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Interfacial interactions and their influence to phase behavior in poly(vinyl pyrrolidone)/silica hybrid materials prepared by sol–gel process

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Abstract

In this research, hybrid materials constructed by poly(vinyl pyrrolidone) (PVP) and inorganic tetraethyloxysilane (TEOS) or methyltriethyloxyslane (MTEOS) were synthesized via sol–gel process. From visual and scanning electron microscopic (SEM) observation, inorganic silicate was not separated from the organic phase in PVP/MTEOS hybrid system and in PVP/TEOS hybrid system with 20 wt.% or less TEOS content. With 40 wt.% TEOS content, microphase separation occurred; furthermore, phase separation and phase inversion can be observed with TEOS content increased to 60 wt.% or more in PVP/TEOS hybrid system. These results were confirmed by the variation of glass transition behavior. From infrared spectra analysis, hydrogen bonds were formed in both PVP/MTEOS and PVP/TEOS hybrid systems. However, higher hydrogen bonding interaction in PVP/TEOS did not induce higher compatibility as compared to PVP/MTEOS. This was due to the greater non-polar interaction between methyl group of MTEOS and polymer backbone in PVP/MTEOS hybrid system.

Keywords: Poly(vinyl pyrrolidone); Sol–gel; Compatibility; Microphase separation; Hydrogen bonding; Polymer

Sol–gel process is a convenient method for the preparation of inorganic films or organic modified hybrid materials, where consecutive reaction steps of hydrolysis and condensation reactions occur between silane groups of the raw materials [1–6]. This technology has advanced fast in the past two decades. At present, sol–gel is not only a manufacturing process for the homogeneous inorganic glasses but also a technique for the synthesis of organic–inorganic hybrid materials for various applications of optical, electrical, and biochemical purposes [3,5,7–10]. In these applications, important properties like appearance, transparency, and phase behavior, depend on the development of inorganic silicate structure and the interfacial interactions between organic and inorganic phases in hybrid materials [11–16]. Hence, studies on these topics are very important for the advancement of this technology.

In this study, poly(vinyl pyrrolidone) (PVP, MW = 58000, Acros) was dissolved in dimethylformamide (DMF, Merck) first. Methyltriethyloxyslane (MTEOS, Acros) solution and tetraethyloxysilane (TEOS, Acros) solution were then prepared with molar ratio of H^+/H_2O/ethanol/TEOS = 0.025:25:5:1 and H^+/H_2O/ethanol/MTEOS = 0.025:25:5:1.333, respectively. Subsequently, these solutions were added into PVP solution in various organic–inorganic ratios, namely 20:80, 40:60, 60:40, 80:20, and 100:0 (w/w) for both TEOS/PVP and MTEOS/PVP, and mixed thoroughly. Sol–gel process was carried out at 30 °C with cover to reduce evaporation loss of the solvent. After 15 min, homogeneous solution can be obtained. These solutions were then heated at 70 °C under vacuum for 6 h to remove residual solvent and by-products (water and alcohol). Post-reaction heat treatment was conducted under 160 °C for 48 h in an vacuum oven. For comparison, neat PVP was also made by the same procedure.

A yellowish, transparent, and smooth specimen can be obtained for neat PVP after the synthesis. Both inorganic silicate matrices constructed by MTEOS and TEOS were transparent with smooth surface. In addition, specimens with same appearance can also be acquired for PVP/TEOS (80/20) and the samples constructed by PVP and MTEOS at

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all mixing levels. With increasing inorganic component content, however, PVP/TEOS (60/40) became translucent, while PVP/TEOS (40/60) and PVP/TEOS (20/80) white and opaque with rough surfaces. The last two samples can be ground into fine powder easily. It is judged that organic and inorganic phases were compatible in PVP/TEOS (80/20) and all levels of the PVP/MTEOS hybrid materials, but phase separation occurred in PVP/TEOS hybrid system with 40 wt.% or more TEOS presented. The large change in visual appearance for PVP/TEOS samples with TEOS content greater than 60 wt.% is thought to be the result of phase inversion.

