Organic–Inorganic Polymeric Hybrids Involving Novel Poly(hydroxymethylsiloxane)

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ABSTRACT: Poly(hydroxymethylsiloxane) (PHMS) has been synthesized by selective oxidation of poly(methylhydrosiloxane) (PMHS) with a dimethyldioxirane solution in acetone. PHMS synthesized *in situ* showed no tendency for self-condensation to siloxane in solution when the concentration of PHMS was less than 1% (g/mL). PHMS gave ceramic materials at 79% yield at 700 °C in a nitrogen atmosphere. Miscibility studies of PHMS with a variety of organic polymers by solution-cast films showed that organic–inorganic polymeric hybrids were formed for poly(*N*-vinylpyrrolidone) (PVPr), poly(ethyloxazoline) (PEOx), and poly(4-vinylpyridine) (PVPy). The hydrogen-bonding interactions in these hybrids were investigated by FT-IR spectroscopy.

Introduction

In recent years, organic-inorganic polymeric hybrids have attracted great interest to researchers with a variety of potential applications. The combination of organic polymers and inorganic oxides by the sol–gel procedure is a main avenue for preparing these hybrids. This can be accomplished either by reacting inorganic alkoxides with polymers end capped with reactive groups to cause cross reaction[1–6] or by incorporating organic polymers which are capable of forming hydrogen bonds into inorganic oxide networks in the sol–gel process by catalyzed hydrolysis.[7–11] In the latter, the incorporation of organic polymers into silicon oxide networks is particularly interesting. Poly(*N*-vinylpyrrolidone) (PVPr), poly(*N*,*N*-dimethylacrylamide) (PDMA), poly(2-methyl-2-oxazoline) (PMOx), poly(vinyl acetate) (PVAc), and poly(methyl methacrylate) (PMMA) were reported to form hybrids with silicon oxide networks by this process. It was shown that heteroassociated hydrogen-bonding interactions between organic polymers and silanols generated in the hydrolysis of tetraalkoxysilane were responsible for the formation of these hybrids.

Silanols are reactive species which play an important role as intermediates in the sol–gel process. The silanol groups produced in hydrolysis tend to further condense to form siloxane networks. Meanwhile, the silanols or residual silanols terminated on the surface of a silicon oxide microphase readily form hydrogen bonds with hydrogen bond acceptor groups in the presence of organic polymers. The choice of different organic polymers influenced the heterogeneous state as well as the structure–property behavior of the hybrids. The structure–property behavior of these hybrids was also affected by pH, nature of the catalyst, tetraalkoxysilane content, amount of water, solvent, and temperature. Hybrid formation was driven either thermodynamically or kinetically, depending on the strength of the heteroassociated hydrogen bonds and the conditions in which the hybrids were prepared.[5,11]

In recent publications,[12,13] we reported the synthesis of silanol-containing polymers and the important role the silanol groups played in the miscibility of polymer blends. Our success in stabilizing silanol groups against self-condensation in either the solution or the solid state provided a further understanding of the properties of the silanol functionality. Although silanol groups are stronger hydrogen bond donors than the corresponding carbinols,[14–16] they are strongly self-associated through hydrogen bonds which compete with heteroassociated hydrogen bonds. The miscibility of silanol-containing polymer blends is determined by the competition between the heteroassociated and self-associated hydrogen bonds.[17–20]

The present paper describes a novel inorganic polymer, poly(hydroxymethylsiloxane) (PHMS) synthesized by the reaction of poly(methylhydrosiloxane) (PMHS) with dioxirane, and the investigation of the miscibility of PHMS with a variety of organic polymers which bear different hydrogen bond acceptor groups. In our previous work, we already demonstrated that the miscibility of a modified siloxane polymer with poly(ethylene oxide) and poly(*n*-butyl methacrylate) could be achieved through hydrogen-bonding interactions.[21] The purpose of the present work is to elucidate the role of the competitive heteroassociated and self-associated hydrogen-bonding interactions of the silanol groups in the preparation of organic–inorganic polymeric hybrids.

