Silicon-Based Materials Prepared by IPN Formation and Their Properties

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Received 26 May 1999; accepted 10 September 1999

ABSTRACT: Both "condensation" and "hydrosilylation" reactions have been successfully applied to the synthesis of silicon-based interpenetrating polymer networks (IPNs) consisting of a stable Si—O and/or a Si—C linkage. 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 were used as the two components for the IPN (Table I). Si-based IPN material was prepared by melt-and-compression-molding method of the B-staged resin. Evaluating the flow-curing nature of the B-staged resin thus obtained with a KOKA-type flow tester led to suitable conditions for melt-and-compression molding. LDS/PCS materials with various shapes (3–4 mm thick) were prepared by melt-and-compression molding. The mechanical properties of the LDS/PCS materials were evaluated. The flexural modulus and Izod impact strength of LDS/PCS (8:2 w/w) were larger than those of each component, a tendency that proved to be a positive effect derived from IPN formation in the LDS/PCS combined system. In addition, the thermal, electrical, and optical properties of these silicon-based materials were studied and are reported on. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 724–731, 2000

Key words: silsesquioxane; polycarbosilane; interpenetrating polymer network; B-staged resin; melt-and-compression molding; mechanical property, thermal property; optical property; electric property

INTRODUCTION

Interpenetrating polymer network (IPN) research has become an area of much interest.[1] IPNs are homogenous polymer mixtures made from two different polymers (each made via different and independent reaction mechanisms) that normally are mutually insoluble, but because of crosslinks 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, poly(phenylene oxide)–polystyrene, and phenolic resin–polyamide.[2] More recently, silicon-based organic–inorganic composites have been prepared by many groups and have been studied at the point of application.[3–8]

In a previous article, the authors reported the synthesis of silicon-based interpenetrating polymer networks (IPNs) consisting of a stable Si—O and/or a Si—C linkage.[9] "Condensation" and "hydrosilylation" reactions were applied to the synthesis of silicon-based IPNs. Ladder silsesquioxane oligomer (LDS **1**, commercial name: Glass Resin™ GR100) and a polycarbosilane (PCS) were used as the components of the Si-based IPN (Table I). The silicon-based IPN produced a condensation reaction with the LDS component and a hydrosilylation reaction with the PCS component.

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Journal of Applied Polymer Science, Vol. 78, 724–731 (2000)
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Table I LDS and PCS Components of IPN Formation

LDS Component		PCS Component	
'RO–[Si(R)–O]–R' / O / 'RO–[Si(R)–O]–R' (n) LDS **1**	R = Ph or Me (Ph/Me = $\frac{1}{2}$) R′ = H or Et n = 7.2	$CH_2{=}CH$–Si(Me)(Me)–C_6H_4–Si(Me)(Me)–$CH{=}CH_2$ **1**	+ cyclo-[H–Si(Me)–O–Si(Me)–H / O / O / H–Si(Me)–O–Si(Me)–H] **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)	

$$—SiOR + H_2O \rightarrow —SiOH + ROH \quad (1)$$

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

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

$$—SiH + CH_2{=}CHSi— \rightarrow —SiCH_2CH_2Si— \quad (2)$$

The casting method was used to prepare the Si-based IPN. However, the specimen was too small to evaluate the practical properties of the silicon-based IPN.

In this article, the authors report on another practical method for the preparation of silicon-based IPN. Furthermore, the thermal, optical, and electrical properties of this silicon-based IPN are also recounted.

EXPERIMENTAL

Materials

The LDS oligomer (commercial name: Glass Resin™) were purchased from OI-NEG TV Products, Inc, USA.[10] The condensation catalyst, titanium (IV) bis(acetylacetonato)diisopropoxide (T-50, NIHON SODA Co., Ltd., Japan), was used without further treatment.

PCS monomers, 1,4-bis(dimethylvinylsilyl)-benzene (**1**), and 1,3,5,7-tetramethylcyclotetrasiloxane (**2**) were purchased from Shin-Etsu Chemical Co., Ltd., Japan. The platinum catalyst, $[Pt\{(CH_2 = CHSiMe_2)_2O\}_2]$ (1.0 wt % xylene solution) was prepared by the reaction of $H_2PtCl_66H_2O$ and 1,1,3,3-tetramethyl-1,3-divinyldisiloxane.[11–12] Dimethyl maleate (TOKYO KASEI Co., Ltd., Japan) and tetrahydrofuran (Nacalai Tesque Co., Ltd., Japan) were used without further treatment.

