their distribution. IR spectra were obtained using JASCO FT/IR-420 spectrometer. Optical transmission spectra were measured with air as the reference using JASCO V-550, UV/VIS spectrophotometer. Differential scanning calorimetry (DSC) was conducted using Rigaku Thermo Plus 2 DSC8230 at a heating rate of 10 °C/min under nitrogen. Scanning electron microscopy (SEM) studies were performed using a Hitachi S-4800, field emission scanning electron microscope (FE-SEM) with the accelerating voltage of 3 kV and emission current of 10 μA. The FE-SEM is equipped with energy dispersed X-ray spectrometry (EDX), Horiba Emax Energy EX-250. The fracture surfaces of the hybrid films were sputter-coated with Pt–Pd under an electric current of 15 mA at 6 Pa for 60 s and then subjected to SEM observation. 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. 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. Thermogravimetric analysis (TGA) was performed with Rigaku Thermo Plus

Table 1
Formulation for the preparation of polybenzoxazine–polysiloxanes hybrid by sol–gel process.[a]

Run	Code	Feed composition		H_2O/g (mmol)	PTS/g (mmol)	Polysiloxane theoretical content[b]/wt%
		Ba/g (mmol)	Diethoxysilane/g (mmol)			
1	PBa	1.50 (3.24)	–	–	–	–
2	PBa–PDMS (5%)	1.43 (3.09)	DEDMS 0.15 (0.95)	0.034 (1.90)	0.011 (0.06)	5
3	PBa–PDMS (10%)	1.35 (2.92)	0.30 (2.03)	0.073 (4.06)	0.023 (0.12)	10
4	PBa–PDMS (20%)	1.20 (2.59)	0.60 (4.05)	0.146 (8.10)	0.046 (0.24)	20
5	PBa–PDMS(30%)	1.05 (2.27)	0.90 (6.08)	0.219 (12.16)	0.067 (0.35)	30
6	PBa–PMPS (5%)	1.43 (3.09)	DEMPS 0.11 (0.51)	0.018 (1.02)	0.006 (0.03)	5
7	PBa–PMPS (10%)	1.35 (2.92)	0.23 (1.10)	0.040 (2.20)	0.013 (0.07)	10
8	PBa–PMPS (20%)	1.20 (2.59)	0.46 (2.21)	0.080 (4.42)	0.025 (0.13)	20
9	PBa–PMPS (30%)	1.05 (2.27)	0.69 (3.31)	0.119 (6.62)	0.038 (0.20)	30
10	PBa–PMPS (40%)	0.9 (1.94)	0.92 (4.41)	0.159 (8.82)	0.049 (0.26)	40
11	PBa–PMPS (50%)	0.75 (1.62)	1.15 (5.51)	0.198 (11.02)	0.063 (0.33)	50
12	PBa–PDPS(5%)	1.43 (3.09)	DEDPS 0.09 (0.35)	0.013 (0.7)	0.004 (0.02)	5
13	PBa–PDPS (10%)	1.35 (2.92)	0.21 (0.76)	0.027 (1.52)	0.009 (0.05)	10
14	PBa–PDPS (20%)	1.20 (2.59)	0.41 (1.51)	0.054 (3.02)	0.017 (0.09)	20
15	PBa–PDPS (30%)	1.05 (2.27)	0.62 (2.27)	0.082 (4.54)	0.027 (0.14)	30
16	PBa–PDPS (40%	0.9 (1.94)	0.83 (3.03)	0.109 (6.06)	0.034 (0.18)	40
17	PBa–PDPS (50%)	0.75 (1.62)	1.04 (3.79)	0.136 (7.58)	0.044 (0.23)	50

[a] Molar ratio: diethoxysilane:H_2O = 1:2, diethoxysilane:PTS = 1:0.06. THF: 8 ml.
[b] Calculated by assuming complete conversion of Ba into PBa and diethoxysilane into polysiloxane.

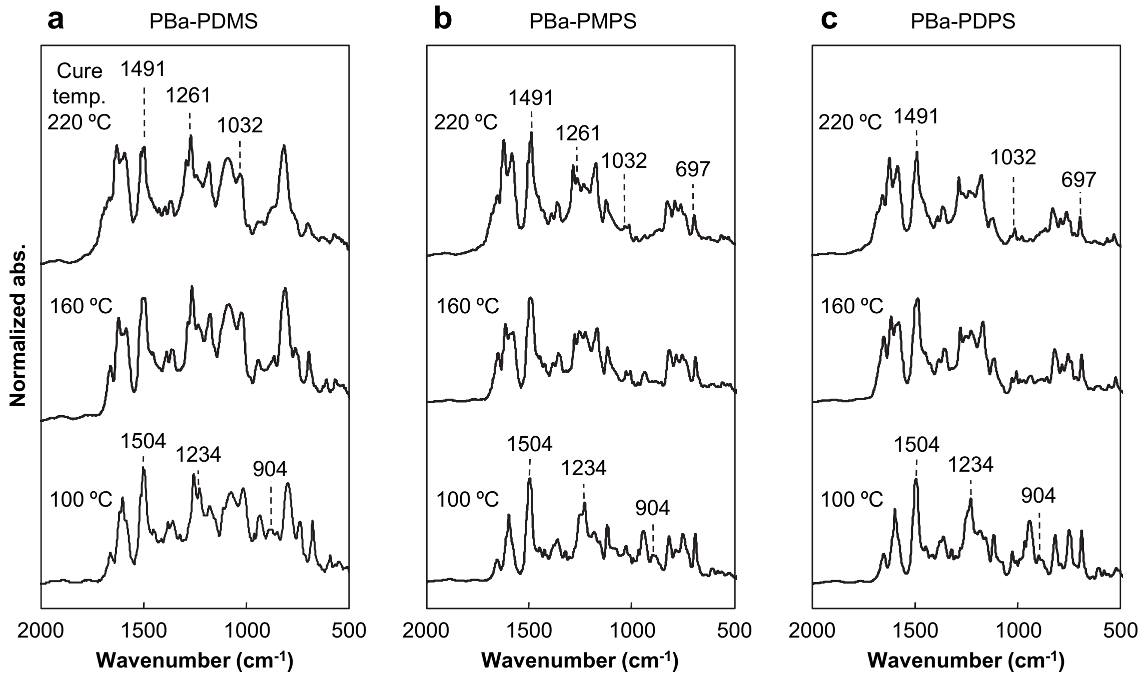


Fig. 1. IR spectra of PBa–PDMS(20%) (a), PBa–PMPS(20%) (b) and PBa–PDPS(20%) hybrids after curing at 100, 160 and 220 °C. The absorbance was normalized using an absorption around 1500 cm^{-1} corresponding to aromatic ring.

2TG-DTA TG8120 at a heating rate of 5 °C/min under argon atmosphere.

2.3. Preparation of polybenzoxazine–polysiloxane hybrids by sol–gel method

A typical experimental procedure for PBa–PDMS hybrid is described below. Ba (1.20 g, 2.60 mmol) was dissolved in THF (8 ml) in a glass bottle equipped with magnetic stirrer at room temperature. DEDMS (0.60 g, 4.05 mmol) and water (0.146 g, 8.1 mmol) were added successively into the solution affording transparent yellowish solution. The amount of water was equal to two molar of diethoxysilane. The addition of excess amount of water such as 4 molar ratio resulted in void formation in the cured hybrid film. PTS was then added into the solution as the acid catalyst for the sol–gel process of diethoxysilane [26] and the color turned into orange because of the oligomerization reaction of Ba due to the acidic catalyst [27]. The amount of PTS was equal to 0.06 M of diethoxysilane. The addition of excess amount of PTS such as 0.1 molar ratio resulted in the formation of orange precipitate during stirring. After the addition of PTS, the solution was stirred for 24 h at room temperature. Then, the solution was cast on a glass plate that was pretreated with dichlorodimethylsilane. The cast film was dried at room temperature for 24 h and at 60 °C for 12 h. Thermal cure was done 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, affording PBa–PDMS(20%) hybrid films with thickness in the range of 0.1–0.3 mm. The less stirring and curing time resulted in unflat and inhomogeneous color appearance of the cured hybrid film. The appearance of final cured hybrid films was ranging from opaque brown to transparent reddish color relating to different type of polysiloxane.