Experimental Part

Materials. Poly(methylhydrosiloxane) (PMHS) end capped with trimethylsilyl groups, with a reported molecular weight of 2270, was purchased from Hüls America Co. Five commercial organic polymers with different hydrogen bond acceptor groups were chosen for a blending study as shown in Table 1. Poly(*N*-vinylpyrrolidone) (PVPr) and poly(4-vinylpyridine) (PVPy) were vacuum dried at 80 °C under a nitrogen atmosphere, poly(ethyl oxazoline) (PEOx) and poly(methyl methacrylate) (PMMA) were vacuum dried at 60 °C, and poly(ethylene oxide-*co*-propylene oxide) (PEO–PPO) were vacuum dried at 40 °C for 3 days each and then stored in a desiccator before use.

Synthesis of Poly(hydroxymethylsiloxane) (PHMS) in Solution. In a typical preparative procedure, 0.76 g of poly(methylhydrosiloxane) (PMHS) was dissolved in 10 mL of acetone. To this solution was added quickly a 275-mL dimethyldioxirane solution in acetone (0.06–0.08 M), and the reaction mixture was stirred at room temperature for 2 h.[12] Poly(hydroxymethylsiloxane) (PHMS) in an acetone solution was obtained after concentrating the solution under reduced

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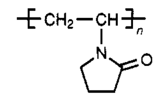
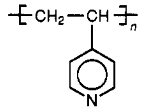
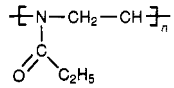
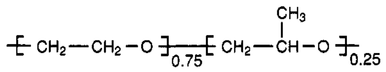
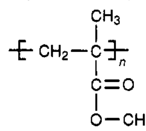
Table 1. Structure and Molecular Weight of Hydrogen Bond Acceptor Polymers Used in Blending Studies

polymer	mol wt	T_g (°C)	source
 poly(*N*-vinylpyrrolidone) (PVPr)	45 000	174	Polyscience, Inc.
 poly(4-vinylpyridine) (PVPy)	40 000	150	Polyscience, Inc.
 poly(ethyloxazoline) (PEOx)	50 000	58	Dow Chemical Co.
 $-\!\left[CH_2-CH_2-O\right]_{0.75}\!\left[CH_2-\overset{CH_3}{CH}-O\right]_{0.25}$ poly(ethylene oxide-*co*-propylene oxide) (PEO–PPO)	13 333	−70	Polyscience, Inc.
 poly(methyl methacrylate) (PMMA)	30 000	106	Aldrich Co.

pressure at room temperature. Isopropyl alcohol or methyl ethyl ketone solution of PHMS was prepared by the addition of isopropyl alcohol or methyl ethyl ketone to the concentrated PHMS acetone solution followed by evaporation of the more volatile acetone solvent under reduced pressure. The process was repeated at least three times to ensure maximum removal of the acetone solvent. The resulting concentrated PHMS solution in isopropyl alcohol or methyl ethyl ketone was transferred into a volumetric flask, and a 0.4% (g/mL) PHMS solution was prepared for solution blending.

Preparation of Blends. 2% (g/mL) solutions of PVPr, PVPy, and PEOx in isopropyl alcohol and PMMA and PEO–PPO in methyl ethyl ketone were prepared. Blend solutions of PHMS with different organic polymers were prepared at weight ratios of 75/25, 50/50, and 25/75, respectively, by mixing appropriate amounts of each polymer in a common solvent while stirring. The resulting blend solutions were stirred at room temperature overnight and then concentrated to approximately 2% concentration under reduced pressure at room temperature. Blend films were prepared by solution casting onto glass slides. After the solvent was slowly evaporated at room temperature, all the films were vacuum dried at 80 °C for 3 days under a nitrogen atmosphere unless otherwise specified in the text.

Thermal Analysis. Differential scanning calorimetry (DSC) was performed by means of either the TA 2920 DSC or the Perkin-Elmer DSC-7 calorimeter. Sample weights of 8–12 mg and a scan rate of 20 °C/min were used. Glass transition temperatures of blends were taken from the second scan unless otherwise noted in the text. Thermogravimetric analysis (TGA) was performed with the use of a TA 2920 Hi-Res thermogravimetric analyzer. Typical sample weights of 8–15 mg and a heating rate of 10 °C/min were employed. The experiments were performed under a nitrogen atmosphere.

