

Properties of Hybrid Materials Derived from Hydroxy-Containing Linear Polyester and Silica Through Sol–Gel Process. I. Effect of Thermal Treatment

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ABSTRACT: The transparent hybrid material, HLP/SiO₂, was prepared by an *in situ* sol–gel process of tetraethoxysilane (TEOS) at 30°C in the presence of hydroxy-containing linear polyester (HLP) obtained by ring-opening reaction of diglycidyl ether of bisphenol A (DGEBA) with adipic acid under the catalyzation of triphenylphosphine (TPP). The hetero-associated hydrogen bonds between the HLP and the residual silanol of silica in the hybrids were investigated by FTIR spectroscopy. Upon heating the hybrid, the interfacial force between the HLP matrix and the silica network changed from hydrogen bonds into covalent Si—O—C bonds through dehydration of hydroxy groups in HLP with residual silanol groups in the silica network. The existence of covalent Si—O—C bonds was proved by solid-state ²⁹Si-NMR spectra. Other properties such as tensile strength, glass transition temperature (*T_g*), solubility, and thermal stability of the hybrids before and after heat treatment were studied in detail. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1179–1190, 2000

Key words: organic–inorganic hybrid materials; sol–gel process; hydroxy-containing linear polyester; interfacial force; hetero-associated hydrogen bonds

INTRODUCTION

As a new class of materials, organic–inorganic hybrids, has recently attracted much attention in the field of material science.^{1–7} For systems containing a mixture of inorganic components, the final products are usually hard and brittle. The incorporation of organic components would expectantly impart flexibility to the inorganic glass. On the other hand, the introduction of inorganic components can improve the hardness and modulus of the organic compounds. This multicomponent system could thus show some characteristics

of the inorganic glassy network and also some properties of the organic species. A sol–gel process is now available which allows the *in situ* development of inorganic phases within an organic matrix at low temperature. In this way, one can readily produce novel organic–inorganic hybrid materials.

In organic–inorganic hybrid materials, polymer and ceramics (e.g., silica) are blended or reacted with each other by mutual dispersion at a molecular dimension. Two approaches are normally utilized: In the first case, the covalent bonds between the polymer and silica are formed. Polymers having —Si(OR)₃ groups at the end or in the pendant groups are subjected to hydrolysis together with Si(OR)₄ in a homogeneous reaction system. Intermediate species of silanol groups derived from Si(OR)₄ and from —Si(OR)₃ in polymers condense with each other to produce homogeneous materi-

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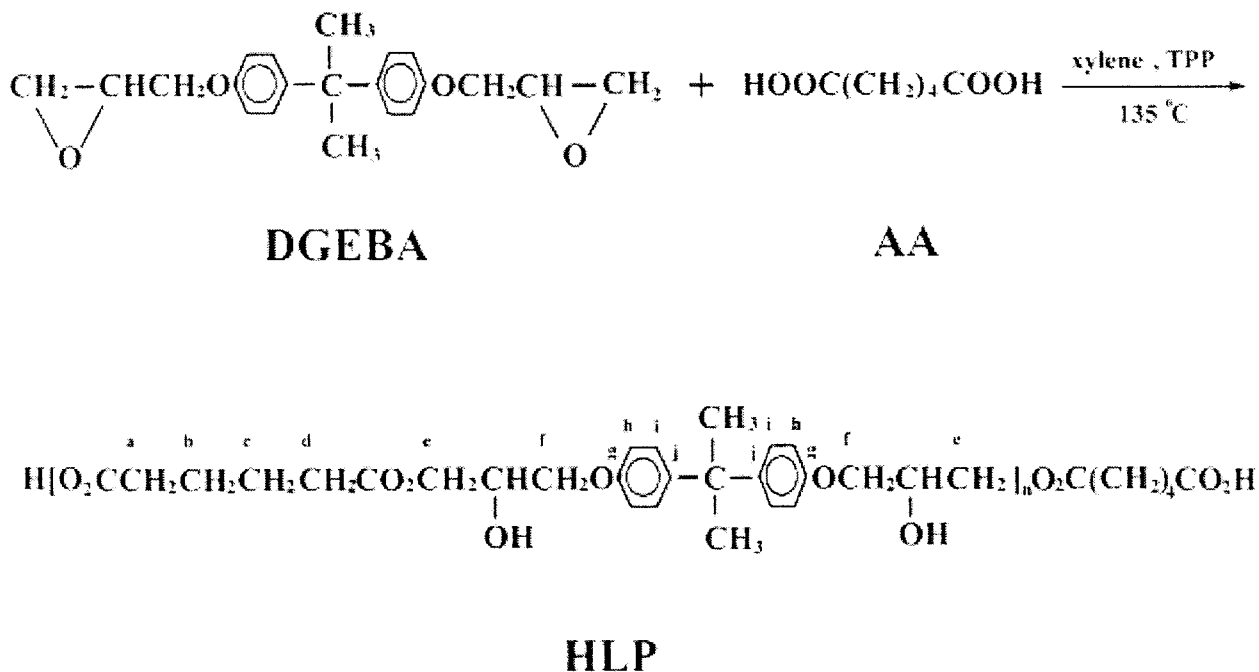


Figure 1 Ring-opening polymerization of DGEBA with AA to synthesize the HLP.

als containing chemically bound components. The other case is the dispersion of polymer molecules in the three-dimensional network of silica (or ceramics) by means of the formation of a hydrogen bond between the basic group of the hydrogen-acceptor function in the polymer and the silanol group ($\equiv\text{SiOH}$) of the intermediate species from $\text{Si}(\text{OR})_4$.^{8,9}

Amide polymers such as polyamide, polyurea, and polyurethane have been found to be most suitable for the preparation of hybrids with silica due to the $-\text{NECO}-$ groups in the polymer chains which very easily form hydrogen bonds with silanol groups.^{9,10} However, $-\text{COO}-$ groups in the polyester chains are not strong enough to form hydrogen bonds with silanol groups, so that the compatibility between the silica network and the polyester are restricted. In this article, we prepared a type of linear polyester which contains hydroxy groups in the polymer chain to increase the interfacial force (i.e., hydrogen bonding) between the polyester and the silica network. This hydroxy-containing linear polyester (HLP) is obtained by a ring-opening reaction of diglycidyl ether of bisphenol A (DGEBA) with adipic acid (AA) in xylene at 135°C under the catalyzation of triphenylphosphine (TPP). The hybrid material, HLP/ SiO_2 , is obtained by the incorporation of HLP with tetraethoxysilane

(TEOS) through a sol-gel process. The hydroxy groups in polyester do not only form hydrogen bonds with silanol groups, but can also form $\text{Si}-\text{O}-\text{C}$ bonds by dehydrating with silanol groups at high temperature. In this study, the interfacial behavior as well as thermal and mechanical properties of HLP/ SiO_2 before and after heat treatment were investigated in detail.