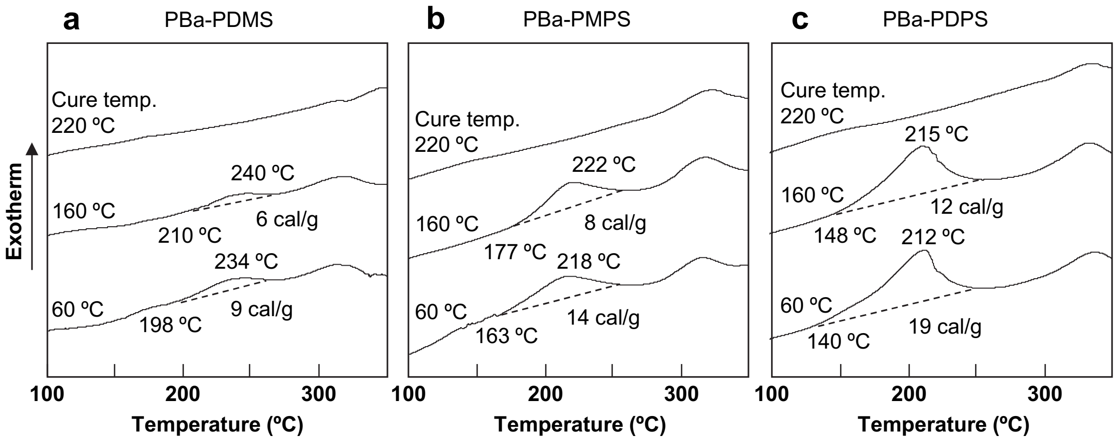


Fig. 2. DSC thermograms of PBa–PDMS(20%) (a), PBa–PMPS(20%) (b), and PBa–PDPS(20%) (c) after curing at 60, 160 and 220 °C.

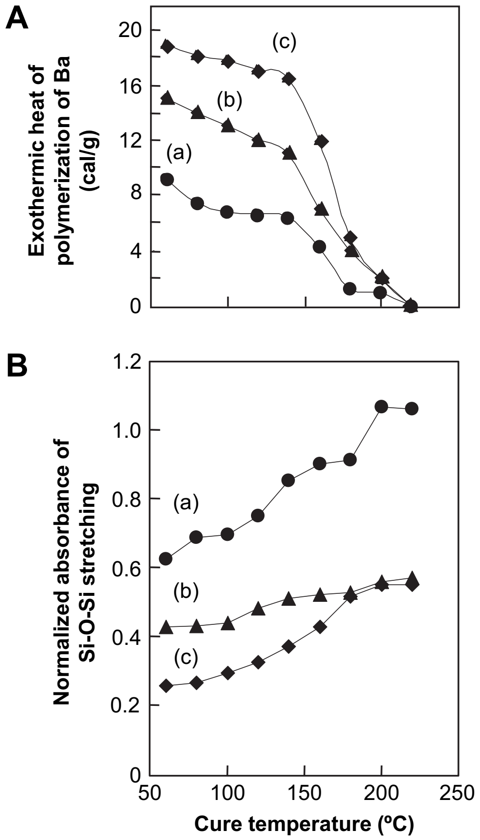


Fig. 3. Progress of ring-opening polymerization of Ba and sol–gel reaction of diethoxysilanes in PBa–PDMS(20%) (a), DEMPS in PBa–PMPS(20%) (b), and DEDPS in PBa–PDPS(20%) (c) hybrid. Changes in exothermic heat determined by DSC (A) and in the normalized absorbance of Si–O–Si stretching from IR spectra (B) with curing temperature.

Pristine PBa, PBa–PMPS and PBa–PDPS hybrids were prepared in the similar way by using DEMPS and DEDPS as polysiloxane monomer, respectively.

2.4. Sol–gel reaction of diethoxysilane without Ba

To investigate the progress of the sol–gel reaction during the preparation of hybrid, the sol–gel reaction of diethoxysilane was carried out without Ba. Typical procedure for the sol–gel reaction of DEDMS is as follows. DEDMS (0.60 g, 4.05 mmol) was mixed with water (0.146, 8.1 mmol) and PTS (45 mg, 0.24 mmol) in THF. The solution was stirred at room temperature for 24 h, affording transparent colorless solution. The obtained solution was divided into two samples. One sample was dried under vacuum and subjected to NMR and SEC analyses. Another sample was cast on a glass plate and cured 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. The product was characterized by NMR and SEC. The sol–gel process of DEMPS and DEDPS were performed in the similar way. Evaporation of the solvent afforded transparent colorless oily liquid in the case of PDMS and PMPS, and white solid in the case of PDPS.

3. Results and discussion

3.1. Preparation of polybenzoxazine–polysiloxanes hybrid by sol–gel process

PBa–polysiloxane hybrids with different type of polysiloxanes were prepared by the ring-opening polymerization of Ba and the sol–gel process of different type of diethoxysilanes. The formulation for the preparation of hybrids is shown in Table 1. The feed of Ba and diethoxysilane was determined by assuming complete conversion of Ba into PBa and diethoxysilane into polysiloxane. The sample code is abbreviated based on the feed of the polysiloxane in the hybrids. For example, PBa–PDMS (10%) stands for PBa–PDMS hybrid at 10 wt% of PDMS feed.

First of all, we attempted to observe the effect of preparation method of PBa–polysiloxane hybrids by modifying the sequence of the addition of Ba relative to diethoxysilane. In the first preparation method, we mixed diethoxysilanes, water and PTS and stirred for 24 h. Then, Ba was added to the solution and continued stirring for an additional for 24 h. The PBa–polysiloxane hybrid films after curing at 220 °C revealed that PBa–PDMS system showed macroscopic phase separation, in which PBa and PDMS phases were apparently observed as reddish solid and oily transparent colorless liquid, respectively. Meanwhile, PBa–PMPS and PBa–PDPS system showed homogeneous films. In the second preparation method, we mixed Ba, diethoxysilane, water and PTS at the same time. After the 220 °C treatment, homogeneous hybrid films were obtained without macroscopic phase separation. Therefore, all the hybrids with various polysiloxane contents were prepared using the second method.

We investigated the progress of reaction during the curing of PBa–polysiloxane by IR and DSC. Fig. 1 shows IR spectra of the hybrids at 20 wt% of polysiloxane feed after various cure stages. The absorptions corresponding to Ba monomer were observed at 1234 cm^{-1} (C–O–C stretching mode of oxazine ring) and 1504 cm^{-1} (trisubstituted benzene ring) after curing at 100 °C [27]. These absorptions decreased with the progress of cure, while the absorptions corresponding to PBa appeared at 1491 cm^{-1} (tetrasubstituted of benzene ring), indicating that the ring-opening polymerization of Ba proceeded during the thermal curing.

The introduction of PDMS into the hybrid was confirmed by the absorptions of Si–OH (904 cm^{-1}), Si–CH_3 (1261 cm^{-1}) and Si–O–Si (1032 cm^{-1}) stretching [19,28] (Fig. 1a). The Si–O–Si absorption increased with the progress of cure, while the absorptions of Si–OH decreased, showing the formation of PDMS [24]. The introduction of PMPS was confirmed by the absorptions of Si-phenyl (697 cm^{-1}), Si–OH (904 cm^{-1}), Si–CH_3 (1263 cm^{-1}), and Si–O–Si (1032 cm^{-1}) stretching [18,29] (Fig. 1b). The introduction of PDPS was confirmed by the absorptions of Si-phenyl (697 cm^{-1}), Si–OH (904 cm^{-1}), Si–O–Si (1032 cm^{-1}) stretching [30] (Fig. 1c). The Si–OH stretching of polysiloxanes was also observed at 3353 cm^{-1} (See, Fig. S1 in Supporting Information). The Si–O–Si absorption of the polysiloxane with phenyl group in the hybrids increased with the progress of cure (Fig. 1), while absorption peaks of Si–OH decreased (Fig. S1), suggesting that the condensation of the diethoxysilanes occurred during thermal curing. The Si–O–Si relative peak intensity of PMPS and PDPS was smaller than that of PDMS because of the lower silicon content at the same polysiloxane weight ratio. At 20 wt% of PDMS, PMPS and PDPS feed, the silicon feed is 7.5, 4.1, and 2.8 wt%, respectively.