FT-IR Spectroscopy. Fourier transform infrared spectroscopy was performed with the use of the Perkin-Elmer 1600 series FT-IR spectrometer. A minimum of 64 scans at a resolution of 2 cm^{-1} was used. Samples for FT-IR studies were prepared by casting blend solutions onto KBr windows followed by vacuum drying at 80 °C for 3 days under a nitrogen atmosphere. Films were sufficiently thin to be within the absorbance range where the Beer–Lambert law was obeyed.

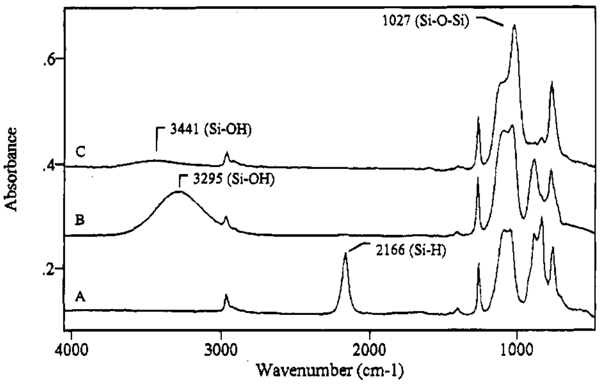
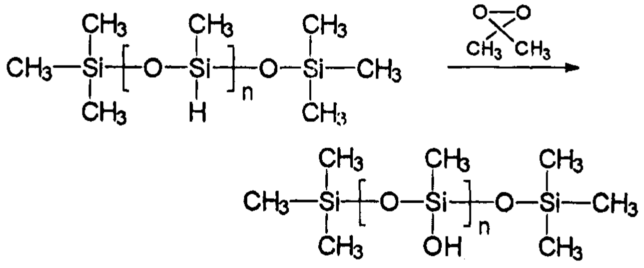


Figure 1. FT-IR spectra of (A) poly(methylhydrosiloxane), (B) freshly made poly(hydroxymethylsiloxane), and (C) poly(hydroxymethylsiloxane) dried at 80 °C for 48 h.

Scheme 1. Synthesis of Poly(hydroxymethylsiloxane) by Selective Oxidation of the Silane (Si–H)



Results and Discussion

Synthesis and Characterization of Poly(hydroxymethylsiloxane) (PHMS). It is well-known that silanol-containing species are highly reactive and tend to condense with themselves to form siloxane linkages.[22] A successful approach for enhanced resistance to self-condensation is to devise a system in which the silanol species are either complexed with other compounds through specific interactions or sterically hindered by bulky substituent groups. In our earlier papers,[12,13] we reported the synthesis of silanol-containing polymers by quantitative and selective oxidation of the precursor polymers containing a Si–H functionality via reaction with dimethyldioxirane. The stability of silanol-containing polymers against self-condensation was achieved either in solution or in the solid state by using different substituents bound directly to the silicon atom. In this study, poly(hydroxymethylsiloxane) (PHMS) was prepared in a similar way by reacting poly(methylhydrosiloxane) (PMHS) with a dimethyldioxirane solution in acetone (Scheme 1). The oxyfunctionalization of the silane group was found to proceed rapidly and stoichiometrically. As can be seen from the infrared spectra in Figure 1, the strong stretching vibration band of the silane (Si–H) in PMHS at 2166 cm^{-1} totally disappeared after reaction, while a new broad band centered at about 3295 cm^{-1} appeared in PHMS which was assigned to the stretching vibration bands of the silanols.

The silanol stretching vibration region in PHMS was characterized by the presence of a strong and broad band centered at 3295 cm^{-1}, but no absorption was detected in the range of 3700–3600 cm^{-1} (Figure 1). The broad band centered at 3295 cm^{-1} consisted of the contributions of silanol–silanol hydrogen bonds and hydrogen bonds between the silanols and the backbone oxygen atoms. The absence of absorption between 3700 and 3600 cm^{-1} suggests very few free silanol groups which normally absorb in this region.