EXPERIMENTAL

Materials

TEOS was purchased from the Acros Chemical Co. (Geel Belgium) and was purified by distillation. AA and TPP were obtained from the Merck Chemical Co. and were purified by recrystallization. DGEBA was used without further purification. Other reagents were purified by the conventional methods.

Synthesis of HLP

DGEBA and AA were dissolved in xylene with the mol ratio of end groups, epoxy and carboxyl groups, at 1.00/1.01. The two reactants then underwent ring-opening polymerization according to the chemical equation in Figure 1 at 135°C under a N_2 at-

Table I Properties of HLPs of Different Reaction Times

Polymer	End Groups (mmol/g)		M_n^a (g/mol)	M_w^a (g/mol)
	[COOH] $\times 10^2$	[Epoxy] $\times 10^3$		
HLP ₄ ^b	45.1	4.2	5273	9739
HLP ₆ ^c	8.2	8.3	8804	22,363

^a Molecular weights were determined with GPC relative to polystyrene.

^b HLP obtained by ring-opening reaction for 4 h.

^c HLP obtained by ring-opening reaction for 6 h.

mosphere. The extent of the reaction was checked by the titration of the epoxy group with HBr.¹¹ At the end of the reaction, petroleum ether was added to the reaction mixture to precipitate the HLP. The pure product was then obtained by redissolving the precipitant in THF, filtering the impurity, and then precipitating the filtrate with petroleum ether three times. The structure and molecular weight of the polyester were determined by elemental analysis, FTIR, ¹³C-NMR, and GPC.

HLP [C ₂₇ H ₃₄ O ₈] _x	C%		H%
	Calc.	66.65	7.05
	Found	66.98	7.20

¹³C-NMR (δ , ppm, DMSO): 23.6 [$>C(-CH_3)_2$]; 33.2 [$>C(CH_3)_2$]; 30.6 (Cb); 41.2 (Ca); 65.4 (Ce); 67.1 (Cf); 69.3 [$>CH-OH$]; 114.8 (Ci); 128.5 (Ch); 144.0 (Cj); 157.6 (Cg); 174.4 [$>C=O$]. IR (cm⁻¹): 3441 ($-OH$); 1733 ($>C=O$, ester); 3060, 1607, 1508, 1457, 830 (benzene ring); 1245, 1140 cm⁻¹ (C—O stretching vibration).

The molecular weight and end-group concentrations are listed in Table I.

Preparation of HLP/SiO₂ Hybrid Materials

The sol-gel liquid solution of HLP with TEOS was prepared by dissolving a stoichiometric amount of TEOS, H₂O, and hydrochloric acid in THF (Table II). The mixture was stirred at room temperature for 30 min to obtain a homogeneous solution called Sol B. Sol B was then combined with the THF solution of HLP (Sol A). The mixture of Sol A and Sol B was then stirred for another 10 min. The resultant homogeneous mixture was subsequently used to prepare the hybrid materials, HLP/SiO₂, through the sol-gel process

of TEOS in the presence of HLP. The silica thus formed was in an open, extended chainlike, ramified structure with the size in the nanoscale.¹² Films of hybrids with uniform thickness were obtained by casting the sol-gel solution of different recipes onto a plate, which was then sealed for gelling at 30°C. The resulting gels were dried slowly in air at the same temperature for a period of time (from several days to 1 month) until the sample reached a constant weight to yield monolithic, transparent, and flexible hybrid materials. All the samples were vacuum-dried at 50°C for 3 days. The materials were subsequently heated to improve their properties. The scheme for the sol-gel process of TEOS and the formation and heat treatment of HLP/SiO₂ are summarized in Scheme 1.

Measurement

FTIR spectra of HLP and the HLP/SiO₂ hybrids were recorded on a Bio-Rad SPC 3200 FTIR with a resolution of 2 cm⁻¹. Samples for FTIR were prepared by coating the polymer (or hybrids) on KBr disks and were then vacuum-dried at 50°C for 3 days. ¹H- and ¹³C-NMR spectra were recorded on JEOL EX-400-MHz FT-NMR spectrometer and ²⁹Si-NMR spectra were recorded on a Bruker MSL-300-MHz solid-state NMR spectrometer. The molecular weight of the polyester was measured by LC-500 GPC (GL Sciences Inc., Japan) with the following conditions: column, PL-gel 5-mM Mixed-D 7.5 \times 300 mm; solvent, THF; concentration, 0.1 g/100 mL; flow rate, 0.8 mL/min; temperature, 40°C; and detector, RI. Thermal properties including the glass transition temperature (T_g) and the initial decomposition temperature (IDT) of the hybrids were characterized

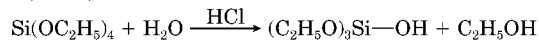
Table II Compositions of Sol-Gel Liquid Solutions of HLP/SiO₂ Hybrid Materials

Sol	Composition	SiO ₂ (wt %)			
		3	8	16	32
Sol A	HLP ^a (g)	2.40	2.40	2.40	2.40
	THF (g)	1.53	1.53	1.53	1.53
Sol B	TEOS (g)	0.26	0.72	1.60	4.00
	THF (g)	0.18	0.50	1.11	2.76
	H ₂ O (g) ^b	0.05	0.14	0.31	0.76
	[HCl]/[TEOS]	0.01	0.01	0.01	0.01

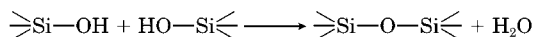
^a HLP₄ or HLP₆.