Preparation of B-Staged Resin of LDS

B-staged resin of LDS was prepared as follows. LDS **1** (50 g) was dissolved in tetrahydrofuran (50 mL) with ultrasonic waves. Titanium (IV) bis(acetylacetonato)diisopropoxide (1.5 g) and deionized water (1.9 g) were then added to this solution. The prepared solution was poured into a tray, the inner surface of which was covered with polyimide film (APICAL 25AH, Kaneka Corporation) in order to easily remove the sample. The tray was then covered with aluminum foil and heated in an oven at 50°C for 17 h. After heating, the obtained sheet was crushed in the presence of dry ice and evaporated under vacuum at ambient temperature for 5 h. The B-staged resin was a pale yellow powder, and its gel content was 49%. 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 for 4 h).

Preparation of Molded LDS

The B-staged resin obtained (6.5 g) was poured into a stainless mold heated at 150°C for 60 s. After that, the sample was pressed at 150°C for 30 s under 30 kg/cm^2, followed by degassing and pressing at 150°C for 30 min under 100 kg/cm^2. Finally, the sample was removed from the mold and placed in an oven at 150°C for 5 h. The sample obtained was pale yellow and transparent, and its gel content was 100%. The bending

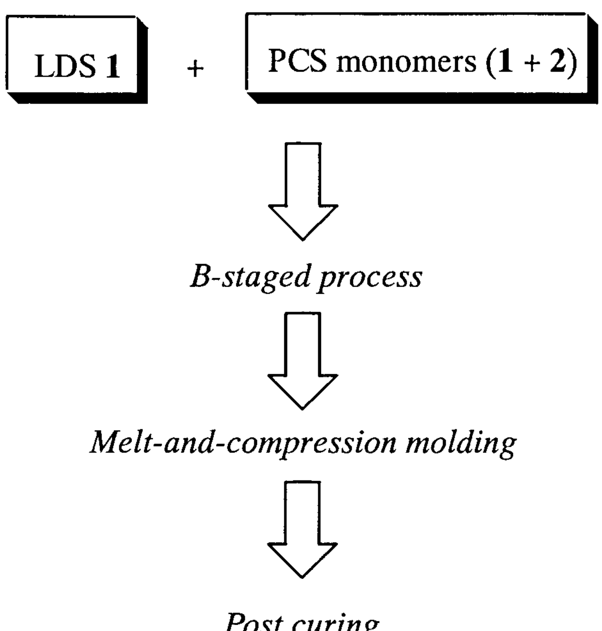

Figure 1 Schematic molding diagram of LDS/PCS materials.

specimen was 117 mm long, 10 mm wide, and 4 mm thick.

Preparation of Cured PCS

PCS monomers (**1**) (17.3 g) and (**2**) (7.9 g), and 10 wt % THF solution of dimethyl maleate 94 mg, and the Pt catalyst (67 mg, 9.71×10^{-6} mmol/mg) were mixed. The solution was poured into a cavity by a silicone rod (3 mm in diameter) between two glass plates, the inner surfaces of which were covered with cellulose film. The solution was heated in an oven at 50°C for 17 h and additionally heated at 100°C for 5 h. Finally, the sample was removed from the glass plates and was postcured at 250°C for 3 h under nitrogen stream. The sample obtained was colorless and transparent, and its gel content was 100%. The bending specimens (98 mm × 10 mm × 2.8 mm) were machined from the plaques obtained.

Preparation of B-Staged Resin of Silicon-Based IPN [LDS/PCS (8/2)]

B-staged resin of LDS/PCS (8/2) [wt/wt] was prepared as follows. LDS **1** (32.5 g) was dissolved in THF (33 mL) with ultrasonic waves. Titanium (IV) bis(acetylacetonato)diisopropoxide (1.0 g) and deionized water (1.2 g) were then added to this solution. In an another flask PCS monomers