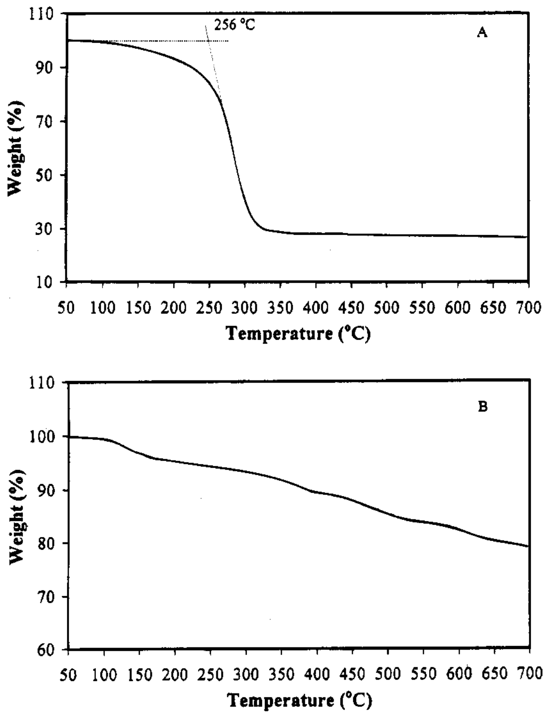


Figure 2. TGA curves of (A) poly(methylhydrosiloxane) and (B) poly(hydroxymethylsiloxane) with a heating rate of 10 °C/min under a nitrogen atmosphere.

PHMS was prone to self-condensation which led to the formation of insoluble siloxane networks. However, it was stable in an acetone solution at room temperature for months when its concentration was less than 1% (g/mL). Optically clear materials were obtained after slowly evaporating acetone from the PHMS solution at room temperature. The resulting solid PHMS was cross-linked and was characterized by the dramatic diminishing of the silanol stretching vibration band in the silanol stretching vibration region and an increase in the absorbance of the siloxane stretching vibration band at 1027 cm^{-1} as shown in Figure 1C.

PMHS has a glass transition temperature at about −128 °C which is similar to that observed for poly(dimethylsiloxane).[23,21] However, for freshly prepared PHMS, the glass transition[24] occurred at 32 °C which was much higher than that of its precursor PMHS. The greatly increased value in the glass transition temperature of PHMS is apparently due to the formation of the siloxane networks by the self-condensation of the silanols and extensive self-associated hydrogen-bonding interactions in PHMS.

The results of thermogravimetric analysis of PHMS and its precursor polymer PMHS are shown in Figure 2. Upon heating, PMHS lost weight gradually probably due to the volatility of PMHS, and then quickly experienced thermal decomposition with an onset temperature at about 256 °C (Figure 2A). The total weight loss of PHMS at 700 °C was 73%. The TGA curve of PHMS (Figure 2B) showed that a weight loss of about 4.5% occurred in the temperature range of 110−180 °C which was probably associated with postcondensation of the silanols. However, there was only a slight weight loss upon further heating, and the total weight loss of PHMS at 700 °C was found to be 21%. The formation of high-yield, lightly brown ceramics at high temperatures suggests a potential new class of preceramic materials.

Miscibility of PHMS with Organic Polymers. The unusual properties of siloxane polymers, such as low surface energy and high gas permeability, are essential to a wide variety of applications.[25] However, the siloxane polymers are essentially immiscible with almost all other polymers.[26] In a previous publication,[21] we demonstrated that the miscibility of the siloxane polymer could be achieved by introducing strong hydrogen bond donor group 4-hydroxy-4,4-bis(trifluoromethyl)butyl via hydrosilylation reaction. The modified siloxane polymer was found to be miscible with poly(*n*-butyl methacrylate) and poly(ethylene oxide), as evidenced by the presence of a single and composition-dependent glass transition temperature and frequency shifts in infrared spectra.