^b [H₂O]/[TEOS] = 2.2 (mol ratio).

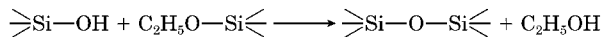
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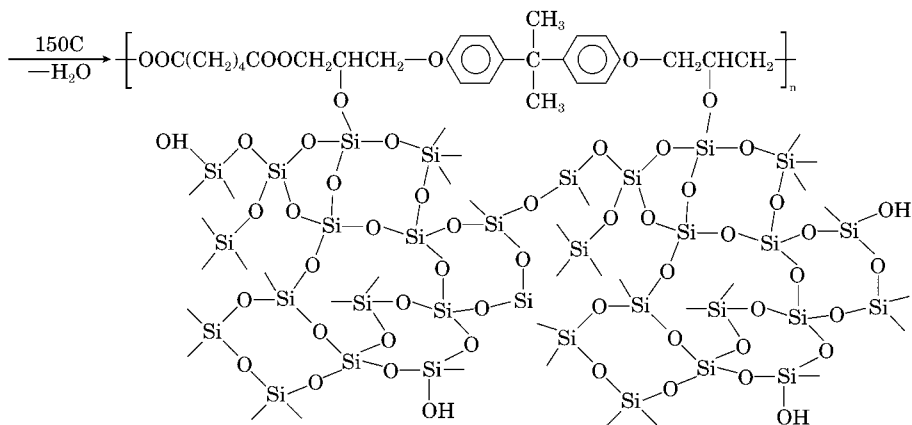
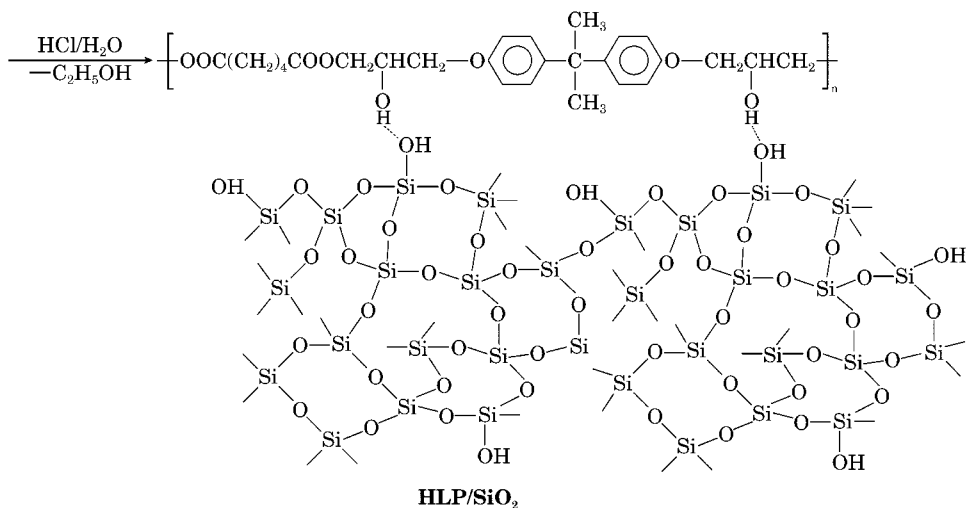
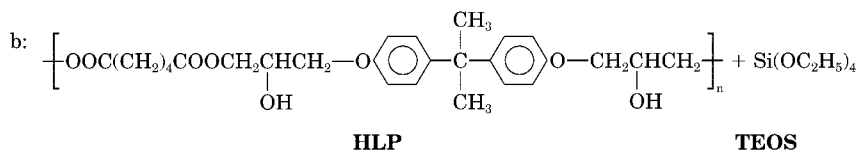
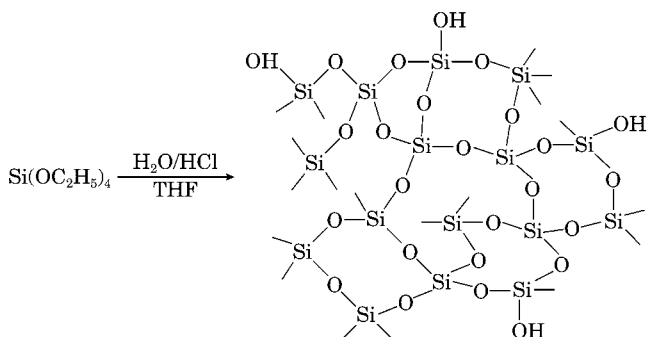
Condensation



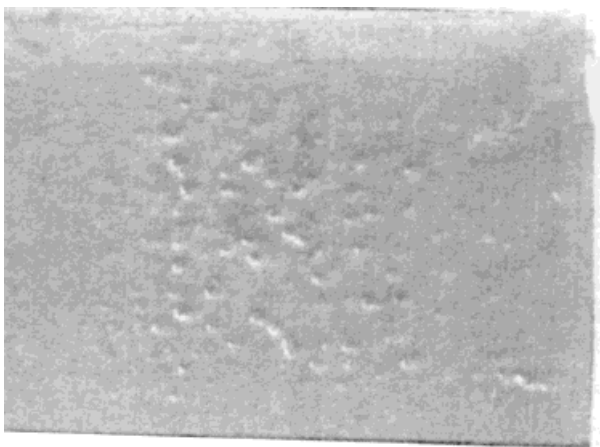
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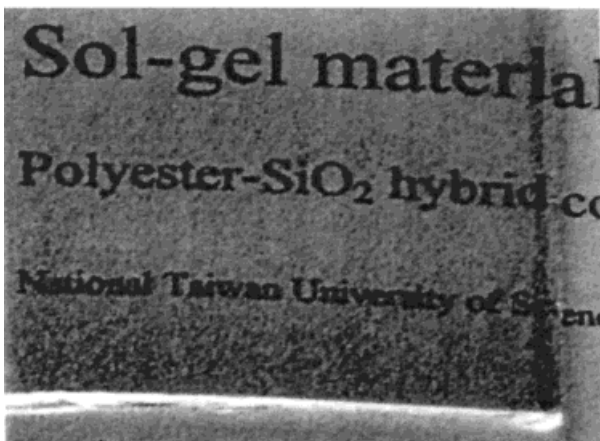
Net Reaction



Scheme 1 Sol-gel process of (a) TEOS and the (b) formation and heat treatment of HLP/SiO₂.



