Silicon-Based Interpenetrating Polymer Networks (IPNs): Synthesis and Properties

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ABSTRACT: Both "condensation" and "hydrosilylation" reactions have been successfully applied for the synthesis of silicon-based interpenetrating polymer networks (IPNs) consisting of a stable Si−O and Si−C linkage. We adopted a ladder silsesquioxane oligomer (LDS **1**; commercial name, Glass Resin GR100) and a polycarbosilane (PCS) by hydrosilylation polymerization of bifunctional Si−H and Si−vinyl monomers as the two components for the IPN. The combined LDS/PCS curing system was studied to try to obtain homogeneously cured material, which may lead to IPN formation, by using both reactions selectively in one pot for chain-extending and cross-linking of both components, respectively. We synthesized the cured LDS/PCS; LDS/PCS = 8/2, 5/5, and 2/8 [wt/wt]. Tuning the rates of the two reactions to each other was important for obtaining a transparent cured product. The morphology of the cured LDS/PCS (8/2) was examined by TEM and AFM. TEM analysis showed a good miscibility with an nm level of LDS/PCS (8/2). The thermal and mechanical properties of the LDS/PCS (8/2) cured sample were better than the calculated values from each component's value. The experimental data imply the IPN structure of the cured LDS/PCS.

Introduction

Interpenetrating polymer network (IPN) research has become an area of much interest.[1] IPNs are "homogeneous polymer mixtures" made from two different polymers (each made via different and independent reaction mechanisms) which normally are mutually insoluble, but due to cross-links and entanglements, mutual "solubility" is induced.[2]

In carbon-based polymers, combinations of various polymers for IPN systems have been synthesized, such as polyurethane−epoxy (PU-E), poly(phenylene oxide)−polystyrene (PPO−PS), and phenolic resin−polyamide (PF−PA) etc.[2] Furthermore, a number of commercial IPN products have been developed. Structural analyses for IPN systems have been performed with SAXS (small-angle X-ray scattering), FTIR (Fourier transform IR spectroscopy), DSC (differential scanning calorimeter), TEM (transmission electron microscopy), and other methods.[2] Though the structural property relationships for IPN systems have not been clarified perfectly, it was clear that the thermal and mechanical properties of materials with IPN synthesis were improved compared with each of the components and the mechanically blended polymer.[3]

More recently, silicon-based organic−inorganic composites have been prepared by many groups and have been studied from the point of application. The hybrid materials were formed by using a sol−gel reaction and an organic reaction. Since the organic−inorganic hybrid materials would be homogeneous at the molecular level, they are expected to have both the properties of an organic material (light, flexible, moldability) and an inorganic material (thermally stable, high strength). Novak and co-workers studied a high glass content "nonshrinking" sol−gel composite via poly(silicic acid esters).[4] The storage modulus of composite material obtained from the simultaneous polymerization in both organic and inorganic components, displays synergistic, nonadditive behavior.[4] These new nonshrinking materials are expected to lead to new optical materials.[5] Wilkes and co-workers synthesized sol−gel-derived hybrid organic−inorganic network ceramer materials.[6] Such materials may serve as useful optical coatings.[6] Schmidt and co-workers developed the methods of synthesizing materials for hard contact lenses by hydrolysis and condensation of an epoxide-substituted alkoxysilane and Ti−alkoxide.[7] The above hybrid materials had covalent bonds between the organic and the inorganic components. On the other hand, Saegusa and Cujo synthesized organic−inorganic hybrid materials with hydrogen bonds prepared from tetraethoxysilane and poly(2-ethyl-2-oxazoline) or poly(*N*-vinylpyrrolidone).[8] Pyrolysis of these polymer hybrids at 600 °C caused porous silica with controlled pore size.[8] A wide variety of applications can be expected by using these molecular hybrids.[8] Furthermore, Toki and co-workers analyzed the microstructure of the organic−inorganic hybrid materials with hydrogen bonds by AFM (atomic force micrography).[9] These may serve as materials for crystalline display and coating films.[9] In this paper, we studied the synthesis of silicon-based interpenetrating polymer networks (IPNs) consisting of stable Si−O and Si−C linkages.

Cross-linked silicic acid (Si−O based polymer) has a high modulus and a thermal stability; however, it is fragile. Therefore, we tried to prepare a thermostable and tough material by means of a silicon-based IPN formation. IPNs containing a silicon-based polymer, such as dimethylpolysiloxane[10] and polysilicic acid,[4] have also been investigated, and interesting properties were derived from the IPN structure. We applied "condensation (eq 1)" and "hydrosilylation (eq 2)" reactions for the synthesis of silicon-based IPN. In our previous work, we made clear that the reactions of both model compounds proceeded selectively by using appropriate catalysts.[11] The cross-linked silicic acid struc-

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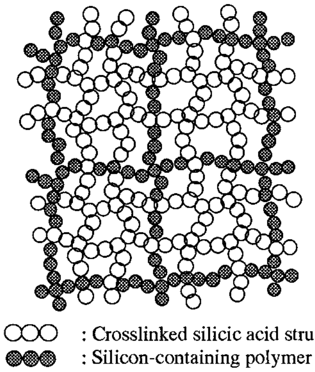


Figure 1. Model structure of the silicon-based IPN.