From scanning electron microscopic (SEM) observation using JSM-5600 (JEOL), detailed morphology for these materials were obtained (Figs. 1 and 2). In Fig. 1, fractured surface of PVP and inorganic silicate matrices constructed by TEOS and MTEOS was very smooth. For hybrid materials of PVP/MTEOS, morphology of fractured surfaces did not show obvious change from that of neat PVP. This indicates that although inorganic component increased, phase behavior was close to PVP without phase separation. On the other hand, with increased TEOS content, PVP/TEOS (40:60) and PVP/TEOS (20:80) exhibited completely different morphology, where linked spheres with diameter of 0.2 to 0.4 μm and 3 to 5 μm appeared, respectively (see Fig. 2(d and f)). These indicate the occurrences of phase separation and phase inversion with high TEOS content in PVP/TEOS hybrid system.

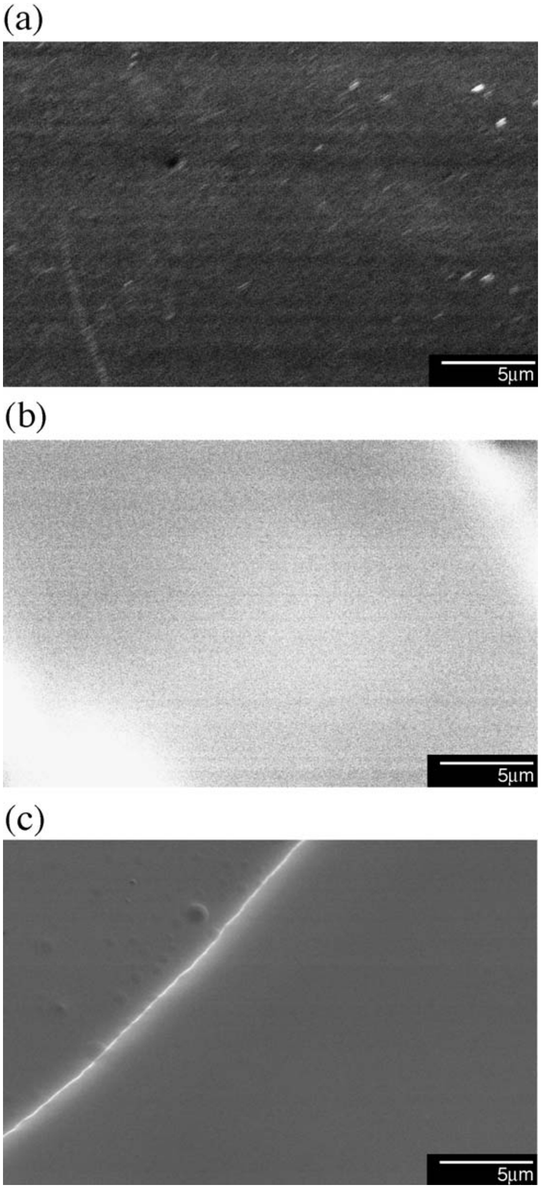

Fig. 1. SEM micrographs of the fracture surfaces of: (a) neat PVP, (b) inorganic matrix constructed by MTEOS, and (c) inorganic matrix constructed by TEOS.

From the investigation of differential scanning calorimeter (DSC, TA 2010) for these synthesized materials, T_gs of hybrid materials were obtained from the glass transition profiles and were tabulated in Table 1. It was found that T_g of neat PVP was 189.6 °C. All the hybrid materials that constituted of PVP and MTEOS exhibited only single T_g located at the region from 150 to 180 °C, which were lower than that of neat PVP. These data confirm the miscibility between MTEOS and PVP [14,18]. Glass transition behavior for PVP/TEOS hybrid system showed more variation than that of PVP/MTEOS hybrid materials. The T_g increased to much higher temperature of 219.3 and 246.0 °C for PVP/TEOS (80:20) and PVP/TEOS (60:40), respectively. With TEOS content increased to 60 wt.% or more, T_g value was lowered to ca. 180 °C, which was slightly less than the T_g of neat PVP (189.6 °C). The increasing crosslinking density of hybrid system with TEOS content from 0 to 40 wt.%, due to the developed inorganic silicate structure, brought about the reduction of molecular mobility and the elevation of the glass transition temperature [13,14,17]. with TEOS content above 60 wt.% or more, inorganic silicate structure was developed more extensive and silica network formed as discussed in the previous section. With the confinement of inorganic silicate matrix, molecular motion of organic polymer chain segments may be hindered and the T_g may be increased even more [11,14]. In general, while phase separation occurred, organic polymer chain segments may form a separated matrix from inorganic silicate structure, but still a portion of PVP was confined in inorganic silicate structure. Hence, two T_gs should be found for PVP/TEOS (40:60) and PVP/TEOS (20:80) from DSC thermoscan. This phenomenon was similar to the previous research, [13,14,19] in which the materials with white, opaque, and rough surface resulted from phase inversion. The single T_g found in this study may be resulted from DSC instrument's limitation and the degradation of the materials so that the possible higher T_g was not observed for these two materials. The shown T_g was the second T_g (lower one) of the hybrid material, which belongs to the organic polymer chains that separated from inorganic silicate structure.