A



B

Figure 2 Photographs of (A) PDGA/SiO₂ hybrid with silica content of 3 wt % (the hybrid is in serious phase separation) and (B) HLP/SiO₂ hybrid with silica content of 32 wt % (the hybrid is transparent).

by a differential scanning calorimeter (DSC, DuPont 2100) under a N₂ flow with a heating rate of 20°C min⁻¹ and a thermogravimetry analyzer (TGA, DuPont 2100) under a N₂ flow with the heating rate of 10°C min⁻¹, respectively. The tensile strength of the hybrids was tested in accordance with the ASTM Test Method D-638M-93.

RESULTS AND DISCUSSION

The driving force of forming an organic-inorganic hybrid of a polyester with a silica network is the

strong hetero-associated hydrogen bonds between the polyester and the residual silanol groups of the silica network.^{8,13} However, without the polar groups (e.g., hydroxy groups) besides the ester moiety in the chains, the hetero-associated hydrogen bonds between the polyester and the silanol groups of the silica network are not strong enough to yield a transparent hybrid because of macrophase separation. Taking poly(diethylene glycol adipate) (PDGA) as an example, the hybrid is not formed when TEOS undergoes the sol-gel process in the presence of PDGA even at a low silica content of 3 wt % (Fig. 2). However, for polyester with hydroxy groups in the chains, (e.g., HLP), a transparent hybrid can be formed by the incorporation of TEOS with HLP even at a much higher silica content (≥40 wt %).

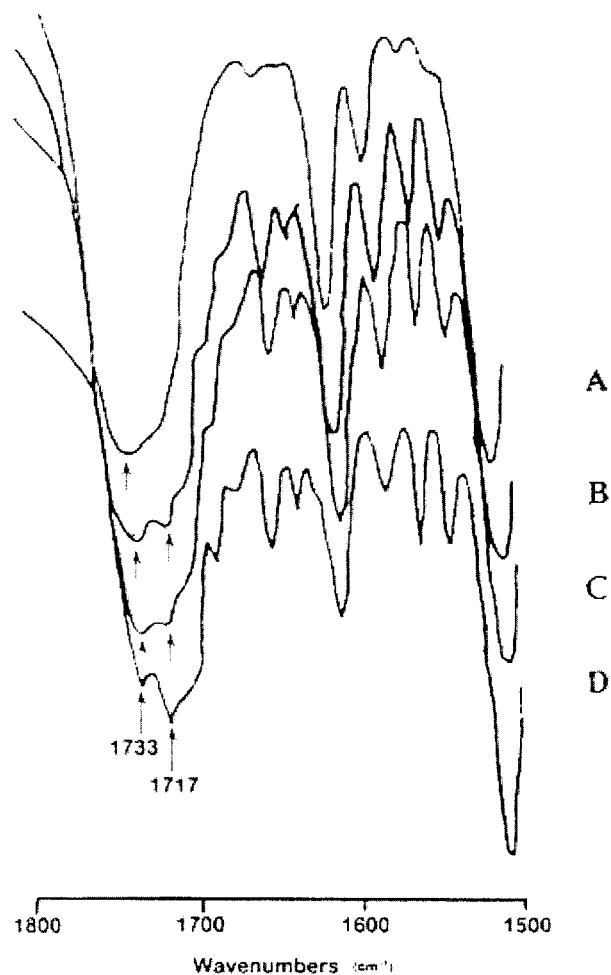


Figure 3 FTIR spectra in the ester carbonyl stretching region for (A) pure HLP and (B) 92/8, (C) 84/16, and (D) 68/32 HLP/SiO₂ hybrids.

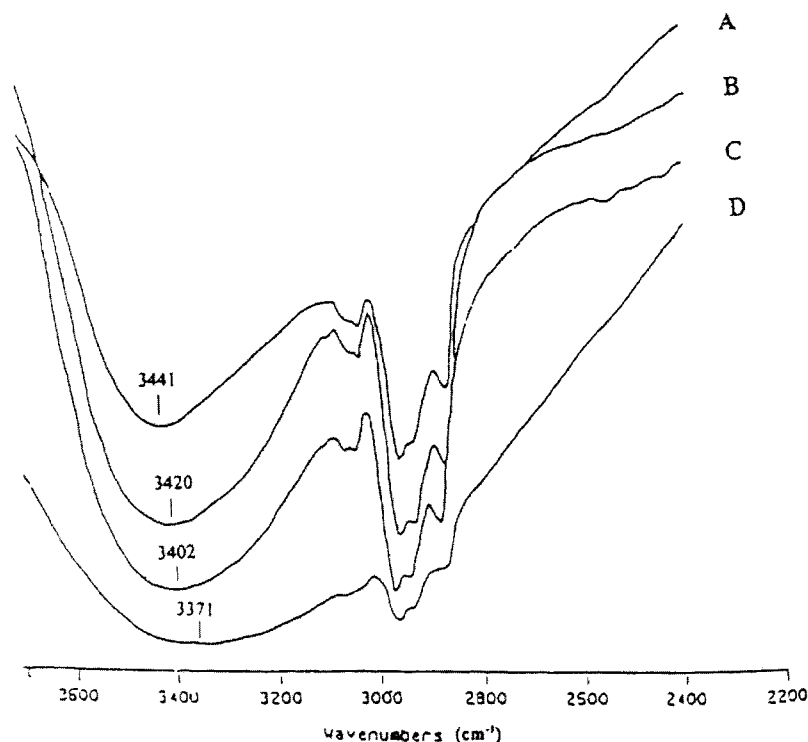


Figure 4 FTIR spectra in the hydroxy stretching vibration for (A) HLP and (B) 92/8, (C) 84/16, and (D) 68/32 HLP/SiO₂ hybrids.