Table 1. LDS and PCS Components for IPN Formation

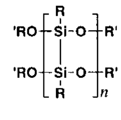
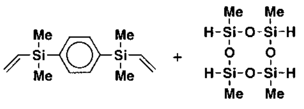
LDS component		PCS component
	R = Ph or Me Ph/Me = 1/2 R' = H or Et n = 7.2	
LDS **1**		**1** + **2**
catalysts	$Ti(O\text{-}i\text{-}Pr)_2(acac)_2$ H_2O	catalyst : $Pt[((CH_2{=}CHMe_2Si)_2O]_2$ retarder : $MeOCOCH{=}CHCO_2Me$ (DM)

Table 2. LDS Oligomers Used in This Work

oligomer code	identification of LDS				
	ratio of Ph/Me[a]	M_w/M_n[b]	n[c]	volatile,[d] %	SiO_2, %
LDS **1**	1/2	7210/1260	7.2	7	59
LDS **2**	1/0	1080/690	2.7	13	40
LDS **3**	4/1	1270/680	2.9	14	45
LDS **4**	0/1	3750/20			78

[a] The ratio of the substituents of LDS oligomers. [b] M_w and M_n are weight-average molecular weight and number-average molecular weight, respectively. [c] The number of units calculated from M_n. [d] Volatile, % = $(M_n - 92)/M_n \times 100$.

ture for the condensation component (eq 1) is expected to be rigid, water-resistant, and incombustible, and the other silicon-containing polymer chain for hydrosilylation component (eq 2) is expected to be flexible (Figure 1).

$$-SiOR + H_2O \rightarrow -SiOH + ROH \qquad (1)$$

$$-SiOH + ROSi- \rightarrow -SiOSi- + ROH$$

$$-SiOH + HOSi- \rightarrow -SiOSi- + H_2O$$

$$-SiH + CH_2{=}CHSi- \rightarrow -SiCH_2CH_2Si- \qquad (2)$$

In this paper, we report as follows: (a) the design of both components; (b) an investigation of the conditions of IPN formation (a control of miscibility; a good-balancing of both of the reactions); (c) evaluation of mechanical and thermal properties and analysis of the morphology of silicon-based IPN.

Experimental Section

Materials. The four LDS oligomers (commercial name: Glass Resin, OI-NEG TV Products, Inc.)[12] used in this study are listed in Table 2. The condensation catalysts were used without further treatment: titanium(IV) bis(acetylacetato)diisopropoxide (T-50) from NIHON SODA; titanium(IV) butoxide from Wako Pure Chemical Industries, Ltd.; ammonium hydroxide from Aldrich; tin(II) octate from NITTO KASEI Co., Ltd.; tetrabutylammonium fluoride from Aldrich.

PCS monomers, 1,4-bis(dimethylvinylsilyl)benzene (**1**), 1,3,5,7-tetramethylcyclotetrasiloxane (**2**), 1,4-bis(dimethylsilyl)benzene (**3**), dimethylsilane (**4**), dimethyldivinylsilane (**5**), 1,1,3,3-tetramethyl-1,3-divinyldisiloxane (**6**), methylphenyldivinylsilane (**7**), 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane (**8**), were purchased from Shin-Etsu Chemical Co., Ltd. The platinum catalyst $[Pt\{(CH_2{=}CHSiMe_2)_2O\}_2]$ (1.0 wt % xylene solution) was prepared by the reaction of $H_2PtCl_6{\cdot}6H_2O$ and 1,1,3,3-tetramethyl-1,3-divinyldisiloxane.[13,14] Dimethyl maleate (Tokyo Kasei Co., Ltd.) and tetrahydrofuran (Nacalai Tesque Co., Ltd.) were used without further treatment.

Preparation of cured LDS from LDS oligomers (Table 3). LDS **1** (5.0 g) was dissolved in tetrahydrofuran (5 mL) with ultrasonic waves. The prepared solution was poured into a metal can (67 mm in diameter; 5 mm in depth), the inner surface of which was covered with polyimide film (APICAL 25AH, Kaneka Corporation) for taking off the cured specimen without difficulty. The can was then covered with a lid and placed in an oven at 50 °C for 19 h, additionally heated stepwisely (80 °C/7.0 h → 100 °C/15 h). The cured sheet obtained (1.1 mm thickness) was pale yellow and transparent. Its gel content was 97%. Gel content was measured by the following procedure: a piece of cured specimen (ca. 200 mg) wrapped in a stainless steel net was immersed in tetrahydrofuran (ca. 200 mL) for 12 h. The gel content here was defined as the residual weight ratio of a sample after dipping and drying (100 °C/4 h). The other cured LDS samples were prepared in the same manner as above.

Preparation of PCS Oligomers (Table 4). Various PCS oligomers were prepared by hydrosilylation polymerization in the same manner as our previous work.[15,16]

Preparation of Cured PCS from PCS Monomers (Table 5). 1, 4-Bis(dimethylvinylsilyl)benzene (**1**) (3.50 g), 1,3,5,7-tetramethylcyclotetrasiloxane (**2**) (1.71 g), 1 wt % THF solution of dimethyl maleate (41.1 mg), and the Pt complex (28.9 mg, 9.71×10^{-6} mmol/mg) were dissolved in tetrahydrofuran (2 mL). The can was then covered with a lid and placed in an oven at 50 °C for 16 h and additionally heated stepwise (80 °C/6.5 h → 100 °C/14.5 h → 150 °C/20 h). The cured sample obtained (1.2 mm thickness) was transparent. Its gel content was 99%. The other cured PCS samples were prepared in the same manner as above.