Fig. 2 shows the DSC curves of PBa–polysiloxane hybrids at 20 wt% of polysiloxane feed after various thermal cure stages to confirm the ring-opening polymerization of Ba. Pristine Ba showed sharp exothermic peak starting at 223 °C with maximum at 249 °C and exothermic heat of 69 cal/g corresponding to the ring-opening polymerization [27]. In the presence of PTS, Ba after treated at 60 °C showed broad exothermic peak starting at 165 °C with maximum at 212 °C. The lowering of the exothermic temperature is due to the acceleration of the ring-opening polymerization by the acidic PTS catalyst [26]. The exothermic heat also decreased to 21 cal/g by the addition of PTS, indicating that the polymerization proceeded even at 60 °C. PBa–PDMS (20%) in the presence of PTS showed

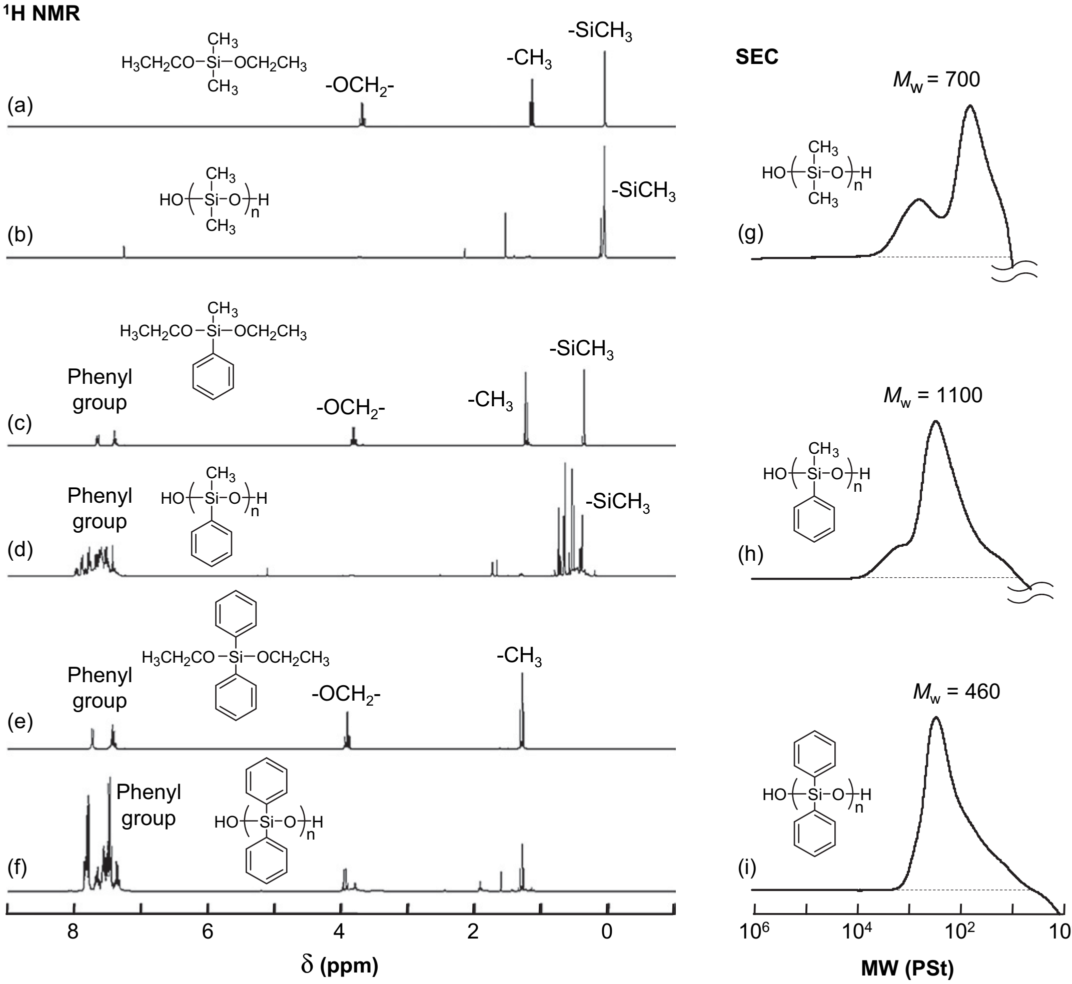


Fig. 4. ^{1}H NMR spectra (a–f) of diethoxysilanes and SEC curves (g–i) of the oligomers prepared by mixing with PTS in THF at room temperature for 24 h.

exothermic peak maximum at 234 °C and exothermic heat of only 9 cal/g (Fig. 2a), much lower than Ba with PTS. PBa–PMPS (20%) and PBa–PDPS (20%) also showed exothermic peak starting at lower temperature and small amount of exothermic heat (Fig. 2b and c), showing that the ring-opening polymerization of Ba was also accelerated by the presence of polysiloxanes. Polysiloxanes might have played as an acidic catalyst based on the silanol groups or as a plasticizer.

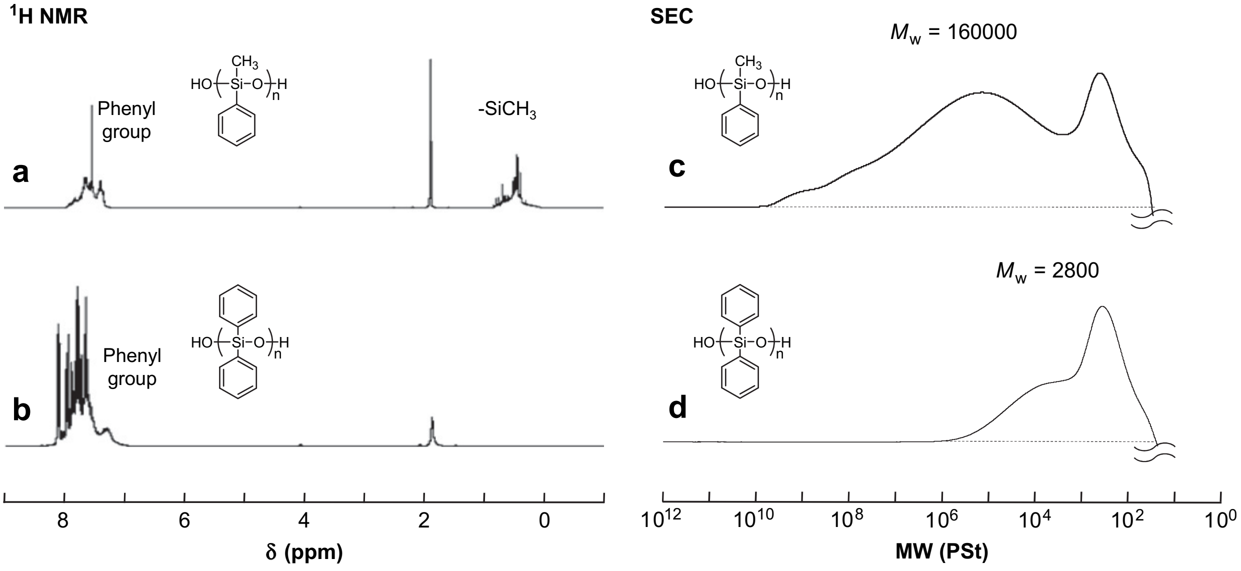


Fig. 5. ^{1}H NMR spectra (a, b) and SEC curves (c, d) of polysiloxanes after thermal treatment at 220 °C for 1 h.