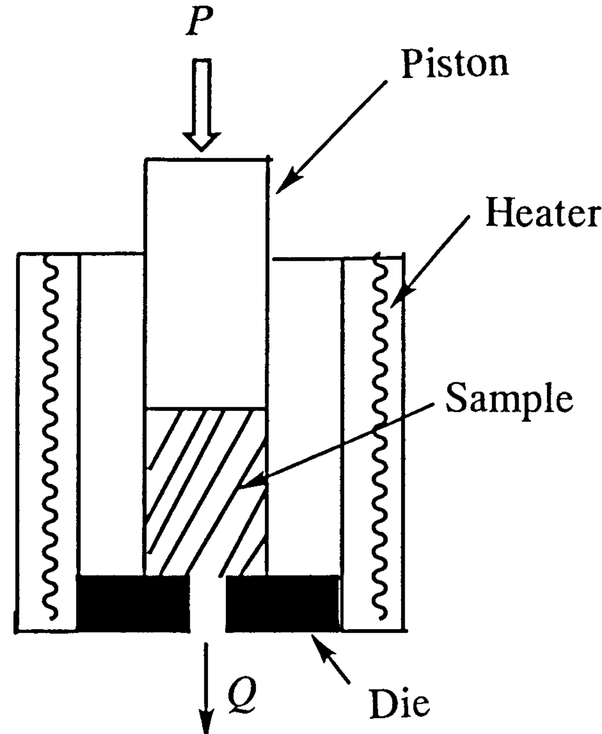

Figure 2 Illustration of Koka-type flow tester.

1 (5.2 g) and **2** (2.6 g), and 1 wt % THF solution of dimethyl maleate (61 mg) were mixed. To the mixed solution was added Pt catalyst (64 mg, 9.71×10^{-6} mmol/mg). The prepared solution was

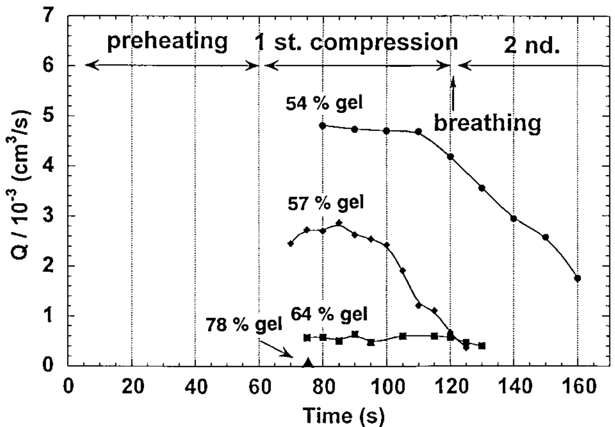

Figure 3 Flow-curing nature of B-staged LDS/PCS (8/2).

Table II Molding Conditions of LDS/PCS Materials

Test Mode	Compression Time (min.) 1st.[a]	Compression Time (min.) 2nd.[a]	Breathing Time (s)
Tensile	1	30	10
Compressive	1	30	45
Electric	4.5	30	60

[a] Molding conditions; preheating: 150°C/60 s, 1st.: 150°C/50 kgf/cm^2, 2nd.: 150°C/100 kgf/cm^2.

poured into a tray, the inner surface of which was covered with polyimide film (APICAL 25AH, Kaneka Corporation). The tray was then covered with aluminum foil and heated in an oven at 50°C for 12 h. After heating, the obtained sheet was crushed in the presence of dry ice and evaporated under vacuum at ambient temperature for 3 h. The B-staged resin was a pale yellow powder, and its gel content was 54%.

Preparation of B-Staged resin of Silicon-Based IPN [LDS/PCS (5/5)]

B-staged resin of LDS/PCS(5/5) [wt/wt] was prepared as follows. LDS **1** (50.0 g) was dissolved in THF (50 mL) with ultrasonic waves. Titanium (IV) bis(acetylacetonato)diisopropoxide (1.5 g) and deionized water (1.9 g) were then added to this solution. In another flask PCS monomers **1** (31.2 g) and **2** (15.3 g) and dimethyl maleate (183 mg) were mixed. To the mixed solution was added Pt catalyst (260 mg, 9.71×10^{-6} mmol/mg). Curing and drying conditions were same as in the case of LDS/PCS (8/2). The B-staged resin was a pale yellow powder, and its gel content was 61%.

Preparation of Molded LDS/PCS (8/2)

The B-staged resin obtained of LDS/PCS (8/2) (5.9 g) was poured into a stainless mold heated at 150°C for 60 s. After that the sample was pressed at 150°C for 60 s under 30 kg/cm^2, followed by degassing and pressing at 150°C for 60 min under 100 kg/cm^2. Finally, the sample was removed from the mold and placed in an oven at 150°C for 5 h. The sample obtained was pale yellow and transparent, and its gel content was 100%. The bending specimen was 98 mm long, 10 mm wide, and 4 mm thick. The molded LDS/PCS (5/5) material was obtained in the same manner as above.