Table 2. Blending Results of PHMS with a Variety of Organic Polymers

no.	blend	ratio (w/w)	solvent	film clarity	T_g (°C)
1	PHMS/PMMA	50/50	MEK	opaque	
2	PHMS/PPO−PEO	50/50	MEK	opaque	
3	PHMS/PVPr	75/25	isopropyl alcohol	clear	170
4	PHMS/PVPr	50/50	isopropyl alcohol	clear	167
5	PHMS/PVPr	25/75	isopropyl alcohol	clear	164
6	PHMS/PEOx	75/25	isopropyl alcohol	clear	72
7	PHMS/PEOx	50/50	isopropyl alcohol	clear	61
8	PHMS/PEOx	25/75	isopropyl alcohol	clear	45
9	PHMS/PVPy[a]	75/25	isopropyl alcohol	clear	163
10	PHMS/PVPy[a]	50/50	isopropyl alcohol	clear	153
11	PHMS/PVPy[a]	25/75	isopropyl alcohol	clear	154

[a] Films were cast from supernatant solutions.

The miscibility of PHMS with a variety of organic polymers containing different hydrogen bond acceptor groups (Table 1) was evaluated preliminarily by the clarity of the films, and the results are compiled in Table 2. 50/50 blends of PHMS/PMMA and PHMS/PEO−PPO were heterogeneous, but blend films of PHMS with PVPr or PEOx were transparent. Interpolymer complexes in the form of precipitates were formed upon mixing the solutions of PHMS with PVPy. The precipitates were optically clear after drying. Films cast from the supernatant layers were also clear.

In the preparation of organic−inorganic polymeric hybrids by the sol−gel process, it has been shown that the properties of the hybrids depended strongly on the conditions in which the hybrids were prepared, such as pH, catalyst, solvent, and temperature. Since the silanols in PHMS perform dual functions, acting either as reactive sites that condense to form siloxane networks or as strong hydrogen bond donors to enhance miscibility with organic polymers, the properties of the hybrids depend on the balance of the two. Accordingly, the sample preparation condition becomes an important parameter which influences the properties of the hybrids in the solid state. The optimal drying condition for the hybrids should achieve the maximum degree of cross-link density while maintaining heteroassociated hydrogen bonds as less intact as possible during drying. The formation and dissociation of the heteroassociated hydrogen bond are thermally reversible in the hybrids, but the self-condensation of the silanol groups is not. If self-condensation takes place at a temperature at which the dissociation of the heteroassociated hydrogen bond has already occurred to a significant extent, the formation of the siloxane networks not only greatly reduces the number of the silanol groups available for reestablishing heteroassociated hydrogen bonds but also hinders the reassociation of the heteroassociated hydrogen bond after cooling. This may influence the state of

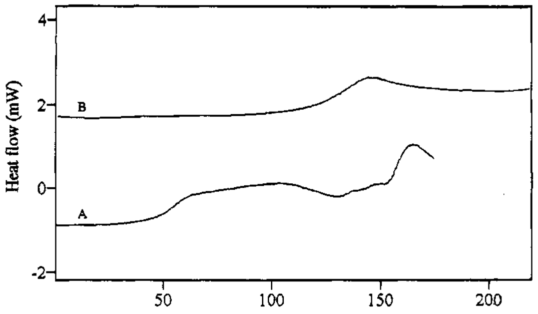


Figure 3. Typical DSC curves of a 50/50 PHMS/PVPy hybrid at a scan rate of 20 °C/min: (A) first scan; (B) second scan.

Table 3. T_g Values of the 50/50 PHMS/PVPr and PHMS/PVPy Hybrids

		T_g (°C)	
blends	ratio (w/w)	1st scan	2nd scan
PHMS/PVPr	50/50	54	134
PHMS/PVPy	50/50	40	111

Table 4. Results of PHMS/PVPy Complexes

complex	feed ratio (w/w)	yield (wt %)	complex composition[a] (PVPy in wt %)	T_g (°C)
PHMS/PVPy	75/25	58	51	160
PHMS/PVPy	50/50	47	68	154
PHMS/PVPy	25/75	30	67	155

[a] Composition of PVPy in the complex was determined by Soxhlet extraction with an ethanol/water (92/8) mixed solvent.

mixing of the two components in the hybrids. For this reason, two sets of experiments were performed.