Table 2
Polybenzoxazine–polysiloxanes hybrid films prepared by sol–gel process.

Run	Code	Polysiloxane theoretical content/wt%	Polysiloxane actual content[a]/wt%	Si content[a]/wt%	Film quality[b]	Transmittance at 700 nm[c]/%
1	PBa	–	–	–	R	99
2	PBa–PDMS(5%)	5	3	3.9	R	61
3	PBa–PDMS (10%)	10	6	7.0	F	59
4	PBa–PDMS (20%)	20	14	10.6	F	55
5	PBa–PDMS(30%)	30	24	0.9	PS	–
6	PBa–PMPS (5%)	5	4	2.6	R	92
7	PBa–PMPS (10%)	10	9	6.9	R	91
8	PBa–PMPS (20%)	20	14	8.1	F	90
9	PBa–PMPS (30%)	30	29	12.2	F	88
10	PBa–PMPS (40%)	40	35	0.9	F	36
11	PBa–PMPS (50%)	50	45	1.7	PS	–
12	PBa–PDPS(5%)	5	4	4.4	R	94
13	PBa–PDPS (10%)	10	9	7.4	R	93
14	PBa–PDPS (20%)	20	15	10.2	F	92
15	PBa–PDPS (30%)	30	25	3.9	F	91
16	PBa–PDPS (40%)	40	36	7.0	F	89
17	PBa–PDPS (50%)	50	47	10.6	PS	–

[a] Determined by EDX of the hybrid films after cured at 220 °C.
[b] R: rigid, F: flexible, PS: macroscopic phase separation.
[c] Determined by UV–vis measurement.

The exothermic heat of PBa–polysiloxane hybrids gradually decreased with the increase of cure temperature and completely disappeared after 220 °C cure, suggesting the completion of the polymerization reaction of Ba.

The progress of two different reactions, ring-opening polymerization and sol–gel process, with the progress of cure was followed by DSC and IR, respectively. Fig. 3A shows the decrease of the exothermic heat from DSC. The plots clearly show the progress of the ring-opening polymerization of Ba with the cure temperature, especially between 150 and 200 °C. The condensation reaction of polysiloxanes was followed by normalizing the Si–O–Si absorbance (1032 cm^{-1}) to the benzene absorbance (1491 cm^{-1}) from IR

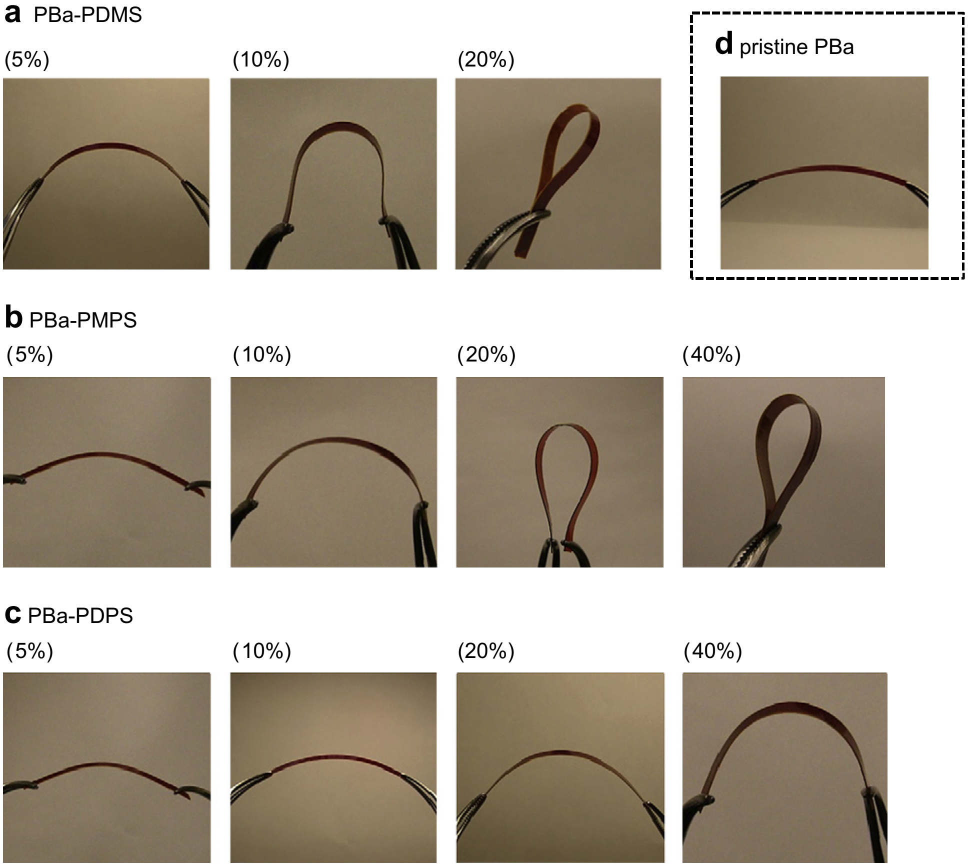


Fig. 6. Photographs of PBa–polysiloxane hybrids with various polysiloxane contents (a–c). The photograps of pristine PBa film is also shown in the dotted square (d). The size of bended films is 4 mm × 50 mm × ca. 150 μm.

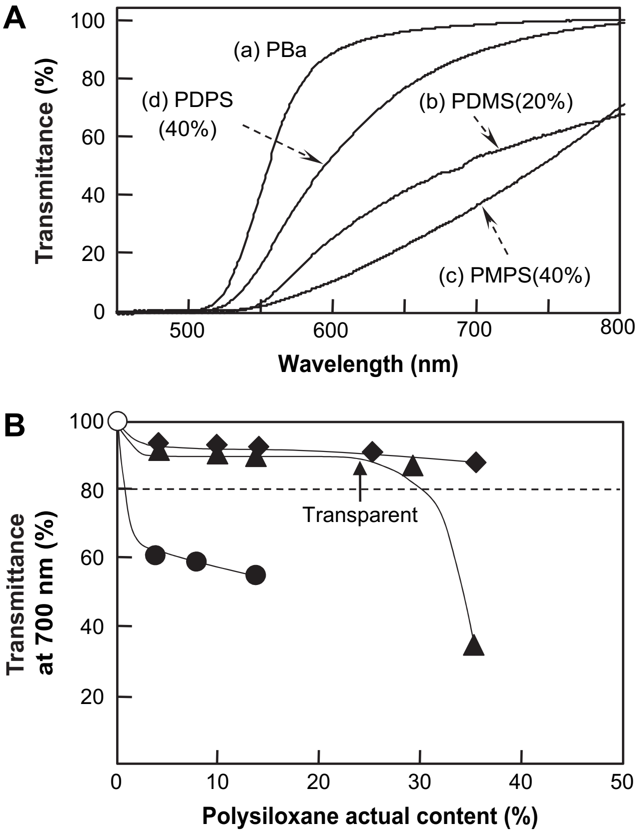


Fig. 7. (A) UV–vis spectra of pristine PBa (a), PBa–PDMS(20%) (b), PBa–PMPS(40%) (c) and PBa–PDPS(40%) (d) films. (B) Plots of transmittance at 700 nm of the PBa–polysiloxane hybrids against the polysiloxane contents;ˆ: pristine PBa, ●: PBa–PDMS hybrid, ▲: PBa–PMPS hybrid, ◆: PBa–PDPS hybrid. The film thickness was ca. 150 μm. See Table 2.