Testing Methods

The mechanical properties were collected by a Shimadzu autograph with a maximum load cell of 100 kg. The flexural, tensile, and compressive test were following the JIS K7203, JIS K7113, and JIS K7208 methods, respectively.[13] The Izod impact strength was measured according to the procedure described in JIS K7110.[13] Samples were tested with a V-shaped notch (2 mm depth). The hardness test procedure followed JIS K7202.[13]

Coefficient of linear thermal expansion of the cured materials were made on a Shimadzu TMA 50 instrument at a heating rate of 10°C/min. Differential scanning calorimetry (DSC) was performed with a Shimadzu DSC-50 instrument at a heating rate of 20°C/min.

Indexes of refraction of the cured materials were determined by using an Abbe-type refrac-

Table III Flexural Properties and Izod Impact Strength of LDS/PCS (8/2) Materials[a]

Sample	Flexural Properties: Modulus of Elasticity (GPa)	Flexural Properties: Maximum Strength (MPa)	Flexural Properties: Maximum Strain (%)	Izod Impact Strength (kJ/m^2)
LDS	1.85	30.2	2.0	1.0
LDS/PCS (8/2)	1.92(1.81)[b]	41.9(34.3)[b]	2.7	2.1(1.1)[b]
PCS	1.63	50.8	5.4	1.4
Polyimide[c]	3.10	130.8	—	7.9

[a] $N = 1$.
[b] The calculated values from each components value.
[c] Vespel™ (SP-1).

Table IV Mechanical Properties and Hardness of LDS/PCS (8/2) Materials[a]

Sample	Tensile Properties			Compressive Strength (MPa)	Hardness (Rockwell)	
	Tensile Modulus (GPa)	Tensile Strength (MPa)	Maximum Elongation (%)		R Scale	M Scale
LDS	1.27	10.0	1.0	136.6	125	115
LDS/PCS (8/2)	1.33	7.1	0.8	111.3	107	90
PCS	0.99	27.9	5.9	—	56	29
Polyimide[b]	—	72.0	8.0	111.8	—	92–102

[a] $N = 3$. Standard deviation (STD) is less than 10%.
[b] Vespel™ (SP-1).

tometer at 14°C. The size of the samples used was approximately 3 × 10 × 30 mm. The transmittance and haze of the cured materials were estimated by a NIHON-DENSHOKU-KOGYO NDH-Σ80.

The electrical test method followed was JIS K6911.[13] The dielectric constants were measured at 1 MHz. The size of the samples used was approximately 3 × 100 × 100 mm.

Chemical and water resistance of the cured material were evaluated according to the procedure described in JIS K7114 and JIS K7209, respectively.[13]

Specific gravities (d) were calculated by the following equation:

$$d = d_0 \times W_1/(W_1 - W_2)$$

where W_1 and W_2 denote the weight in air and in water, respectively, and d_0 represents the specific gravity of water at 22°C.

RESULTS AND DISCUSSION

Material Preparation

Figure 1 shows a molding diagram of LDS/PCS materials. B-staged process was applied to obtain appropriate flow at molding. For the B-stage of the process, the LDS oligomer (**1**) and PCS monomers (**1**) + (**2**) were mixed and heated at 50°C for 12 h. The gel content of B-staged LDS/PCS resin was 54%.

The fluidities of various B-staged resins obtained were evaluated by a Koka-type flow tester. Figure 2 illustrates a sketch of Koka type flow tester. It consists of a piston, a heater, and a die that has a hole. Estimation of the amount of flowed resin from a die was determined by the molding condition of the LDS/PCS materials. Figure 3 displays the flow-curing nature of B-staged resins with various gel contents. The test was performed at 150°C under 100 kgf/cm^2. The vertical axis shows the amount of flowed B-staged resin a second and the horizontal axis shows time per second. It is clear that the fluidity of B-staged resins decreases as the gel content increases. The B-staged resin whose gel content was 78% did not flow. As a result, the molding conditions were determined as follows: (1) Preheating: heating the B-staged resin in a mold at 150°C for 60 s; (2) First compression: pressing at a lower pressure (30 kgf/cm^2); (3) Breathing: removing air, H_2O, and ethanol; (4) Second compression: pressing at a higher pressure (150 kgf/cm^2).

Bars (thickness: 3–4 mm) of LDS/PCS materials could be prepared according to the melt-and-compression molding of the B-staged resin under the above conditions. The LDS/PCS materials obtained were transparent, with no cracks and bubbles. Specimens for various testing mode were prepared with modified molding conditions (Table II).