The initial experiments were conducted for the 50/50 blends of PHMS with PVPr and PVPy.[27] The blends were vacuum dried at 40 °C for 3 days, and then the glass transition temperatures were measured. Typical DSC curves for the 50/50 PHMS/PVPy blend are shown in Figure 3. In the first scan, the glass transition occurred at 40 °C followed by an exothermic peak at above 100 °C. In the second scan, the glass transition shifted to 111 °C. The greatly increased T_g values in the second scans were probably caused by the postcondensation of the silanols during the first scan at above 100 °C (Figure 3A). The results of the glass transition temperature measurements for the 50/50 PHMS/PVPy and PHMS/PVPr were shown in Table 3. Infrared spectroscopy indicated that more self-associated silanol groups were transformed into siloxane networks after the first scan which accounted mainly for the great increase in T_g values of the hybrids in the second scan.

In the second set of the experiments, the hybrids were vacuum dried at 80 °C for 3 days.[28,29] Single and almost constant T_g values for the first and second scans were observed for all of these hybrids as well as the precipitated interpolymer complexes (Tables 2 and 4). The great dependence of the hybrid properties on the drying temperature here provides a striking evidence for great care in the practice during the hybrid preparation.

FT-IR Studies of the Hybrids. The driving force for PHMS to form organic–inorganic polymeric hybrids with PVPr, PVPy, and PEOx is strong heteroassociated hydrogen bonds between the silanol groups of PHMS and the acceptor groups of organic polymers. To obtain a better understanding of the role of the hydrogen-bonding interactions, FT-IR spectroscopy has been utilized to probe the heteroassociated and self-associated hydrogen bonds in the hybrids.

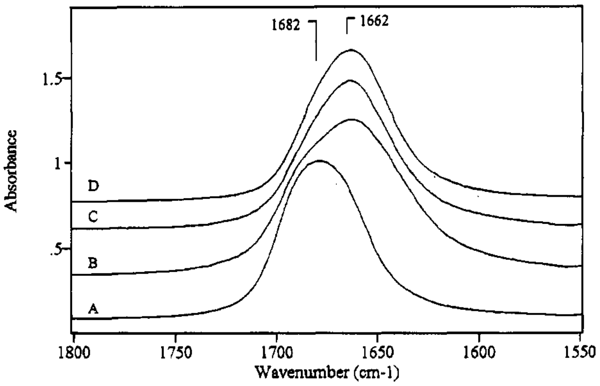


Figure 4. FT-IR spectra in the amide carbonyl stretching vibration region for (A) PVPr and (B) 25/75, (C) 50/50, and (D) 75/25 PHMS/PVPr hybrids.

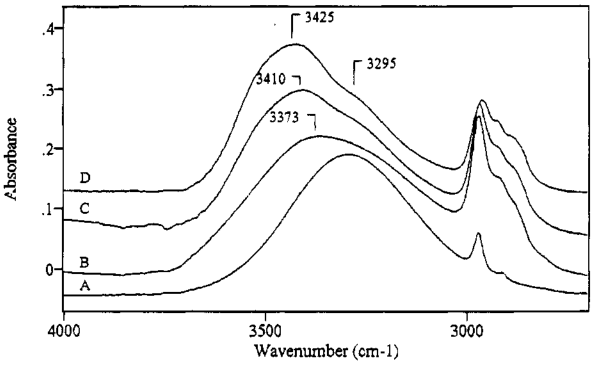


Figure 5. FT-IR spectra in the silanol stretching vibration region for (A) PHMS and (B) 75/25, (C) 50/50, and (D) 25/75 PHMS/PVPr hybrids.

PHMS/PVPr hybrids: Figure 4 shows the infrared spectra in the amide carbonyl stretching vibration region for PHMS/PVPr hybrids. The amide carbonyl stretching vibration band of PVPr was characterized by a strong absorption band centered at 1682 cm^{-1}. Upon forming hybrids, a new major band centered at 1662 cm^{-1} was observed which was assigned to the silanol stretching vibration band of bound amide carbonyl. For the 25/75 PHMS/PVPr hybrid, the free amide carbonyl band at 1682 cm^{-1} was still discernible. However, with increasing amounts of PHMS in the hybrids, the free amide carbonyl band appeared only as weaker shoulders.