(Fig. 3b). We see clearly that the normalized absorptions of Si–O–Si increased with increasing the cure temperature, showing the progress of the condensation of polysiloxanes. The normalized Si–O–Si absorbance for PBa–PMPS and PBa–PDPS are lower than that for PBa–PDMS. This is possibly because of the high benzene absorbance from the additional Si-phenyl content in the PMPS and PDPS. The plots in Fig. 3A and 3B showed that both reactions proceeded at the same time during the cure stages, corresponding to the synchronized reactions of the ring-opening polymerization of Ba and the sol–gel process of diethoxysilanes.

We investigated how the sol–gel reaction of diethoxysilanes (DEDMS, DEMPS, and DEDPS) proceeds during the formation of the hybrids. But, it was very difficult to observe the progress of hydrolysis and condensation reaction of diethoxysilanes during the preparation of PBa–polysiloxane hybrids. Therefore, we examined the sol–gel reaction of diethoxysilanes without Ba, as a model reaction, employing the same procedure for the preparation of the hybrids.

The mixtures of diethoxysilanes, water, and PTS in THF were stirred at room temperature for 24 h and then dried under vacuum. Fig. 4 shows ^{1}H NMR spectra of the resulting products together with those of diethoxysilanes. The spectrum of DEDMS showed the characteristic peaks assignable to Si-bonded methyl (CH_3–Si), methyl (–CH_3), and methylene (–OCH_2–) protons at 0.36, 1.18, and 3.73 ppm, respectively (Fig. 4a). In the reaction product of DEDMS (Fig. 4b), the signals of ethoxy group disappeared, indicating that hydrolysis reaction proceeded in the presence of water and PTS in THF (Fig. 4b). Moreover, the splitting of CH_3–Si signal in the spectrum suggests that oligomerization of the hydrolyzed compound occurred during the stirring. Similar phenomenon was observed for DEMPS. After stirring with water and PTS, the ethoxy signals disappeared and the Si-bonded methyl and phenyl signals broadened (Fig. 4c and d). In the reaction product of DEDPS, the ethoxy signals became small and phenyl peak was broadened (Fig. 4f). These results indicate that the hydrolysis and oligomerization occurred by stirring with water and PTS at room temperature in THF.

The molecular weight of the reaction products was determined by SEC (Fig. 4). The weight-average molecular weights (M_w) of PDMS, PMPS and PDPS were estimated to be 700, 1100, and 460, respectively, which are not high.

To investigate the progress of the sol–gel reaction during cure stage, the mixtures of diethoxysilane, water, and PTS in THF after stirring at room temperature for 24 h were cast on glass plates, and then thermally treated up to 220 °C. The resultant products after thermal cure were characterized by NMR and SEC. All the hydrolyzed oligomer of DEDMS evaporated and we could not find product after 220 °C treatment. On the other hand, the oligomers of DEMPS and DEDPS gave products after the cure. Fig. 5 shows ^{1}H NMR spectra and SEC curves of the products from DEMPS and DEDPS. The ^{1}H NMR signals of the products from DEMPS and DEDPS were broader (Fig 5a and b) than those before curing (Fig 4d and f). The M_ws of the products from DEMPS and DEDPS were estimated by SEC to be 160,000 and 2800, respectively, which are higher than those before the curing. The high M_w of the resultant product after the cure indicates that condensation reaction proceeded during the thermal treatment. Additionally, the lower M_w of PDPS than that of PMPS indicates lower reactivity for condensation reaction because of the bulkiness of the pendant group.

During the thermal curing for the preparation of hybrids, some part of diethoxysilanes might be evaporated. Therefore, the actual content of polysiloxanes in the hybrids might be lower than the feed. To evaluate the actual content of polysiloxanes in the hybrid film, we performed EDX characterization (Table 2) and determined the actual polysiloxane contents based on the C/Si ratio. In the case of PBa–PDMS hybrid, the actual PDMS content was 60–80 wt%, probably because of the evaporation of the polysiloxane precursor. On the other hand, the PMPS and PDPS contents were 70–99 wt%, which were near the feed because of the lower volatility of the polysiloxane precursors.

3.2. *The appearance and morphology of polybenzoxazine–polysiloxane hybrids*

The cured PBa film is very brittle and cannot be bent further than as is shown in Fig. 6d. The cured PBa–polysiloxane hybrid films showed much higher flexibility than the pristine PBa film (Fig. 6a–c). The flexibility of the films increased with increasing the polysiloxanes content. PBa–PDMS hybrids were obtained as opaque homogeneous films up to 20 wt% of PDMS feed and the films can be bent easily (Fig. 6a). PBa–PMPS and PBa–PDPS hybrids were obtained as transparent homogeneous films up to 30 wt% and 40 wt% polysiloxane feed, respectively. The PBa–PMPS films can be bent (Fig. 6b), but the PBa–PDPS films were not flexible enough to be bent (Fig. 6c).

The PBa–PDMS hybrid films were homogeneous and opaque up to 20 wt% of PDMS feed (actual polysiloxane content: 14 wt%). But, the hybrid showed severe macroscopic phase separation above 30 wt% of PDMS feed (actual content: 24 wt%). In contrast, PBa–PMPS and PBa–PDPS hybrid films were transparent even at high polysiloxane content, up to 30 wt% of PMPS feed (actual content: 29 wt%) and up to 40 wt% PDPS feed (actual content: 36 wt%). The transparency of PBa–polysiloxane hybrid films was measured by