Synthesis of IPN (Table 6, LDS/PCS = 8/2). LDS oligomer **1** (5.0 g) was dissolved in tetrahydrofuran (5 mL) with ultrasonic waves. To this solution was then added titanium(IV) bis(acetylacetato)diisopropoxide (151 mg). In an another flask, 1,4-bis(dimethylvinylsilyl)benzene (**1**) (807 mg), 1,3,5,7-tetramethylcyclotetrasiloxane (**2**) (397 mg), and 1 wt % THF solution of dimethyl maleate (9.7 mg) were dissolved. These solutions were mixed, and to the mixed solution was then added H_2O (190 mg) and the Pt complex (63.0 mg, 9.71×10^{-7} mmol/mg). The can was then covered with a lid and placed in an oven at 50 °C for 16 h, additionally heated stepwisely (80 °C/6.5 h → 100 °C/14.5 h → 150 °C/20 h). The cured sheet obtained (1.4 mm thickness) was pale yellow and transparent. Its gel content was 100%.

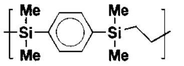
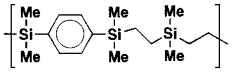
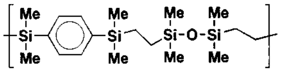
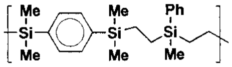
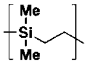
Measurements. Molecular weights (M_n and M_w) and polydispersity (M_w/M_n) were determined with respect to polystyrene standards by gel permeation chromatography (GPC: Waters LC moldule 1), with chloroform as eluent. Thermogravimetric analyses (TGA) were made on a Shimadzu TGA 50 instrument (20 °C/min or 10 °C/min) under a nitrogen stream. ^{29}Si NMR measurements were made using a Bruker AMX-400 spectrometer. The high-resolution solid-state ^{29}Si NMR spectra were obtained by the combined use of dipolar-decoupling (DD) and magic-angle spinning (MAS).[17,18] The spinning frequency was about 5.0 kHz. Mechanical data were collected from flexing bars ($4.0 \times 0.7 \times \sim 0.14$ cm) made from

Table 3. Properties of Cured LDS[a]

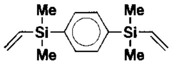
expt no.	type of LDS[b]	appearance (gel content, %)	flexing modulus, GPa	maximum strength, MPa	maximum strain, %	LOI,[c] %	TGA[d] wt loss, % at 500 °C	TGA[d] T_{d5},[e] °C
1	LDS **1**	transparent (97)	1.71	29.0	1.8	28−29	3.1	530
2	LDS **2**	transparent (45)					4.0	545
3	LDS **3**	transparent (94)	2.14	27.5	1.2	30−31	3.1	535
4	LDS **4**	transparent (99)	1.27	9.2	0.7	36−38	2.2	>560

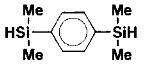
[a] Curing conditions: 50 °C/19 h → 80 °C/7 h → 100 °C/15 h (LDS **1**); 50 °C/7.5 h → 80 °C/16 h → 100 °C/8 h → 150 °C/65 h (LDS **2**); 50 °C/19 h → 80 °C/7 h → 100 °C/15 h → 150 °C/15 h (LDS **3**); 50 °C/16 h → 80 °C/8 h → 100 °C/65 h (LDS **4**). [b] The identification of LDS oligomers is listed in Table 2. [c] Limiting oxygen index. [d] Curing conditions: 180 °C/1 h (LDS **1-3**); 150 °C/16 h (LDS **4**). [e] The temperature at 5% weight loss under N_2, 20 °C/min.

Table 4. Properties of the Polycarbosilanes Synthesized

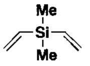
polymer code	polymer structure	monomers[a] SiH	monomers[a] Si-vinyl	apperance m. p., °C	M_n (M_w / M_n)[b]	TGA wt loss, % 400 °C	TGA wt loss, % 500 °C	solvent solubility, mL/mg[c]
PCS 1		3	1	powder 196-198	15000 (2.6)	1	27	530
PCS 2		3	5	solid 135-138	15000 (2.6)	4	42	0.8
PCS 3		3	6	sticky solid	15000 (2.9)	5	48	-
PCS 4		3	7	sticky solid	14000 (3.5)	17	33	<1
PCS 5		4	5	viscous liquid	3700 (3.3)	16	74	-

[a] monomers;


1


3

$(Me)_2SiH_2$
4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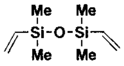
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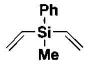
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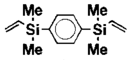
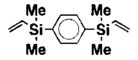
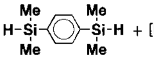
[b] M_w and M_n are weight-average molecular weight and number-average molecular weight, respectively, by GPC. [c] Solvent volume necessary for dissolving 1 g of polymer.

Table 5. Properties of Cured PCS[a]

cured PCS code	components	appearance (gel content, %)	flexing modulus, GPa	maximum strength, MPa	maximum strain, %	LOI,[b] %	TGA wt loss, % 500 °C	TGA T_{d5},[c] °C
PCS 12	 + $[MeSi(H)O]_4$ 1 2	transparent (99)	1.55	47.4	5.0	22	3.0	521
PCS 82	$[(CH_2{=}CH)Si(Me)O]_4$ + $[MeSi(H)O]_4$ 8 2	transparent (100)	1.06	9.8	0.9	34	0.6	>580
PCS 132	 +  + $[MeSi(H)O]_4$ 1 3 2	translucent (97)	1.79	49.8	3.6	20	9.0	472

[a] Curing conditions: 50 °C/18 h → 80 °C/9 h → 100 °C/14 h → 150 °C/22 h. SiH/Si−vinyl = 1/1 (mol). [b] Limiting oxygen index. [c] The temperature at 5% weight loss under N_2, 20 °C/min.

cured film in a Shimadzu AUTO-GRAPH with maximum load cell of 100 kg, and a cross-head speed of 0.9 mm/min was used for all flexing analysis (JIS K7203). The specimen was cut from the cured sample by a cutter with a diamond-blade. The flammability of the cured film was estimated by using the limiting oxygen index (LOI) method (JIS K7201). Morphological studies were obtained using a JEOL JEM-1200EX (TEM) and a TOPOMETRIX TMX-2000 (AFM).