FTIR Studies of the Hybrids

To better understand the hydrogen-bonding interactions between organic and inorganic phases in the hybrid, FTIR spectroscopy was utilized to probe the hetero-associated and self-associated hydrogen bonds in the hybrids. Figure 3 shows the infrared spectra of HLP and HLP/SiO₂ with different silica contents. The C=O stretching band of HLP was characterized by a strong absorption centered at 1733 cm⁻¹. Upon forming the hybrids (92/8 HLP/SiO₂ hybrids), in addition to the absorption at 1733 cm⁻¹, a new absorption band at 1717 cm⁻¹ is observed which is assigned to the silanol-bound carbonyl stretching. The intensity of this new band increases as the amounts of silica in the hybrids increases to 16 and 32 wt %.

The hetero-associated hydrogen bonds between hydroxy groups of HLP and silanol groups of silica in the hybrids can also be proved to take place in the same situation. The hydroxy stretching band of HLP appears as a strong broad band at 3441 cm⁻¹. Upon forming the hybrids with silica, the band appears at 3420 cm⁻¹ for the 92/8 HLP/SiO₂ hybrids and gradually shifts to 3402 and 3371 cm⁻¹ as the silica composition increases to 16 and 32%, respectively (Fig. 4). The vibration

bands are also broadened with increasing silica content in the hybrids. These observations are attributed to the strong hetero-associated hydrogen bonds between the hydroxyl groups of HLP and the silanol groups of silica.

Heat Treatment of HLP/SiO₂ Hybrid Materials

FTIR spectra of the 84/16 HLP/SiO₂ hybrid before and after heat treatment is shown in Figure 5 along with that of pure HLP. The split silanol-bound carbonyl bands between 1733 and 1717 cm⁻¹ in the hybrid become a single absorption peak at 1733 cm⁻¹ after heat treatment of the hybrid at 150°C for 3 h. The absorption frequency is just the same as that of pure HLP. The carbonyl-bound hydroxy band in the HLP/SiO₂ hybrid shifts back from 3402 to 3440 cm⁻¹. The pattern and frequency of the absorption peak of the hydroxy group is very similar to that of pure HLP. The stretching band of Si—OH at about 958 cm⁻¹ in the hybrid disappears after heat treatment. This indicates that the hetero-associated hydrogen bonds between HLP and the silanol groups in the hybrid changed after the heat treatment. Other information about the change of the

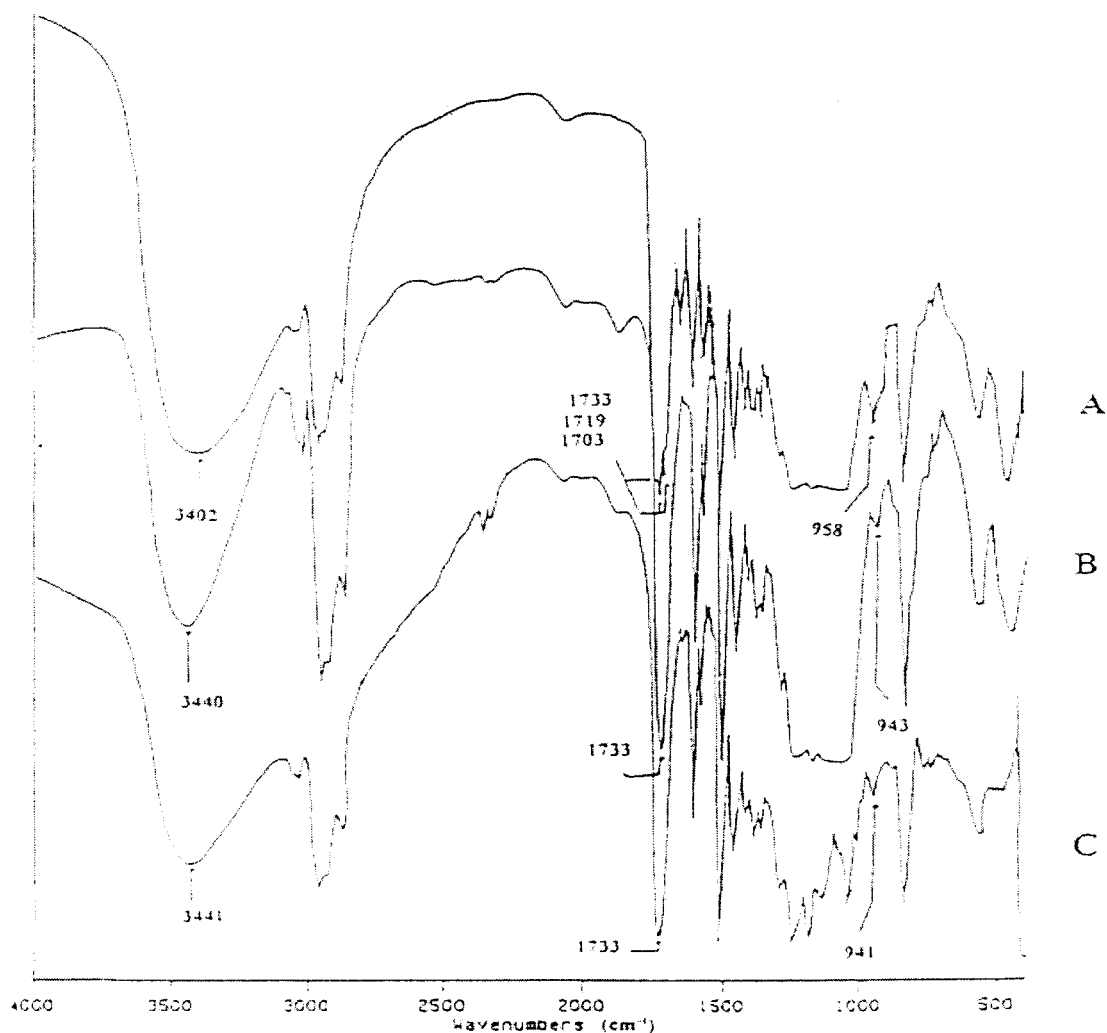


Figure 5 FTIR spectra of 84/16 HLP/SiO₂ hybrid (A) without heat treatment and (B) after heat treatment at 150°C for 3 h and (C) of pure HLP.