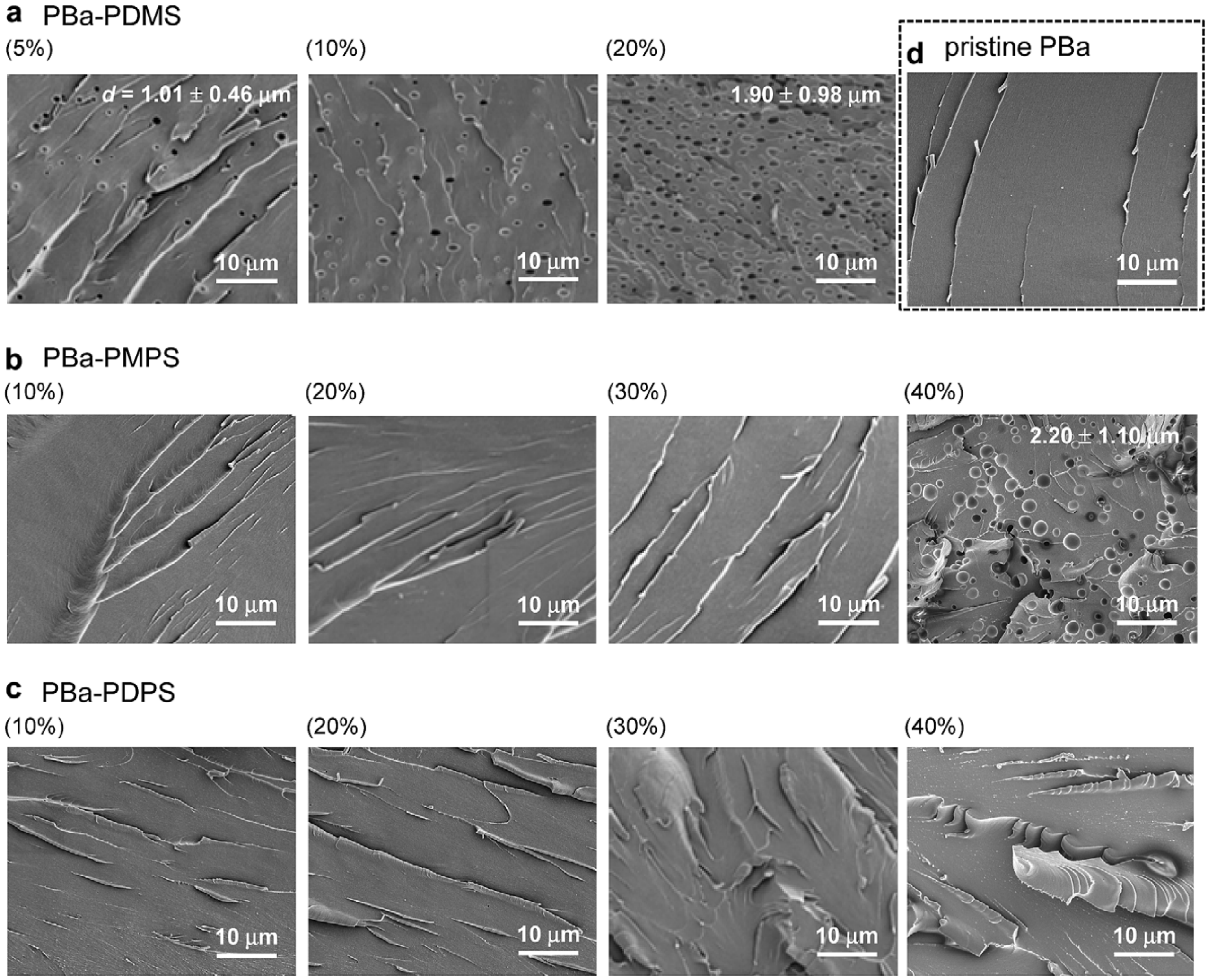


Fig. 8. SEM images for the fracture surface of PBa–polysiloxane hybrids with various polysiloxane contents (a–c). The SEM image of pristine PBa film is also shown in the dotted square (d).

UV–Vis spectrophotometer (Fig. 7 and Table 2). The pristine PBa film (ca. 150 μm thickness) showed high transparency in the visible region from 600 nm to 800 nm (a in Fig. 7A) and transmitted 99% of 700 nm light. The transmittance of the PBa–PDMS hybrid significantly decreased even as small as 5 wt% of PDMS feed (Table 2 and Fig. 7B). In contrast, the PBa–PMPS hybrids showed much higher transparency up to 30% feed, though the transmittance considerably decreased at 40% feed (Fig. 7B). On the other hand, the PBa–PDPS hybrid films showed high optical transmittance even at the polysiloxane content as high as 40% feed (Fig. 7A-d), transmitting 89% of 700 nm light.

The transparency of the hybrid films comes from the dispersion of polysiloxanes in the PBa matrix. Thus, we investigated the fracture surface morphology of PBa–polysiloxane hybrids by SEM (Fig. 8). The fracture morphology of the pristine PBa film revealed homogeneous phase relating to the transparent appearance of the film (Fig. 8d). The PBa–PDMS hybrid films revealed two phases, relating to the opaque appearance of the film. The diameter of the dispersed spherical PDMS domains was 1–2 μm, indicating that micrometer-scale phase separation occurred because of the low compatibility of PDMS with PBa (Fig. 8a). On the other hand, the PBa–PMPS and PBa–PDPS hybrids revealed homogeneous phase without phase separation (b and c in Fig. 8) up to 30 and 40 wt% feed, respectively, indicating the high compatibility of the polysiloxanes with PBa, probably because of the π–π interaction between the phenyl groups of the two components. The PBa–PMPS(40%) revealed the spherical phase with average diameter of ca. 2.2 ± 1.1 μm, that indicated micrometer-scale phase separation (Fig. 8b) relating to the opaque appearance of the film.

In addition, the fracture morphology of the pristine PBa film revealed smooth and lack of plastic deformation line indicating brittle fracture. The fracture morphology of the PBa–polysiloxane hybrids (Fig. 8a–c) showed rough surface and increasing deformation lines because of increasing plastic deformation, indicating ductile fracture. The increasing plastic deformation lines of the hybrids relate the enhancement of toughness by the introduction of polysiloxanes [31,32].

3.3. Physical and thermal properties of the hybrids

Tensile properties of the hybrid films were examined and the results were summarized in Fig. 9 and Table 3. Pristine PBa reveals high modulus (3.3 GPa), but low elongation at break (1.5%). Fig. 9B and C showed the tensile strength and elongation at break of the hybrids against polysiloxane content. The incorporation of PDMS as in the PBa–PDMS hybrid showed higher tensile strength and

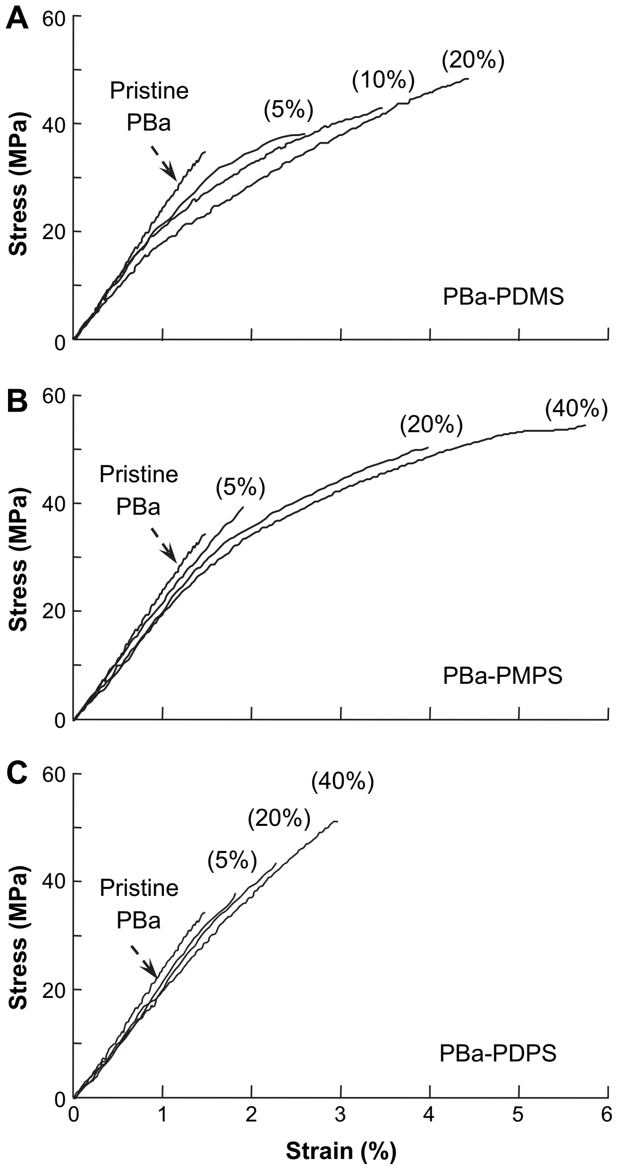


Fig. 9. Stress–strain curves (A) of pristine PBa film and PBa–polysiloxane hybrid films with various polysiloxane contents (a–c). Plots of tensile strength (B) and elongation at break (C) of the hybrids with various polysiloxane contents; ^: pristine PBa, ●: PBa–PDMS hybrid, ▲: PBa–PMPS hybrid, ◆: PBa–PDPS hybrid. The film thickness was ca. 0.15 mm. See Table 3.

Table 3
Tensile properties of pristine PBa and PBa–polysiloxane hybrids.