Results and Discussion

Design of a Si−O−Si Based Polymer (Condensation Component). To obtain a thermally stable, hard and tough material by means of silicon-based IPN, we considered that it was necessary for the condensation component to be hard and thermally stable, and furthermore, before the reaction the solvent solubility was necessary to apply casting method. A one-dimensional Si−O−Si based polymer (polysiloxane) has the disadvantage of hardness and thermal stability, and a three-dimensional Si−O−Si based polymer (silicic acid) has the disadvantage of solvent solubility. Therefore, we used the ladder silsesquioxane oligomer (LDS) as a condensation component. LDS is known as a highly thermally stable and rigid polymer.[19] LDS could be prepared by hydrolysis and condensation of trichlorosilanes[20] and trialkoxysilanes (mostly trimethoxysilanes or triethoxysilanes).[21] In this work, we used ladder silsesquioxane oligomers (LDS **1−4**), which were purchased from OI-NEG TV Products, Inc. (commercial name: Glass Resin).[12] The general analytical data of the oligomers are summarized in Table 2. The weight-

Table 6. LDS/PCS (8/2) Combined Curing Systems

	LDS components[b]			PCS components[c]		LDS/PCS cured sample	
expt no.	[Ti] (parts)[d]	H_2O (parts)[d]	gel content (%)[e]	DM (equiv)[f]	gel content (%)[e]	appearance	gel content (%)[g]
1	3	3.8	17, 65, 100	10	93, 94, 100	transparent	66, 71, 100 [33][h]
2	1	3.8	14, 54, 100	10	93, 94, 100	transparent[i]	*j*, 57, 100
3	1	0	0, 47, 100	10	93, 94, 100	opaque	*j*, 43, 100

[a] Curing conditions: 50 °C/16 h → 80 °C/6.5 h → 100 °C/14.5 h → 150 °C/20 h. [b] LDS; LDS **1** in Table 1. [c] PCS monomers: 1,4-bis(dimethylvinylsilyl)benzene + $[MeSi(H)O]_4$. [d] Relative amount to the LDS **1**. [e] For either LDS or PCS alone. Numbers in the left are for curing at 50 °C/16 h, those in the middle are for a further 80 °C/2 h, those on the right are for a further 150 °C/20 h. [f] Relative amount to the Pt catalyst. [g] For LDS/PCS combined curing system. [h] The calculated values from each component's value at 50 °C/16 h. [i] The surface was not smooth. [j] The cured material was highly viscous, so we couldn't evaluate their gel contents.

average molecular weights (M_w) of the oligomers, as determined by gel permeation chromatography using polystyrene standards, were in the range 1080−7210. The oligomers were highly soluble in common organic solvents such as THF, chloroform, acetone, *n*-hexane, toluene, and so on. The ^1H NMR spectrum gave signals for SiOEt groups. This implies that the oligomers were prepared by hydrolysis and condensation of triethoxysilanes. As described below, the cured materials of the oligomers were thermally stable. Therefore, we presumed that the structure of the oligomer was ladder-like.[22]

Table 3 shows the appearance of the cured LDS (**1**−**4**) materials. Testing samples were synthesized by the casting method. The cured LDS materials had no cracks or bubbles by means of heating stepwise (50/80/100/150 °C). The gelation of LDS **1** and LDS **4** proceeded almost perfectly; however, the gel content of LDS **2** was 45%. We consider that increasing the number of phenyl substituents on silicon atom would inhibit gelation on account of their steric effect. With the cured LDS specimens (**1**, **3**, and **4**), we were able to get mechanical and LOI tests. However, the cured LDS **2** (Ph/Me = 1/0) was too fragile to get a specimen for the tests. The cured LDS **3** specimen was cracked with a diamond blade.

The flexing properties, LOI (Limiting Oxygen Index), and thermal properties of cured LDS materials were summarized in Table 3. Flexing moduli increased by increasing the Ph/Me ratio. It was clear that the LOI depended on the content of the "%SiO_2 content", and the LOI of LDS **4** (%SiO_2 = 78) was the highest of all of them. All of the cured LDS materials were highly thermally stable ($T_{d5} > 530$). Therefore, we used LDS **1** with well-balanced properties as a condensation component of the silicon-based IPN.

Next, we developed a condensation catalyst. Alkoxysilanes are hydrolyzed with an acidic or basic catalyst.[23] However, a strong acidic or basic catalyst would decompose hydrosilanes. In our previous work, to make both the reactions "condensation (eq 1)" and "hydrosilylation (eq 2)" proceed selectively, selection of catalysts was important. An organic weak acid, $(C_8H_{17}O)_2P({=}O)OH$ had been used previously, but the condensation rate was slow (2−10 days).[11] The hydrosilylation reaction proceeds more rapidly than the hydrolysis/condensation reaction. Therefore, we tried to prepare the cured materials with various condensation catalysts. Table 7 shows the effects of catalysts on the cured LDS **1** modulus. Titanium(IV) bis(acetylacetato)diisopropoxide caused a cured material with a high modulus. The cured sample was transparent, without cracks and bubbles. Furthermore, since titanium(IV) bis(acetylacetato)diisopropoxide was a neutral catalyst, it would not decompose hydrosilane. Because Ti(O-n-Bu)$_4$ had caused precipitation of LDS, we could not employ it. As a result, titanium(IV) bis(acetylacetato)diisopropoxide was a suitable catalyst for silicon-based IPN.