interaction between the organic and inorganic phases can be deduced from the changes in the tensile strength and solubility of the hybrid before and after heat treatment.¹⁴ Table III shows the effect of the heat-treatment temperature on the tensile strength of HLP with different molecular weights (HLP₄ and HLP₆) and their corresponding hybrids, HLP₄/SiO₂ and HLP₆/SiO₂ (of different silica content). After being treated at 150°C for 3 h, the tensile strengths of HLP₄ and HLP₆ were not changed. However, their corresponding hybrids of different silica content exhibit significant improvement in strength upon heat treatment. This indicates that the trace amount of epoxy and carboxy groups (Table I) in the polyester do not significantly influence the mechanical properties of HLP. The increase in

tensile strength of the hybrids after heat treatment is thus attributed to the presence of the silica network and the change of the interfacial force between the silica network and HLP. The solubilities of HLP/SiO₂ hybrids of different silica content in THF before and after heat treatment are listed in Table III. If the interfacial force between HLP and silica is only hydrogen bonding, then THF should dissolve the unreacted HLP and leave the "silica phase" as particles or gel. If there are strong interactions or covalent bonds between the two phases, then the content of the "silica phase" will exceed that of SiO₂, which can be tested through TGA.¹⁵ It is found that the solubility of the hybrids decreases significantly after being heated at 150°C, and the higher the silica content in the hybrid, the more the decrease of

Table III Tensile Strengths and Solubilities of HLP₄/SiO₂ and HLP₆/SiO₂ Hybrids with Different Silica Content Before and After Heat Treatment at 150°C

SiO ₂ (wt %)		Tensile Strength (MPa)		Solubility in THF (wt %) ^a	
Calcd	Observed ^b	30°C	150°C	30°C ^c	150°C ^c
0	0	1.6/3.7 ^d	1.7/4.9	100.0/100.0 (A) ^d	100.0/100.0 (A)
3	3.6/3.1 ^d	4.8 ± 0.1/10.2 ± 0.5	12.6 ± 0.3/40.7 ± 1.3	91.0/86.2 (B)	89.5/57.3 (C)
8	8.7/9.1	10.5 ± 0.4/21.4 ± 0.9	44.4 ± 1.1/79.4 ± 2.4	86.6/80.3 (B)	19.7/17.8 (C)
16	17.1/16.3	7.6 ± 0.2/15.6 ± 0.7	33.8 ± 0.9/66.8 ± 1.9	79.8/71.7 (C)	5.1 (C)/0.6 (D)
32	33.4/31.6	6.3 ± 0.3/13.8 ± 0.6	21.6 ± 0.7/47.2 ± 2.2	60.3/47.8 (C)	0.7/0.5 (D)

^a HLP/SiO₂ film 0.5 g, dissolved in 100 mL of THF at 25°C with stirring for 3 days.

^b Film appearance after dissolving in THF for 3 days: (A) clear solution; (B) broken into fine particles; (C) intact and opaque; (D) intact and transparent.

^c SiO₂ content in the hybrids were determined by TGA.

^d Numerator is the properties of the HLP₄/SiO₂, while denominator is the properties of the HLP₆/SiO₂.

the solubility. This indicates that the interfacial force between the silica network and HLP was changed from hydrogen bonding to another chemical bond, perhaps the Si—O—C covalent bond, through the dehydration of the hydroxy group in HLP with the residual silanol group in the silica network.

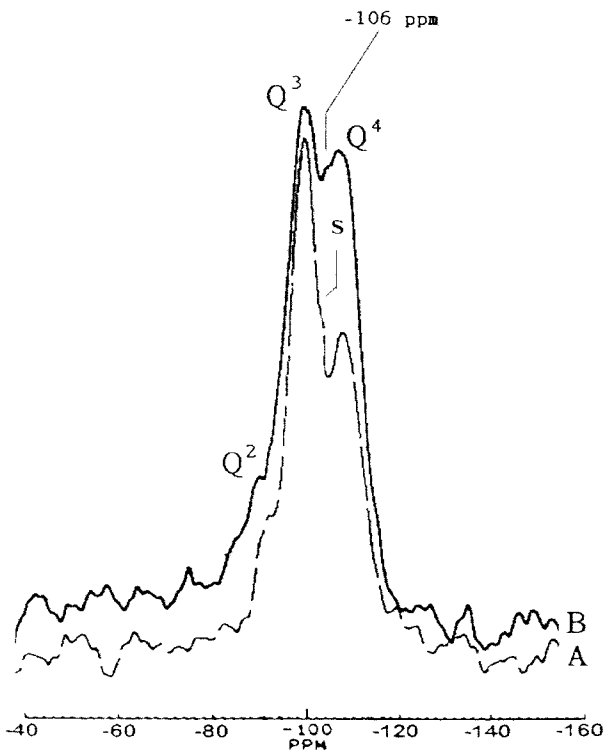


Figure 6 Solid-state ²⁹Si-NMR spectra of 84/16 HLP/SiO₂ hybrid (A) without heat treatment and (B) after heat treatment at 150°C for 3 h.