Code	Polysiloxane actual content (wt%)	Si content (wt%)	Modulus (GPa)	Strength (MPa)	Elongation at break (%)
PBa	–	–	3.3	35	1.5
PBa–PDMS (5%)	3	3.9	2.8	38	2.6
PBa–PDMS (10%)	6	7.0	2.6	42	3.5
PBa–PDMS (20%)	14	10.6	2.2	48	4.4
PBa–PMPS(5%)	4	0.9	3.0	40	2.0
PBa–PMPS (10%)	9	2.6	2.8	46	3.1
PBa–PMPS (20%)	14	6.9	2.7	50	4.2
PBa–PMPS(30%)	29	8.1	2.5	53	4.8
PBa–PMPS (40%)	35	12.2	2.2	55	5.7
PBa–PDPS (5%)	4	0.9	3.0	37	2.1
PBa–PDPS (10%)	9	1.7	2.8	42	2.2
PBa–PDPS (20%)	15	4.4	2.7	44	2.3
PBa–PDPS (30%)	25	7.4	2.7	47	2.5
PBa–PDPS (40%)	36	10.2	2.5	52	3.0

elongation at break than the pristine PBa. This is because PDMS has low glass transition temperature (T_g) (PDMS homopolymer $T_g = -120$ °C [23,33]) and acts as a toughener. By increasing the PDMS content, modulus slightly decreases but tensile strength and elongation at break increase [14]. Similarly, the incorporation of PMPS as in the PBa–PMPS hybrids revealed higher tensile strength and elongation at break than pristine PBa, since the PMPS component in the hybrids also acts as a toughener (PMPS homopolymer $T_g = -20$ °C [29,34]). It is worth noting that the PBa–PMPS hybrids have even higher tensile strength than PBa–PDMS hybrids at the same polysiloxane feed (Fig. 9B). The incorporation of PDPS as in the PBa–PDPS hybrids also revealed higher tensile strength and elongation at break than pristine PBa, however, lower than PBa–PDMS and PBa–PMPS. This is probably due to the lower toughening effect of the rigid PDPS that has relatively high T_g (PDPS homopolymer $T_g = 40$ °C [33]). As a result, all the hybrids revealed enhanced toughness over the pristine PBa because of the toughening effect of polysiloxanes. Among the hybrids, PBa–PMPS hybrid reveals the optimum enhancement of tensile properties.

Viscoelastic properties of PBa–polysiloxane hybrids were examined by DMA (Fig. 10 and Table 4). Pristine PBa film revealed one T_g at 159 °C from the maxima of loss modulus (E'') and at 174 °C from tan δ. The PBa–PDMS hybrid films revealed two T_g's corresponding to the PDMS component at low temperature and PBa component at high temperature, indicating micrometer-scale phase separation in the hybrid as evidenced by the SEM observation. Fig. 11 shows plots of the higher T_g as a function of the polysiloxane content. The T_g of PBa shifts to higher temperature in the presence of in-situ formed PDMS [14,24]. The increase of T_g suggests higher crosslinking density of PBa due to the plasticizing effect of PDMS that assists the polymerization of Ba [26]. The decrease of storage modulus above T_g was also suppressed owing to the increased crosslinking density.

The PBa–PMPS hybrid films up to 30 wt% of PMPS feed revealed one T_g because of the high compatibility of PMPS with PBa. The PBa–PDPS hybrid films up to 40 wt% of PDPS feed also showed one

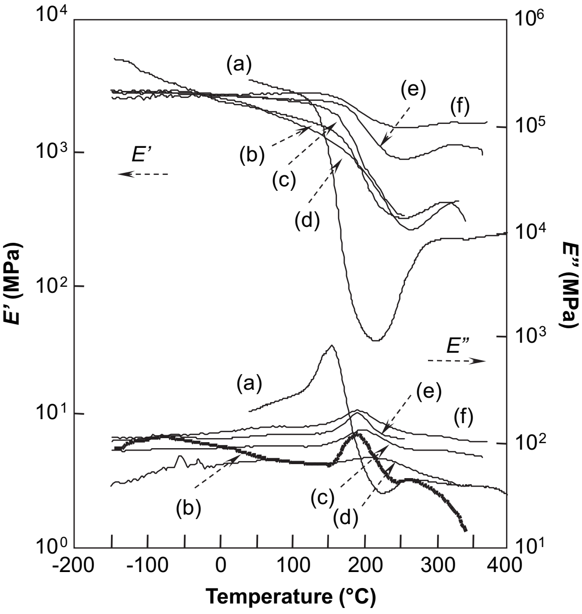


Fig. 10. DMA results of pristine PBa (a), PBa–PDMS(20%) (b), PBa–PMPS(20%) (c), PBa–PMPS(40%) (d), PBa–PDPS(20%) (e), and PBa–PDPS(40%) (f) hybrid films.

Table 4
Thermal properties of PBa and PBa–polysiloxane hybrids.

Code	Polysiloxane actual content (wt%)	Si content (wt%)	DMA					TGA		
			E' at 30 °C (GPa)	Lower T_g (°C)		Higher T_g (°C)		T_5 (°C)	T_{10} (°C)	Weight residue at 850 °C (%)
				E''	tan δ	E''	tan δ			
PBa	–	–	3.2	–	–	159	174	298	325	34
PBa–PDMS (5%)	3	3.9	2.9	−57	−51	171	186	320	341	36
PBa–PDMS (10%)	6	7.0	2.5	−63	−55	176	189	325	352	40
PBa–PDMS(20%)	14	10.6	2.1	−72	−61	185	210	339	368	46
PBa–PMPS (5%)	4	0.9	2.9	–	–	177	213	310	335	40
PBa–PMPS (10%)	9	2.6	2.7	–	–	181	222	313	336	46
PBa–PMPS(20%)	14	6.9	2.5	–	–	186	231	324	342	50
PBa–PMPS(30%)	29	8.1	2.3	–	–	192	246	326	348	55
PBa–PMPS (40%)	35	12.2	2.1	−30	−27	207	252	329	349	58
PBa–PDPS (5%)	4	0.9	2.9	–	–	180	216	310	339	43
PBa–PDPS (10%)	9	1.7	2.7	–	–	186	225	316	342	50
PBa–PDPS (20%)	15	4.4	2.6	–	–	189	234	326	348	52
PBa–PDPS (30%)	25	7.4	2.5	–	–	192	240	335	359	58
PBa–PDPS (40%)	36	10.2	2.4	–	–	195	243	336	360	59

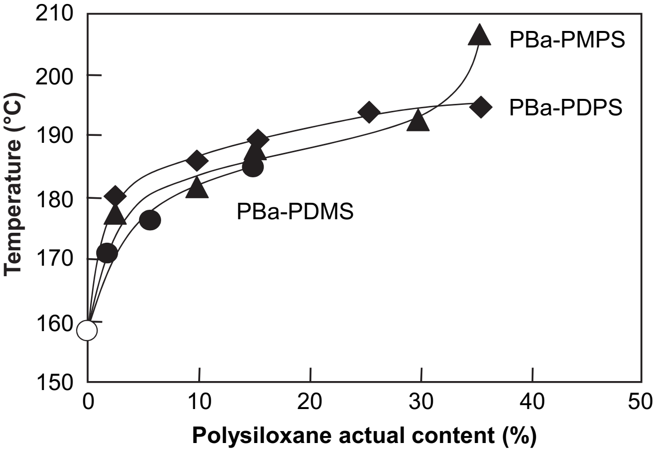


Fig. 11. Effect of PDMS (a), PMPS (b), and PDPS (c) with various polysiloxane contents on the T_g of PBa–polysiloxane hybrids;ˆ: pristine PBa, •: PBa–PDMS hybrid, ▲: PBa–PMPS hybrid, ◆: PBa–PDPS hybrid.

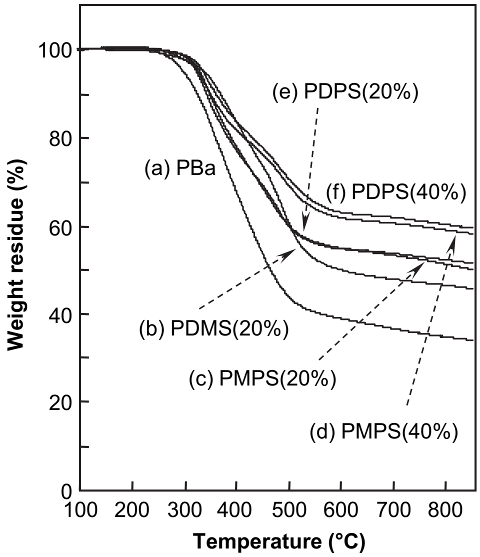


Fig. 12. TGA curves of pristine PBa (a), PBa–PDMS(20%) (b), PBa–PMPS(20%) (c), PBa–PMPS(40%) (d), PBa–PDPS(20%) (e) and PBa–PDPS(40%) (f) hybrid films.