Table V Coefficient of Linear Thermal Expansion of LDS/PCS (8/2) Materials

Sample	Coefficient of Linear Thermal Expansion (× 10^{-5}/°C)
LDS	12.0
LDS/PCS (8/2)	14.8
PCS	10.3($<T_g$),21.3($>T_g$)[b]
Polyimide[a]	5.4

[a] Vespel™ (SP-1).
[b] T_g: 85.3°C by DSC analysis.

Table VI Optical Properties of LDS/PCS (8/2) Materials and Other Plastics[a]

Sample	Index of Refraction	Transmittance T_t (%)[b]	Transmittance T_d (%)[c]	Hase (%)
LDS	1.48	75.7	11.3	15.0
LDS/PCS (8/2)	1.49	84.0	8.2	9.7
PCS	1.52	92.0	3.5	3.8
PMMA	1.49	>92.0	—	3.0
PS	1.58	88.6	—	9.7
PC	1.58	86.8	—	7.1

[a] PMMA: poly(methyl methacrylate); PS: polystyrene; PC: polycarbonate.
[b] Total transmittance.
[c] Diffusion transmittance.

Flexural Properties and Izod Impact Strength

Table III summarizes flexural properties and Izod impact strength of LDS, PCS, and LDS/PCS (8/2) materials compared with those of polyimide (Vespel™, SP-1).[14] Vespel™ was used as a heat-resistant engineering plastic. The flexural modulus and Izod impact strength of LDS/PCS (8/2) materials were greater than those of each component. It can be inferred based on the IPN structure that the features of LDS/PCS (8/2) materials would have a synergistic effect. However, the mechanical properties of the LDS/PCS materials obtained were lower than those of Vespel™ (SP-1). To use the LDS/PCS material as a structural material, the mechanical properties have to be improved.

Tensile and Compressive Properties and Hardness

Table IV lists tensile and compressive properties and hardness of obtained materials. The tensile modulus was bigger than those of each component. The same trend was reported in the carbon-based IPN system of epoxy resin and unsaturated polyester.[15] Compressive strength and hardness of LDS/PCS materials were the same as those of Vespel™ (SP-1).[14]

Coefficient of Linear Thermal Expansion

Table V lists the coefficients of linear thermal expansion of obtained materials. The cured PCS had a glass-transition temperature (T_g) of 85°C. The LDS, PCS, and LDS/PCS materials obtained had large coefficients of expansion compared with carbon-based materials, Vespel™ (SP-1).[14] This would be because the longer Si—C bond (bond length: Si—C := 0.190 nm, C—C = 0.154 nm) is flexible.

Optical Properties

The optical properties of LDS/PCS obtained are shown in Table VI. All materials obtained were transparent. The refractive index of LDS/PCS was almost the same as those of carbon-based polymers. In particular, the transmittance of PCS material was similar to that for PMMA, which is often used in optical materials. The PCS material had a high thermal stability.[9] Therefore, the ma-

Table VII Electric Properties of LDS/PCS (8/2) Materials and Other Plastics

Sample	Dielectric Breakdown Strength (kV/mm)	Dielectric Constant	Dielectric Loss Tangent, tan δ	Volume Resistivity (Ω cm)	Surface Resistivity (Ω)
LDS	18.6	2.7	0.002	2.6×10^{17}	1.9×10^{15}
LDS/PCS (8/2)	15.0	2.6	0.002	5.2×10^{17}	2.4×10^{15}
PCS	18.2	2.5	0.002	4.6×10^{14}	6.6×10^{12}
PI[a]	22	3.6	0.003	10^{16}	—

[a] Vespel™ (SP-1).

Table VIII Chemical and Water Resistance of LDS/PCS (8/2) Materials[a]

Solvent	LDS		LDS/PCS (8/2)		PCS	
	Appearance[b]	Ratio of Absorption (%)	Appearance[b]	Ratio of Absorption (%)	Appearance[b]	Ratio of Absorption (%)
H_2O at r.t.	+−	0.14	+	0.06	+	−0.02
10 wt % H_2SO_4	+	0.05	+	0.03	+	−0.01
10 wt % NaOH	+	0.03	+	0.01	+	0.02
H_2O at 100°C (1 h)	−	0.41	−	0.27	−	0.10
MeOH	−−	7.96	+	4.10	+	0.68
EtOH	−−	—	+	2.21	−−	0.31
Toluene	+−	−0.82	+	2.02	−−	—
THF	−−	—	−−	—	−−	—
$CHCl_3$	−−	—	−−	—	−−	—

[a] For 24 h at 23°C.
[b] +: no changes; +−: a few cracks; −: many cracks at cooling; −−: test pieces didn't hold initial shapes.

terial could be useful for heat-resistant optical fiber.