Formation of Si—O—C Bond Between HLP and Silica Network

Dehydration of the hydroxy group in HLP with the residual silanol group in the silica network to form a Si—O—C bond at high temperature was further investigated by a solid-state ²⁹Si-NMR spectrum. Figure 6 shows that the solid state of the ²⁹Si-NMR spectra of the 84/16 HLP/SiO₂ hybrids before heat treatment exhibits three kinds of chemical shifts (δ) at -91.3, -101.1, and -110.8 ppm due to Q², Q³, and Q⁴ groups which are assigned as Qⁿ in (HO)_{4-n}Si(—OSi≡)_n, with n equal to 2, 3, and 4, respectively. Q³, (HO)Si(—OSi—)₃, is preponderant over Q⁴ and Q² groups in

Table IV Tensile Strengths of the Hybrids Derived from Polymers with and without Hydroxy Groups and Silica Network Before and After Heat Treatment

Hybrids (SiO ₂ :8 wt %)	OH Group in Polymer	Tensile Strength (MPa)	
		30°C	150°C
SBS/SiO ₂ ^a	No	15.9	15.7
ABS/SiO ₂ ^a	No	36.3	37.8
PVA/SiO ₂ ^b	Yes	223.3	395.1
HLP ₄ /SiO ₂	Yes	10.5	44.4
HLP ₆ /SiO ₂	Yes	21.4	79.4

^a Preparation and characterization of hybrids will be described in the later publications.

^b Hybrid, PVA/SiO₂, was prepared using DMSO as solvent and dried at 80°C. PVA was purchased from Aldrich Chemical Co. (St. Louis, MO) with an average *M_w* of 1.5 × 10⁵ and 99% hydrolyzed.

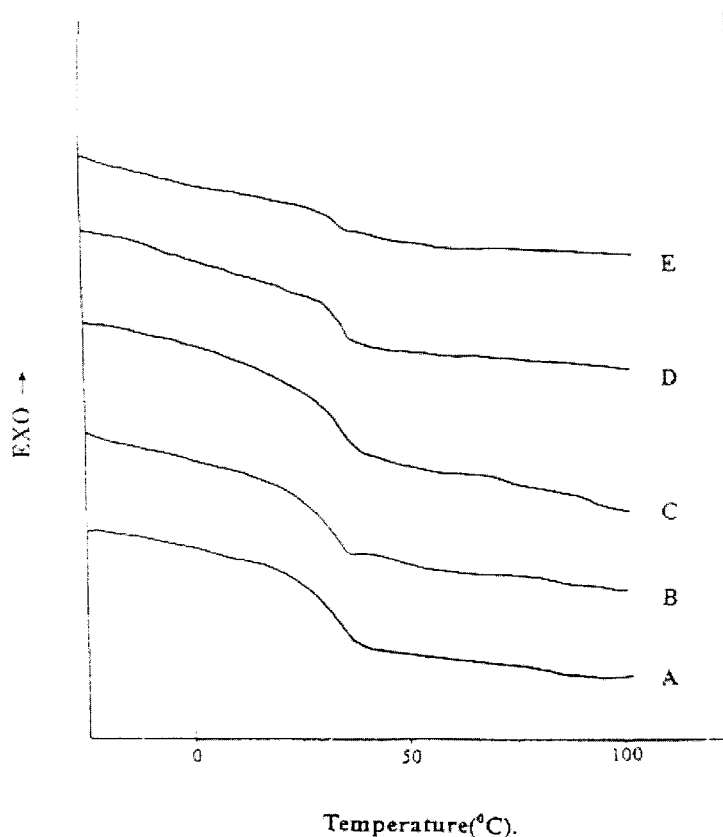


Figure 7 DSC traces of (A) pure HLP, (B) 97/3, (C) 92/8, (D) 84/16, and (E) 68/32 HLP/SiO₂ hybrids.

the silica network for the sol-gel reaction condition of TEOS in the recipes prescribed in Table I (curve A).¹⁶ After heat treatment, the peaks of Q³ and Q⁴ are broadened and the intensity ratio between Q³ and Q⁴ are changed because of the change of the environment and/or the composition of the Q³ and Q⁴ groups.¹⁷ Especially, a new absorption peak at about 106 ppm is observed which is associated with the silicon center of HLP-O-Si-(O-Si≡)₃ obtained by the dehydration of silanol groups in Q³ with hydroxy groups in HLP (curve B). Because the alkyl group in R-O-Si is an electron-donating group, the chemical shift of Q³ will shift downfield and the extent of the shift increases with increasing molecular weight of the alkyl group (i.e., Si-OH < Si-OMe < Si-OEt < Si-OPr).^{18,19} Therefore, it is very reasonable that the silicon center of HLP-O-Si-(O-Si≡)₃ moves from -101.1 (Si-OH) to around -106 ppm.²⁰⁻²² In curve A, there is a shoulder (S) between Q³ and Q⁴; its chemical shift is near -106 ppm, which can be defined as the absorption of the silicon center of C-O-Si-(O-Si≡)₃. It

seems that some Si-O-C bonds have already formed in the hybrid before the heat treatment. This is why the hybrids did not completely dissolve in THF before the heat treatment (Table III).

From the investigation of the solid-state ²⁹Si-NMR, it is found that the intensities of both Q² and Q³ are reduced when the hybrid is treated at 150°C. When the HLP/SiO₂ hybrid is heated at 150°C, the silanol groups may not only react with the hydroxy of HLP to form Si-O-C bonds, but may also undergo self-condensation to form Si-O-Si bonds. The newly formed Si-O-C bond had a great influence on the properties of the hybrid as described above. The role played by the newly formed Si-O-Si in enhancing the properties of the hybrid is evaluated as well. Table IV shows the variation in tensile strengths of the hybrids with or without hydroxy groups after the heat treatment. The hybrids, SBS/SiO₂ and ABS/SiO₂, were prepared through sol-gel processing of the poly(styrene-*b*-butadiene-*b*-styrene) copolymer (SBS) and the poly(acrylonitrile-*co*-buta-