Table 7. Effects of Catalysts on the Flexing Modulus of the Cured LDS 1[a]

expt no.	catalyst type	catalyst wt %	gel content, %	flexing modulus, GPa
1	$Ti(O\text{-}i\text{-}Pr)_2(acac)_2$	3	98	2.26
2	$Ti(O\text{-}n\text{-}Bu)_4$	3	100	1.94
3	NH_4OH	1	92	1.74
4	$(C_7H_{15}CO_2)_2Sn$	2	99	1.52
5	$n\text{-}Bu_4NF$	0.2	100	1.07
6			88	1.54

[a] Curing conditions: 50 °C/14 h → 80 °C/7 h → 100 °C/15 h → 150 °C/15 h.

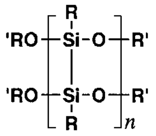
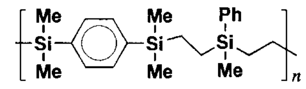
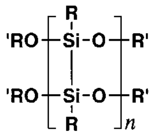
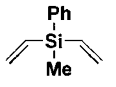
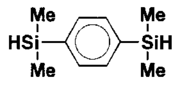
Design of Si−C Based Polymer (Hydrosilylation Component). As the other component for silicon-based IPN, we used a polycarbosilane (PCS). Hydrosilylation polymerization has been reported as a well-known reaction leading to polycarbosilanes (PCS) and related polymers.[24−27] Recently, we reported on polycarbosilanes with thermal stability and solubility.[15,16]

In this paper, we first synthesized polycarbosilanes (PCS) by hydrosilylation polymerization of bifunctional Si−vinyl and Si−H monomers. Table 4 shows the structure of synthesized PCSs, and thermal property and solvent solubility. It was clear that PCS **1** was highly thermally stable; however, the solvent solubility was very low. Introducing the flexible unit (PCS **2**−**5**) increased solubility of PCS, but it decreased the thermal stability. The thermal stability of PCS **5** was very low. As a result, it was clear that the bis(silyl)-*p*-phenylene unit $[Si(Me)_2\text{-}p\text{-}C_6H_4{-}Si(Me)_2]$ would be an optimal candidate.

Homogeneity prior to IPN formation was important for obtaining an IPN in a one-pot reaction system. We evaluated the miscibility of LDS oligomer (LDS **1**) and PCS oligomer (PCS **4**) as well as PCS monomers (**3** + **7**). Table 8 shows the miscibility evaluated with a phase-differential microscope. Both components were miscible in the presence of solvent. LDS **1** and PCS **4** was immiscible in the absence of solvent. We evaluated the miscibility between LDS oligomer (LDS **1**) and PCS monomers (**3**, **7**). In that case, the combined system was miscible under the following conditions: LDS/PCS (wt/wt) = 8/2, 5/5, and 2/8 at room temperature. Therefore, we used monomers as the starting materials for hydrosilylation component owing to the miscibility before and on IPN formation.

We synthesized the cured PCS materials via an in-situ cross-linking reaction and evaluated their mechan-

Table 8. Miscibility between LDS Oligomer and PCS Oligomer or PCS Monomers without Solvent

LDS oligomer	PCS oligomer or PCS monomers	miscibility
 LDS 1[a]	 PCS 4	−
 LDS 1[a]	 7 +  3	+

[a] R = Ph or Me; Ph/Me = 1/2; R′ = H or Et, n = 7.2.

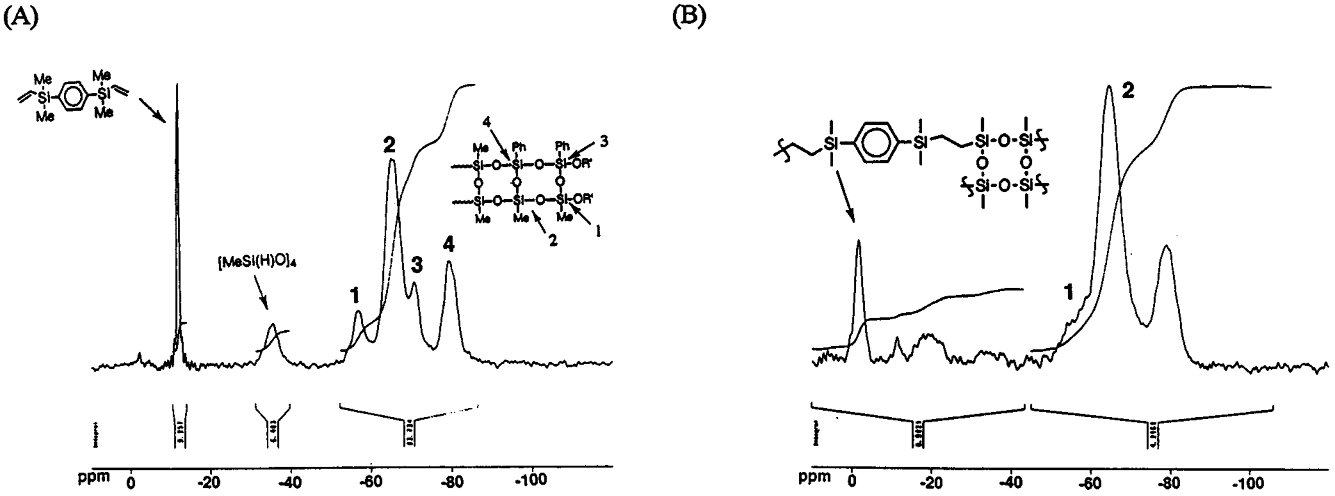


Figure 2. ^{29}Si DD/MAS spectra for the cured LDS/PCS: (A) curing condition, 50 °C/12 h; curing conditions, 50 °C/16 h → 80 °C/6.5 h → 100 °C/14.5 h → 150 °C/20 h. Peak assignments are also depicted.