T_g. The T_gs of hybrids are higher than that of pristine PBa, and increase with increasing of the polysiloxane content (Fig. 11). Interestingly, the PBa–PMPS (40%) hybrid film, which showed micro-scale phase separation by the SEM observation, showed two T_gs corresponding to the PMPS and PBa components. The T_g of PBa component, estimated to be 207 °C from E'' and 252 °C from tan δ, was the highest among the hybrids.

Thermal stability of the PBa–polysiloxane hybrids was investigated by TGA under argon atmosphere (Fig. 12 and Table 4). All the hybrids showed higher degradation temperature and flame retardancy with increasing polysiloxane content, because the polysiloxanes possess high thermal stability [15–18]. Fig. 13A shows the influence of polysiloxane content on the 5% weight loss

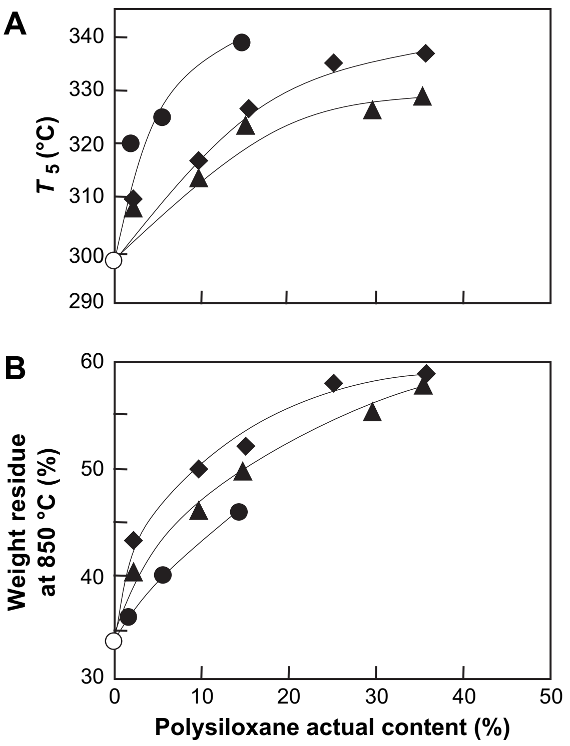


Fig. 13. Plots of (A) T_5 and (B) weight residue at 850 °C of the PBa–polysiloxane hybrids with various polysiloxane contents;ˆ: pristine PBa, •: PBa–PDMS hybrid, ▲: PBa–PMPS hybrid, ◆: PBa–PDPS hybrid.

temperature (T_5). The T_5s of PBa–PDMS are higher than those of PBa–PMPS and PBa–PDPS hybrids. Although we could not determine the molecular weight of PDMS in the hybrids, we expect that the molecular weight is relatively high compared with PMPS and PDPS from the result of the model reactions of diethoxysilanes as mentioned above. The difference of molecular weight might affect the T_5. Additionally, the PBa–PDPS hybrids showed higher weight residue at 850 °C than PBa–PDMS and PBa–PMPS hybrids due to the high aromatic content (Fig. 13B).

4. Conclusions

The PBa–polysiloxane hybrids with different type of polysiloxanes were successfully prepared by synchronizing reactions of the ring-opening polymerization of Ba and the sol–gel process of diethoxysilanes. This technique is useful to prepare various organic–inorganic hybrids based on polybenzoxazine. The phenyl group of polysiloxanes enhanced their compatibility with PBa. By using PMPS and PDPS, we could obtain the transparent hybrid films. The PBa–polysiloxane hybrids showed better tensile strength and elongation at break because of the toughening effect of the polysiloxanes. Especially, the PBa–PMPS hybrid revealed the optimum enhancement of the mechanical property. The hybridization also brought about improvement of T_g due to the high crosslinking density of PBa by the plasticizing effect of the polysiloxanes that assists the polymerization of Ba. Furthermore, the degradation temperature and weight residue at 850 °C also increased by the hybridization. The PBa–PDMS hybrid showed the optimum enhancement of the degradation temperature, while the introduction of PDPS was the most effective for the flame retardancy. The pendant group of the polysiloxanes strongly affects the optical, thermal, and mechanical properties, and those properties of the hybrids can be controlled by the type of polysiloxanes.

Acknowledgment

H. A. acknowledges AUN/SEED-Net JICA for the research grant and scholarship.

Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2009.10.001.

References

[1] Takeichi T, Kawauchi T, Agag T. Polym J 2008;40:1121.
[2] Ning X, Ishida H. J Polym Sci Part A: Polym Chem 1994;32:1121.
[3] Ishida H, Allen DJ. J Polym Sci Part B: Polym Phys 1996;34:1019.
[4] Kim HD, Ishida H. J Appl Polym Sci 2001;79:1207.
[5] Su YC, Chang FC. Polymer 2003;44:7989.
[6] Allen DJ, Ishida H. J Appl Polym Sci 2006;101:2798.
[7] Takeichi T, Kano T, Agag T. Polymer 2005;46:12172.
[8] Jang J, Seo D. J Appl Polym Sci 1998;67:1.
[9] Agag T, Takeichi T. High Perform Polym 2001;13:S327.
[10] Takeichi T, Guo Y, Agag T. J Polym Sci Part A: Polym Chem 2000;38:4165.
[11] Rimdusit S, Pirstpindvong S, Tanthapanichakoon W, Damrongsakkul S. Polym Eng Sci 2005;45:288.
[12] Ishida H, Lee Y-H. Polymer 2001;42:6971.
[13] Takeichi T, Guo Y, Rimdusit S. Polymer 2005;46:4909.
[14] Takeichi T, Agag T, Zeidam R. J Polym Sci Part A: Polym Chem 2001;39:2633.
[15] Jovanovic JD, Govedarica MN, Dvornic PR, Popovic IG. Polym Deg Stab 1998;61:87.
[16] Takayama Y, Takeichi T. J Chromatogr A 1994;61:685.
[17] Deshpande G, Rezac ME. Polym Deg Stab 2002;76:17.
[18] Tiwari A, Nema AK, Das CK, Nema SK. Thermochim Acta 2004;417:133.
[19] Park Y-W, Lee D-S, Kim S-H. J Appl Polym Sci 2004;91:1774.
[20] Ochi M, Takemiya K, Kiyohara O, Nakanishi T. Polymer 1998;39:725.
[21] Gong W, Xeng K, Wang L, Zheng S. Polymer 2008;49:3318.
[22] Kricheldorf HR. Silicon in polymer synthesis. Berlin: Springer; 1996.
[23] Kripotou S, Pissis P, Bershtein VA, Sysel P, Hobzova R. Polymer 2003;44:2781.
[24] Abe Y, Gunji T. Prog Polym Sci 2004;29:149.
[25] Abbasi F, Mirzadeh H, Katbab A-A. Polym Int 2001;50:1279.
[26] Ardhyananta H, Wahid MH, Sasaki M, Agag T, Kawauchi T, Ismail H, et al. Polymer 2008;49:4585.
[27] Agag T, Tsuchiya H, Takeichi T. Polymer 2004;45:7903.
[28] Vuk AS, Fir M, Jese R, Vilcnik A, Orel B. Prog Org Coat 2008;63:123.
[29] Lo TY, Huang SK. J Appl Polym Sci 1998;69:1523.
[30] Lu C, Wang Z, Liu F, Yan J, Gao L. J Appl Polym Sci 2006;100:124.
[31] Chen Z-K, Yang G, Yang J-P, Fu S-Y, Ye L, Huang Y-G. Polymer 2009;50:1316.
[32] Thomas R, Yumei D, Yuelong H, Le Y, Moldenaers P, Weimin Y, et al. Polymer 2008;49:278.
[33] Gadda TM, Weber WP. J Polym Sci Part A: Polym Chem 2006;44:3629.
[34] Yang M-H, Huang W-J, Chin T-C, Chen C-M, Chang H-Y, Chang Y-S, et al. Polymer 2001;42:8841.