In this study, all the synthesized hybrid materials have the infrared absorption at ca. 1675 cm^{-1}, which corre-

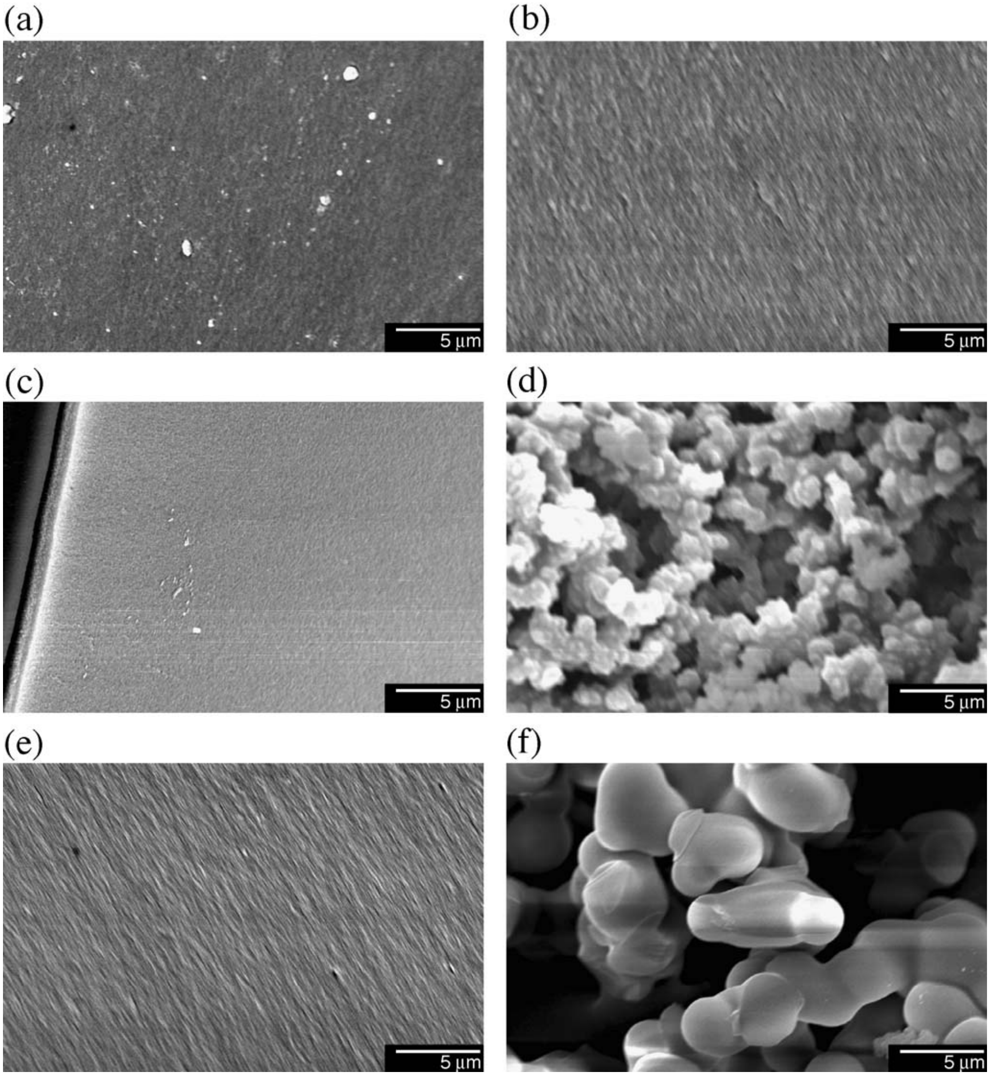

Fig. 2. SEM micrographs of the fracture surfaces of: (a) PVP/MTEOS (60:40), (b) PVP/TEOS (60:40), (c) PVP/MTEOS (40:60), (d) PVP/TEOS (40:60), (e) PVP/MTEOS (20:80), and (f) PVP/TEOS (20:80).