The infrared spectra in the silanol stretching vibration region of PHMS/PVPr hybrids are shown in Figure 5. The silanol stretching vibration band of PHMS appeared as a strong broad band centered at 3295 cm^{-1}. For the hybrids, a new broad band at higher wavenumber appeared which gradually shifted to a higher wavenumber and eventually became a major band centered at 3425 cm^{-1} as the amount of PVPr increased in the hybrids. The broad band centered at 3425 cm^{-1} was assigned to the amide carbonyl-bound silanol stretching vibration band.

PHMS/PEOx hybrids: The carbonyl stretching vibration band of PEOx was observed at 1642 cm^{-1} (Figure 6). Upon forming hybrids with PHMS, this band gradually shifted from 1639 cm^{-1} for 25/75 PHMS/PEOx to 1628 cm^{-1} for 75/25 PHMS/PEOx hybrids. Unlike the PHMS/PVPr hybrids, the hydrogen-bonded and free carbonyl bands in the PHMS/PEOx hybrids were severely overlapped and can not be distinguished.

The infrared spectra in the silanol stretching vibration region for the PHMS/PEOx hybrids are shown in

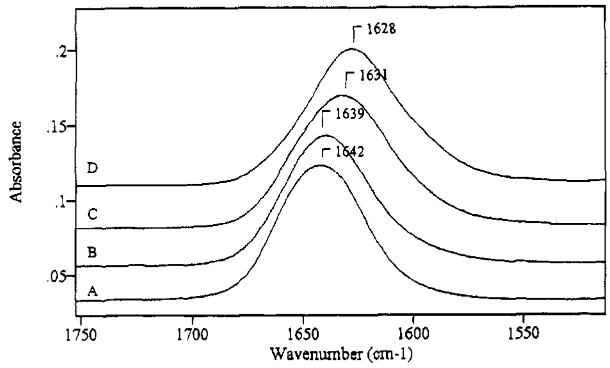


Figure 6. FT-IR spectra in the amide carbonyl stretching vibration region for (A) PEOx and (B) 25/75, (C) 50/50, and (D) 75/25 PHMS/PEOx hybrids.

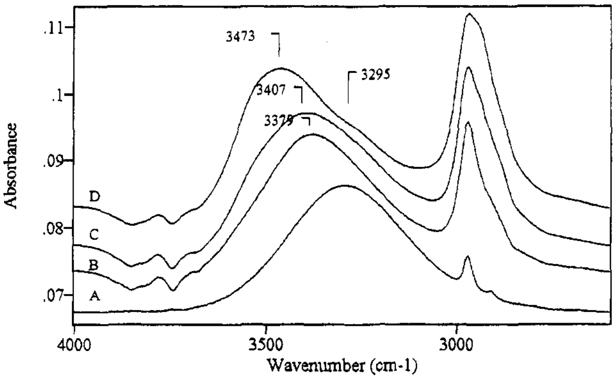


Figure 7. FT-IR spectra in the silanol stretching vibration region for (A) PHMS and (B) 75/25, (C) 50/50, and (D) 25/75 PHMS/PEOx hybrids.

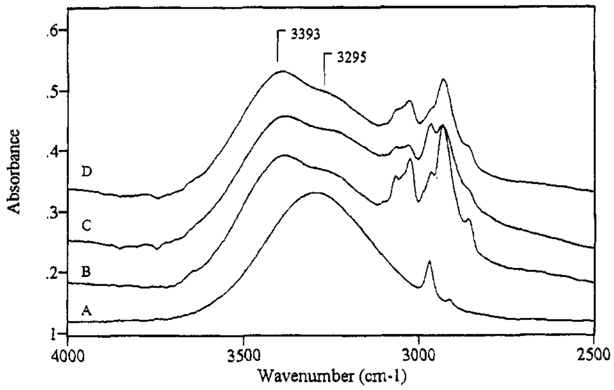


Figure 8. FT-IR spectra in the silanol stretching vibration region for (A) PHMS and (B) 75/25, (C) 50/50, and (D) 25/75 PHMS/PVPy hybrids.

Figure 7. For the hybrids of PHMS/PEOx, the carbonyl-bound silanol band appeared at 3379 cm^{-1} for the 75/25 PHMS/PEOx hybrid and gradually shifted to 3473 cm^{-1} as PEOx composition increased to 75% in the hybrid.