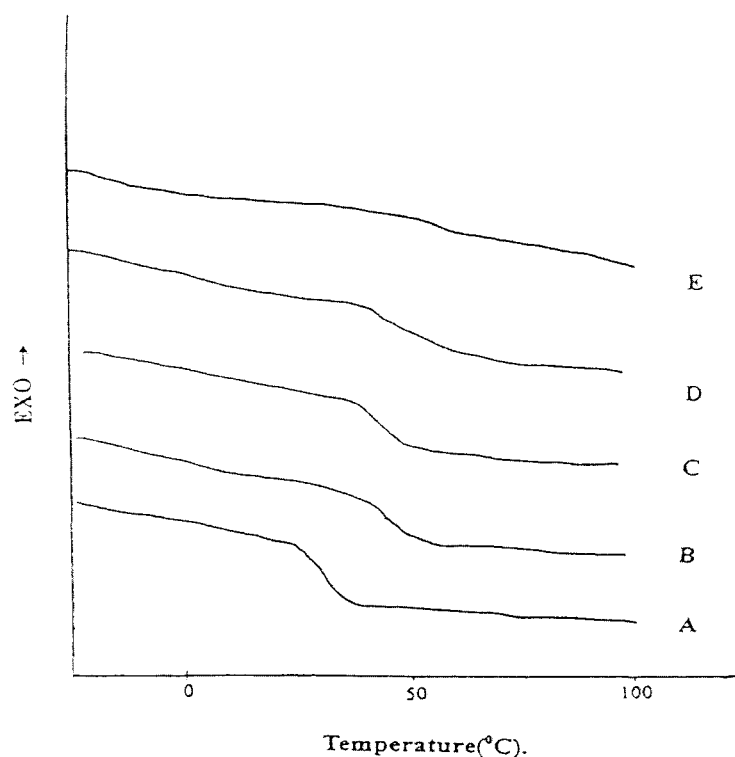


Figure 8 DSC traces of HLP and HLP/SiO₂ hybrids after heat treatment at 150°C for 3 h: (A) pure HLP, (B) 97/3, (C) 92/8, (D) 84/16, and (E) 68/32 HLP/SiO₂ hybrid.

diene-*co*-styrene) copolymer (ABS) with TEOS, respectively.²³

Both copolymers contain no hydroxy groups in the chains and the residual silanol groups only undergo self-condensation to form Si—O—Si bonds. Because the tensile strengths of the hybrids are not increased after the heat treatment, the formation of Si—O—Si bonds through the self-condensation of silanol groups did not contribute to the improvement of the tensile strength of the hybrids after the heat treatment. In the PVA/SiO₂ hybrid, however, the tensile strength

increased significantly after the heat treatment. This supports that the hydroxy group in the polymer chain plays the decisive role in increasing the tensile strength and other properties of the hybrids after heat treatment because of the formation of Si—O—C bonds between the two phases.

Phase Behaviors of the Hybrids Before and After Heat Treatment

The glass transition temperature (T_g) of the hybrid material is associated with a cooperative mo-

Table V T_g 's and IDT of HLP/SiO₂ Hybrids with Various Silica Content Before and After Heat Treatment at 150°C for 3 h

SiO ₂ (wt %)		30°C		150°C	
Calcd	Observed	T_g (°C)	IDT (°C)	T_g (°C)	IDT (°C)
0	0	31	389	30	388
3	3.5	30	391	42	398
8	8.3	32	395	43	421
16	17.1	33	407	47	423
32	33.4	34	411	53	427

^a HLP used was HLP₆.

tion of long-chain segments, which may be hindered by the inorganic metal oxide network.²⁴ The DSC traces of the HLP/SiO₂ hybrids with different silica content before and after heat treatment are shown in Figures 7 and 8, respectively. Figure 7 displays the DSC traces of the hybrids with different silica content prepared at 30°C and dried in a vacuum at 50°C for 3 days. The T_g 's of the hybrids of various silica content are very close irrespective of the silica content and are similar to that of pure HLP. Although the number of hydrogen bonds between the two phases may increase with the silica content in the hybrids (Figs. 3 and 4), the density of Si—O—C bonds between the two phases is still not enough to influence the motion of chain segments of HLP in the hybrids; consequently, the T_g of the hybrid does not increase with the silica content.^{24,25}

The DSC traces of the heat-treated pure HLP and the hybrids are shown in Figure 8. The T_g of the pure HLP does not change after being heated at 150°C for 3 h, while that of the hybrids increases by more than 10°C for all silica contents investigated. This indicates that the newly formed Si—O—C bonds between the organic and inorganic phases are stronger than are the hydrogen bonds to hinder the motion of the polymer chains. The increase in T_g with the silica content is only to a small extent (Table V), while the increase in transition breadth and the decrease in ΔC_p with the silica content are found to a significant extent.^{24,25}

Thermal Stability of the Hybrids Before and After Thermal Treatment

The enhancement of thermal stability of the organic-inorganic hybrid may be attributed to the interaction between the polymer (e.g., HLP) chains and silica network and the consequential uniform distribution of the silica in the polymer matrix.^{26,27} Table V shows the IDT of the HLP/SiO₂ hybrids with various silica content before and after heat treatment. The IDT of the heat-treated hybrids is higher than that of the corresponding hybrid without heat treatment. This result indicates that the change of interfacial force between HLP and the silica network from the weaker hydrogen bonding to the stronger Si—O—C bond has increased the IDT of the HLP/SiO₂ hybrid.

CONCLUSIONS

The nonbonded hybrid materials of HLP/SiO₂ of various silica content were prepared by the *in situ* sol-gel process of TEOS at 30°C in the presence of HLP. The hybrid is transparent and flexible even when the silica content exceeded 40%. The interfacial force, that is, the hetero-associated hydrogen bonds, between HLP and the residual silanol in the hybrids was investigated by FTIR spectroscopy. In addition to the absorption at 1733 cm⁻¹, a new absorption band at 1717 cm⁻¹ associated with the silanol-bound carbonyl groups was observed, and the intensity of these new bands increased with increasing silica content. The strong hetero-associated hydrogen bonds between the hydroxyl groups of HLP and the silanol groups of silica also caused the bands associated with the hydroxy of HLP (at 3441 cm⁻¹) to shift toward the lower frequency and the band was broadened with increasing silica content. The T_g 's of the hybrids with various silica content were similar to that of the pure HLP. After heat treatment at 150°C for 3 h, the Si—O—C bonds were formed by the dehydration of the hydroxy and silanol groups and the existence of Si—O—C bonds were proved by solid-state ²⁹Si-NMR. Because of the increase in interfacial force, the tensile strength, T_g , and thermal stability of the hybrids were increased to a significant extent after heat treatment, while the solubility of the hybrids was decreased to an extremely low degree.

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