Electric Properties

Table VII lists the electric properties of obtained materials compared with those of polyimide. The dielectric breakdown strength was similar to the one of Vespel™ (SP-1). The dielectric constant of LDS/PCS materials was very low. That would be because the silicon-based polymer has very large free volume in the network structure. Recently, silsesquioxane was used as low-κ material.[16] Si-based material would be low-κ material with high thermal stability and good mechanical properties.

Chemical Resistance

The chemical resistances of obtained materials are shown in Table VIII. LDS, PCS and LDS/PCS materials had high resistance to water, acid and base. The stability of the LDS/PCS materials in MeOH, EtOH, and toluene was improved compared with LDS or PCS. Those feature of LDS/PCS materials would be attributed to the synergism of its IPN structure.

Physical Properties

The T_g and specific gravity are listed in Table IX. The T_g of PCS materials was observed at 85.3°C; however, LDS/PCS (8/2) materials did not have T_g. Furthermore, the specific gravities of LDS/PCS materials were larger than the calculated values from each component's values. Figure 4

Table IX Physical Properties of LDS/PCS Materials[a]

Sample	T_g (°C)[a]	Specific Gravity (g/cm^3)
LDS	N.D.	1.258
LDS/PCS (8/2)	N.D.	1.216(1.210)
LDS/PCS (5/5)	—	1.161(1.139)
PCS	85.3	1.019

[a] DSC (23°C ~ 250°C).
[b] Calculated values from each component's value.

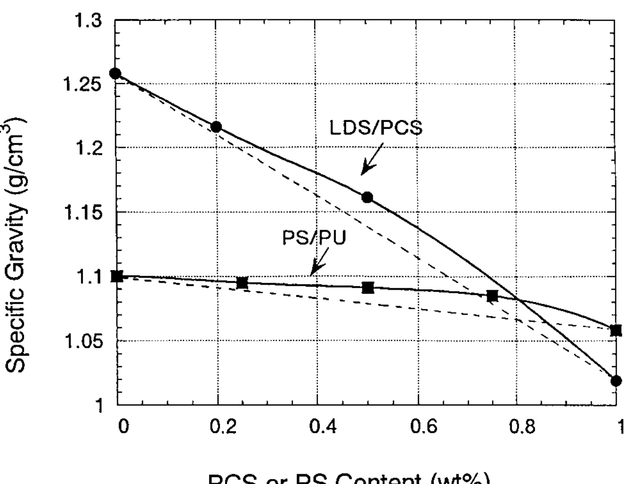

Figure 4 Specific gravity of the LDS/PCS materials and the polystyrene–polyurethane (PS–PU) IPN.

illustrates the relationship of observed to calculated density compared with the trend of the polystyrene–polyurethane (PS–PU) IPN.[17,18] The disappearance of the T_g and the trend of specific gravity would seem to indicate the formation of the IPN structure in the LDS/PCS materials. However, we do not have direct evidence for IPN formation. In our previous work, the solid-state NMR analysis suggested that the two components (LDS and PCS) independently formed the networks.[9] Now we are analyzing the structure of our Si-based IPN.

CONCLUSION

According to the results presented here, the melt-and-compression-molding method is suitable for obtaining practical test pieces of silicon-base IPN material. It is also clear that evaluating the flow-curing nature of the B-staged resin is useful in determining molding conditions.

The flexural modulus and Izod impact strength of LDS/PCS (8/2) materials were found to be bigger than those of each component. The features of LDS/PCS (8/2) materials can be inferred from the synergistic effect based on the IPN structure. Furthermore, the specific gravities of LDS/PCS materials were larger than the calculated values from each component's values. The trend of specific gravity would also seem to indicate the formation of IPN structure of LDS/PCS materials.

The transmittance of PCS material was similar to that for PMMA. PCS material is expected to be applicable to heat-resistant optical fibers. Furthermore, it is clear that the obtained Si-based materials have a very low dielectric constant.

This work was performed by Kaneka Corporation, under the management of the Japan Chemical Innovation Institute, as part of the Industrial Science and Technology Frontier Program supported by the New Energy and Industrial Technology Development Organization (NEDO).

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