PHMS/PVPy hybrids: Figure 8 shows the infrared spectra in the silanol stretching vibration region for the films of PHMS/PVPy cast from supernatant solutions. As seen from Figure 8, a new band centered at 3393 cm^{-1} appeared in the silanol stretching vibration region which was assigned to the carbonyl-bound silanol band.

The infrared spectral features of PHMS/PVPy complexes in the silanol stretching vibration region were almost identical with that of supernatant solutions presented in Figure 8.

It is well-known that the amide carbonyl groups of PVPr and PEOx and the pyridine nitrogen atom in PVPy are strong hydrogen bond acceptors. The locations of hydrogen-bound silanol stretching vibration bands in the blends with these three organic polymers appeared at 3393 cm^{-1} for PVPy, 3425 cm^{-1} for PVPr, and 3473 cm^{-1} for PEOx (Table 5). Although the free silanol band in PHMS was not observable, it appears in organosilicon compounds at about 3690 cm^{-1}.[30] The frequency shifts of the bound silanols with these organic polymers so calculated were listed in Table 5. The shift of the silanol stretching band in the hybrids from the absorption of the free silanol groups is a measure of the strength of hydrogen bonding which, according to our data, could be ranked in the following order: PHMS/PVPy > PHMS/PVPr > PHMS/PEOx.

Table 5. Comparison of Locations and Frequency Shifts of Heteroassociated Silanol Hydrogen Bonds among the Hybrids

hybrid	location of heteroassociated H-bond (cm^{-1})[a]	frequency shift (cm^{-1})[b]
PHMS/PVPy	3393	297
PHMS/PVPr	3425	265
PHMS/PEOx	3473	217

[a] Self-associated silanol band of PHMS located at 3295 cm^{-1}.
[b] Calculated by assuming a free silanol stretching vibration band at 3690 cm^{-1}.

In our previous paper,[17] we found that the heteroassociated hydrogen bond between the carbonyl group of PBMA and the silanol groups of poly[styrene-*co*-(4-vinylphenyl)dimethylsilanol] (~94 cm^{-1}) was much weaker than the self-associated silanol bands (187–303 cm^{-1}). The heterogeneity of the blends of PHMS with PMMA or PEO–PPO is attributed probably to a direct result of the competition between the weak heteroassociated hydrogen bonds of the acceptor polymers and silanol groups and the much stronger self-associated silanol hydrogen bonds.

Conclusions

Poly(hydroxymethylsiloxane) (PHMS) in solution was synthesized by the selective oxidation of poly(methylhydrosiloxane) (PMHS). The oxyfunctionalization of the silane (Si–H) by dimethyldioxirane proceeded in a rapid and quantitative way which provided a new convenient route in practice to synthesize a wide variety of novel silanol-containing polymers from silicon precursor polymers containing the Si–H function. PHMS was found to be prone to self-condensation which led to the siloxane network formation. However, PHMS was stable in an acetone solution when PHMS concentration was less than 1%. Thermal gravimetric analysis indicated that PHMS formed ceramic materials at 700 °C with 79% yield which showed promise as a new class of preceramics.

Miscibility studies of PHMS with a variety of organic polymers indicated that PHMS was inherently immiscible with PMMA and PEO–PPO, but organic–inorganic polymeric hybrids were formed with PVPr, PVPy, and PEOx. The heterogeneity of PHMS with PMMA and PEO–PPO was attributed to the much weaker heteroassociated hydrogen bonds compared to the self-associated silanol hydrogen bonds. The choice of different organic hydrogen bond acceptor polymers influenced greatly the heterogeneous state of mixing of the hybrids. It was found that the properties of the hybrids, such as glass transition temperature, were depended mainly on the temperature at which the hybrids were dried which provided evidence for caution in preparing these hybrids. Evidences concerning heteroassociated hydrogen-bonding interactions in the hybrids were obtained by FT-IR spectroscopy. The strength of the heteroassociated hydrogen bonds of PHMS with these organic polymers was decreased in the order of PVPy > PVPr > PEOx.

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