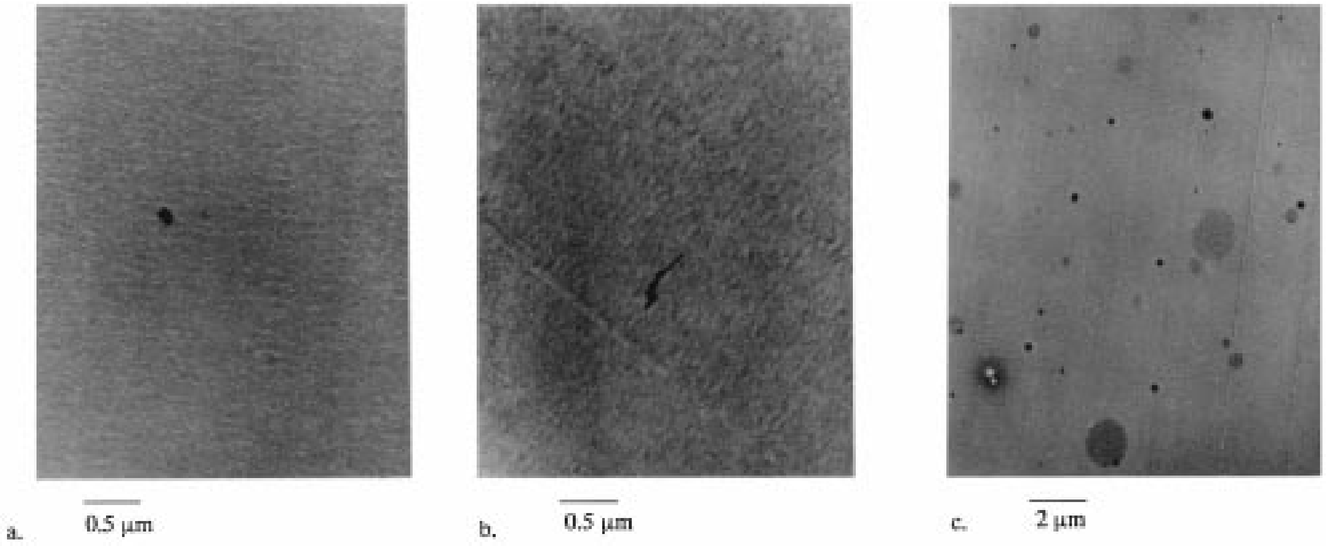


Figure 3. Transmission electron micrographs of the LDS/PCS (8/2) cured samples stained by RuO$_4$: (a) no. 1, (b) no. 2, and (c) no. 3 in Table 6.

ical and thermal properties (Table 5). The cured PCS **12** was transparent, but the cured PCS **132** was translucent owing to the high crystallinity of the polymer backbone. The maximum strength and strain of PCS **12** were a little higher than those of cured LDS materials (Table 3). Furthermore, it was clear that the bis(silyl)-*p*-phenylene unit was important for improving the mechanical properties of the cured PCS. The LOI of cured PCS **12** was low; however, thermal stability was very good. As a result, we adopted the combination of 1,4-bis(dimethylvinylsilyl)benzene (**1**) and 1,3,5,7-tetramethylcyclotetrasiloxane (**2**) as the other component for a silicon-based IPN for good thermal and mechanical properties.

Table 9. LDS/PCS Combined Curing Systems[a]

expt no.	LDS/PCS[b] (wt/wt)	DM (equiv)[c]	LDS/PCS cured sample appearance
1	5/5	10	translucent
2	5/5	500	transparent[d]
3	2/8	10	translucent
4	2/8	500	transparent

[a] Curing conditions; 50 °C/16 h → 80 °C/8 h → 100 °C/16 h → 150 °C/5 h (no. 1, 3) or 20 h (no. 2, 4). [b] LDS: LDS **1** in Table 1 (LDS components; added 3.8 parts of H_2O, 3 parts of Ti catalyst), PCS monomers; 1,4-bis(dimethylvinylsilyl)benzene + $[MeSi(H)O]_4$. [c] Relative amount of dimethyl maleate (DM) to the Pt catalyst. [d] The surface was not smooth.

Synthesis of Silicon-Based IPNs. As noted above, we used LDS **1** as a condensation component, and the combination of 1,4-bis(dimethylvinylsilyl)benzene (**1**) and 1,3,5,7-tetramethylcyclotetrasiloxane (**2**) as a hydrosilylation component for a silicon-based IPN (Table 1). As a condensation catalyst, we used titanium(IV) bis(acetylacetato)diisopropoxide, H_2O, and $[Pt\{(CH_2{=}CHSiMe_2)_2O\}_2]$ as a hydrosilylation catalyst, as well as dimethyl maleate as a retarder of hydrosilylation.