sponds to carbonyl group (C=O) stretching vibration on the side chain of PVP. These absorption peaks of carbonyl group for hybrid materials were obtained using Fourier transform infrared spectrophotometer (FTIR, Nicolet Avatar 320) and were sketched in Fig. 3 with spectral range of 1825 to 1525 cm^{-1}. In this figure, there is an obvious shoulder found at ca. 1700 cm^{-1} with increasing content of inorganic component. This absorption was constructed by two distinct peaks at ca. 1700 and 1645 cm^{-1}, which belong to free and hydrogen boned carbonyl groups, respectively. With curve fitting analysis, the absorption band of carbonyl groups may be readily separated into two peaks by Gaussian curve fitting [13,19–21]. The fraction of hydrogen bonded carbonyl can be calculated from the following equation suggested by Coleman et al. [21–23]:

Table 1
Glass transition temperature (T_g) of synthesized hybrid materials

Hybrid materials	Glass transition temperature (°C)
Neat PVP	189.6
PVP/MTEOS (80:20)	155.2
PVP/MTEOS (60:40)	165.6
PVP/MTEOS (40:60)	150.4
PVP/MTEOS (20:80)	177.0
Inorganic matrix (MTEOS)	–
PVP/TEOS (80:20)	219.3
PVP/TEOS (60:40)	246.0
PVP/TEOS (40:60)	180.5[a]
PVP/TEOS (20:80)	173.6[a]
Inorganic matrix (TEOS)	–

[a] There may be two possible T_gs in these hybrid materials, the higher one was not observed due to instrumental limitation.

$$f_{\text{bonded}} = \frac{A_{\text{bonded}}}{A_{\text{bonded}} + A_{\text{free}}} \tag{1}$$

where A_{bonded} is the area of hydrogen bonded carbonyl absorption, A_{free} is the area of free carbonyl absorption, and f_{bonded} is the fraction of hydrogen bonded carbonyl groups. In addition, the ratio of absorptive coefficients of two bands