We tried to prepare a silicon-based IPN via a casting method, and the method was described as follows: a THF solution of both components and the catalysts was poured into a metal can and placed in an oven at 50 °C for 16 h, subsequently, and heated stepwisely (80 °C/6.5 h → 100 °C/14.5 h → 150 °C/20 h). The cured sheet obtained was pale yellow and transparent without bubbles or cracks (Table 6, experiment no. 1). Its gel content was 100%. It was clear that the curing conditions, *stepwise heating*, 50 °C/16 h → 80 °C/6.5 h → 100 °C/14.5 h → 150 °C/20 h, was important in getting cured LDS/PCS materials without bubbles or cracks. We could not observe H_2-forming under these curing conditions. We considered the reason the neutral catalysts were used. In our previous work, it was clear that the Pt−vinylsiloxane complex was much more favorable than the conventionally used Speier's catalyst (H_2PtCl_6) in the presence of alcohol.[11]

We examined the possibilities of balancing both the reaction rate of the combined LDS/PCS (LDS/PCS = 8/2 [wt/wt]) curing system by means of adjusting amounts of the catalyst (Table 6). The extent of "condensation" and "hydrosilylation" was roughly estimated by gel content. Table 6 summarized the gel contents of the cured LDS, PCS and LDS/PCS (8/2), which were cured under 50 °C/16 h and 80 °C/2 h, respectively. It was clear that the gelation of the LDS oligomer did not proceed without H_2O, which was necessary to hydrolyze the SiOEt groups, and that the gelation of the PCS almost proceeded under mild conditions (50 °C/16 h). In the case of the combined curing system, the gel content after 50 °C/16 h was 66% (Table 6, experiment no. 1). It was larger than the calculated values ($17 \times 0.8 + 93 \times 0.2 = 33\%$). However, in the case of decreasing the condensation catalysts (Table 6, experiment no., 2 and 3), the reaction did not proceed rapidly at 50 °C/16 h. Furthermore, the appearance of the cured LDS/PCS was opaque without H_2O.

To obtain more information about the curing reaction of the combined LDS/PCS system, we analyzed the cured material that was heated for 12 h at 50 °C with solid-state ^{29}Si NMR. Figure 2A shows that the PCS monomers still remained after 50 °C/12 h. The PCS monomers would be swollen into the LDS network. Figure 2B of the cured LDS/PCS after 150 °C/20 h shows that the cross-linking reaction of both the components proceeded selectively. The results probably suggests that our IPN would be a sequential IPN formation; that is, the condensation reaction may proceed at first, and a sequential hydrosilylation reaction may proceed.

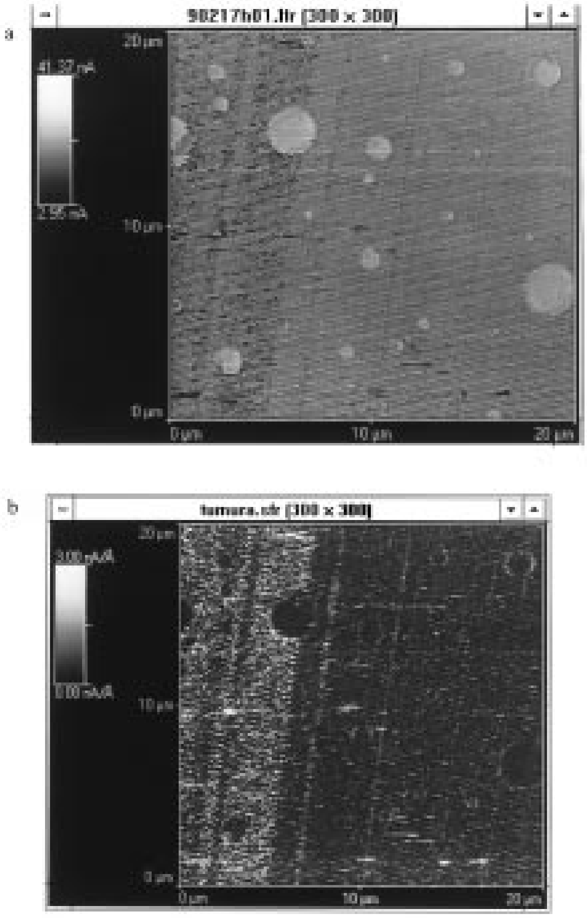


Figure 4. Atomic force micrographs (AFM) of the LDS/PCS cured samples: (a) lateral force mode; (b) force modulus mode of experiment no. 3 in Table 6.

We were interested in the effect of composition ratio on the property. Therefore, we attempted to prepare the LDS/PCS cured material (LDS/PCS = 5/5 and 2/8 [wt/wt]). In a PCS-rich combined curing system, by increasing the amount of dimethyl maleate, we were able to obtain a homogeneously cured transparent material (Table 9). We presume that the beginning of the hydrosilylation reaction would be delayed by increasing the amounts of the retardant.

Morphology Silicon-Based IPNs. We evaluated the morphology of silicon-based IPN by means of transmission electron microscopy (TEM, Figure 3) and atomic force micrography (AFM, Figure 4). TEM techniques indicated good miscibility at a nanometer level for the homogeneous and transparent material; however, an opaque LDS/PCS contained domains whose size was at micrometer level (Figure 3).