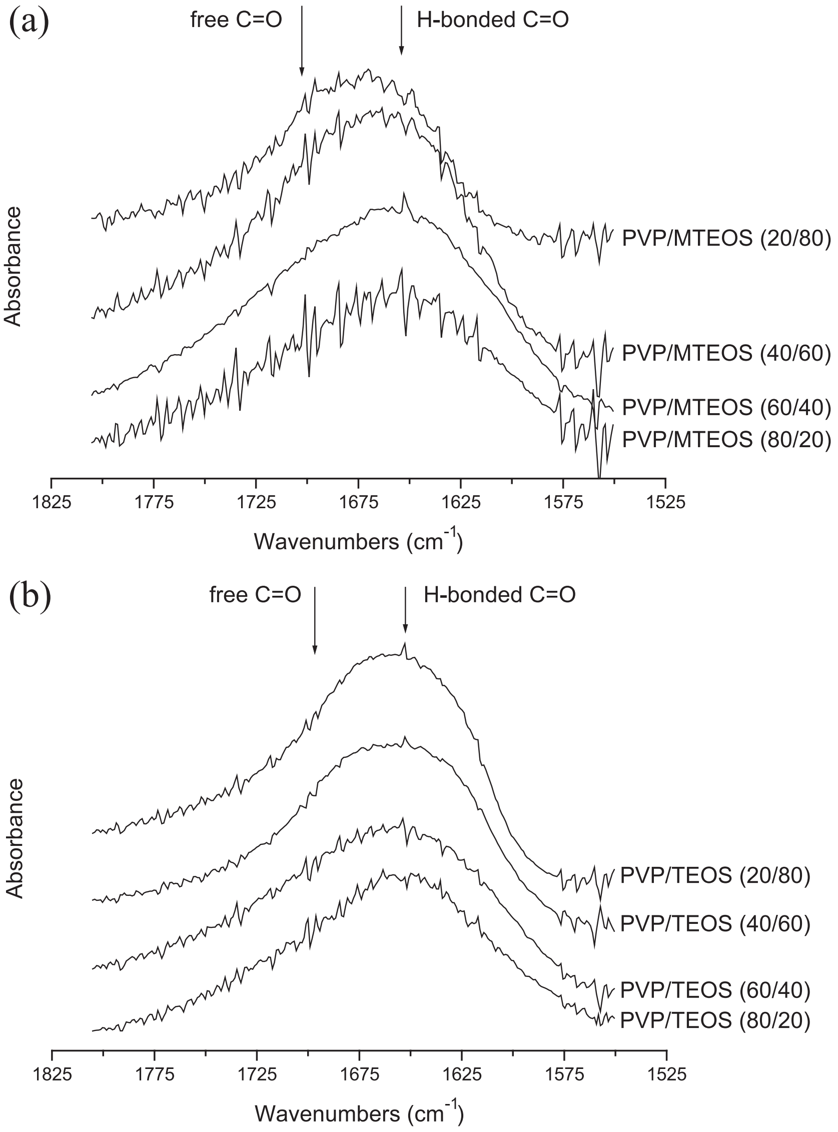

Fig. 3. Scale-expand infrared spectra in carbonyl stretching region of hybrid materials: (a) PVP/MTEOS and (b) PVP/TEOS hybrid systems.

for hydrogen bonded and free carbonyl is presumed to be equivalent in this study [20]. These values for materials were calculated and were tabulated in the Table 2.

From hydrogen bonding analysis, fraction of hydrogen bonded carbonyl group for PVP/MTEOS (80:20) was 67.2%. While MTEOS content increased, hydrogen bonded carbonyl group for PVP/MTEOS hybrid system was diminished continuously to extreme low value of 21.4%. In addition, fraction of hydrogen bonded carbonyl group for PVP/TEOS (80:20) was 79.3%, which was higher than that for PVP/MTEOS (80:20). While increasing the TEOS content to over 40 wt.%, hydrogen bonded carbonyl group for PVP/MTEOS hybrid system was diminished to ca. 55%. It was found that the fraction of hydrogen bonded carbonyl group for PVP/TEOS hybrid system was greater than that for PVP/MTEOS hybrid system with identical organic polymer content. This means the interfacial interaction contributed from hydrogen bonds for PVP/TEOS hybrid system was greater than PVP/MTEOS hybrid system. From the discussion in the previous sections, however, compatibility of organic and inorganic phases in PVP/MTEOS system was

Table 2
The curve fitting results from infrared spectra of the hybrid materials

Hybrid materials	Free C=O		Hydrogen bonded C=O		Fraction of hydrogen bonded C=O (f_{bonded}, %)
	v (cm^{-1})	A_{free} (%)	v (cm^{-1})	A_{bonded} (%)	
Neat PVP	1699.9	100.0	–	0.0	100.0
PVP/MTEOS (80:20)	1716.8	32.8	1646.7	67.2	67.2
PVP/MTEOS (60:40)	1696.5	58.9	1640.6	41.1	41.1
PVP/MTEOS (40:60)	1683.5	75.2	1643.3	24.8	24.8
PVP/MTEOS (20:80)	1686.1	78.6	1650.5	21.4	21.4
PVP/TEOS (80:20)	1724.3	20.7	1651.2	79.3	79.3
PVP/TEOS (60:40)	1702.5	47.9	1644.2	52.1	52.1
PVP/TEOS (40:60)	1689.9	41.4	1651.2	58.6	58.6
PVP/TEOS (20:80)	1695.0	48.7	1649.3	51.3	51.3

substantially greater than in PVP/TEOS system. It resulted from the existence of non-polar interaction between methyl group on MTEOS and polymer backbone in these hybrid materials. This interaction provided the main interfacial interaction to prevent the occurrence of phase separation. In this study, hydrogen bonding interaction was indeed found to exist in both PVP/MTEOS and PVP/TEOS hybrid systems. It provides weak interaction to stabilize phase behavior of hybrid materials; however, it did not play an important role to influence the phase behavior as other hybrid material systems [13,15,21]. When homogeneous (transparent) hybrid materials are acquired for optical or other applications, the usage of MTEOS is a more efficient method to provide higher compatibility between organic and inorganic phases.

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