Atomic force micrography (AFM) revealed the properties of the domains that had phase-separated the LDS/PCS materials (Table 6, experiment no. 3).[28] The lateral force mode measured the lateral variation (Figure 4a). The white area shows the highly frictional area. The force modulus mode measured the force variation (Figure 4b). The dark domain shows the low modulus area. Since the cured PCS had a higher strain than the cured

Table 10. Properties of LDS/PCS Compared with Each Component's

sample[a]	flexing modulus, GPa	LOI,[b] %	TGA[c] wt loss, % at 500 °C	T_{d5},[d]
LDS	2.2	40	2.1	577
LDS/PCS (8/2)	2.2 (2.0)[e]	40 (32)[e]	1.8 (2.4)[e]	<580
PCS	1.5	24	3.8	51

[a] Curing conditions: 50 °C/21 h → 80 °C/20 h → 100 °C/7 h → 150 °C/24 h → 180 °C/65 h. LDS: LDS **1** in Table 1 (LDS components; added 3.8 parts of H_2O, 3 parts of Ti catalysis), PCS monomers; 1,4-bis(dimethylvinylsilyl)benzene + $[MeSi(H)O]_4$. [b] Limiting oxygen index. [c] Under N_2, 20 °C/min. [d] The temperature at 5% weight loss. [e] The calculated values from each component's value.

Table 11. Influence of Miscibility on the Thermal Stability of LDS/PCS[a]

expt no.[b]	domain size,[c] μM	T_{d5},[d] °C	TGA wt loss, %[e] 400 °C	500 °C	1000 °C
1	N.D.	417	4.1	10.8	35.2
2	N.D.	387	5.6	12.1	36.5
3	1 ~ 2	374	6.2	12.1	36.7
4[f]		366	6.8	12.0	36.9

[a] LDS: LDS **1** in Table 1. PCS monomers: 1,4-bis(dimethylvinylsilyl)benzene + $[MeSi(H)O]_4$. [b] Curing conditions; 50 °C/16 h → 80 °C/6.5 h → 100 °C/14.5 h → 150 °C/20 h. [c] By TEM analysis. [d] The temperature at 5% weight loss. [e] Under N_2, 10 °C/min. [f] Blended polymer.

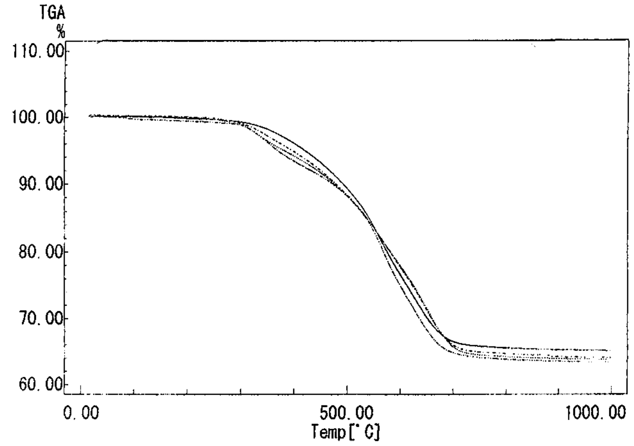


Figure 5. TGA curves of LDS/PCS with various miscibility under nitrogen stream (solid line, experiment no. 1; dash–dotted line, experiment no. 2; dotted line, experiment no. 3; dash–two dotted line, experiment no. 4 in Table 11).

LDS, we presumed that the domains mainly consisted of PCS.

Properties of Silicon-Based IPNs. We evaluated a flexing modulus, limiting the oxygen index (LOI) and thermal properties of the cured LDS, PCS, and LDS/PCS (8/2), respectively. The flexing modulus, LOI, and weight loss percentage at 500 °C of LDS/PCS (8/2) were greater than the calculated values of each component's values (Table 10). Furthermore, we evaluated the influence of miscibility on thermal stability. Table 11 summarizes the thermal stability of the cured LDS/PCS (8/2), which is the same as in Table 6, experiment no. 4, which is a mechanical blend mixture of 80 wt % cured LDS to 20 wt % cured PCS. Figure 5 shows the TGA curves. It was revealed that good miscibility tended to inhibit the decomposition between 25 and ca. 550 °C. The higher thermal stability results from the highly cross-linked structure.

Table 12. Effects of the LDS/PCS Ratios on the Flexing Properties of the Cured Samples

expt no.	LDS/PCS,[a] wt/wt	flexing modulus, GPa	maximum strength, MPa	maximum strain, %
1	8/2	2.2 (2.0)[b]	54	3.5
2	5/5	1.2 (1.8)[b]	40	3.4
3	2/8	1.8 (1.6)[b]	78[c]	10.7[c]
4	10/0	2.2	43	3.4
5	0/10	1.5	64[c]	9.5[c]

[a] LDS: LDS **1** in Table 1. PCS monomers: 1,4-bis(dimethylvinylsilyl)benzene + $[MeSi(H)O]_4$. [b] The calculated values from each component's value. [c] The sample was only distorted without break.

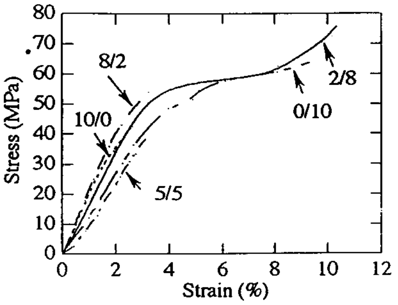


Figure 6. Stress–strain curves of the cured LDS/PCS with various ratios in Table 12.

We evaluated the effects of the LDS/PCS ratios on the flexing properties. Table 12 summarizes the results, with stress–strain curves in Figure 6. The flexing modulus of the cured LDS/PCS (8/2, 2/8) was larger than the calculated one from each component's value. The maximum strength and strain of the cured LDS/PCS (2/8) were interestingly and unexpectedly larger than each of the component values. Such a tendency was reported in a carbon-based IPN of polyester and epoxy resins.[29] The various features of the cured LDS/PCS imply an IPN structure.

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