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Glass transition temperatures of poly(hydroxystyrene-*co*-vinylpyrrolidone-*co*-isobutylstyryl polyhedral oligosilsesquioxanes)

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Abstract

A series of poly(hydroxystyrene-*co*-vinylpyrrolidone-*co*-isobutylstyryl polyhedral oligosilsesquioxanes) (PHS-PVP-POSS) hybrid polymers with various POSS contents was prepared by free radical copolymerization of acetoxystyrene, vinylpyrrolidone with styrylisobutylpolyhedral oligosilsesquioxanes (POSS), followed by selective removal of the acetyl protective group. The POSS content of a hybrid polymer can be effectively controlled by varying the feed ratios of reactants. The T_g of the POSS hybrid increases with the POSS content of PHS-PVP-POSS hybrids. The mechanism of T_g enhancement in these PHS-PVP-POSS hybrids was investigated using DSC, FTIR and GPC. The formation of the physically cross-linked POSS in these hybrid polymers trends to restrict polymer chain motion and results in significant T_g increase. © 2002 Published by Elsevier Science Ltd.

Keywords: Hybrid materials; Hydrogen bonding; Nanocomposites

1. Introduction

Polyhedral oligosilsesquioxane (POSS) based hybrid polymers have recently generated much interest [1–3]. These polymers have potential in the development of a wide range of hybrid materials with diverse properties. Polyhedral silsesquioxane consists of well-defined nanoscale inorganic silica-like core that is surrounded by eight organic groups, such as $[\text{RSiO}_{1.5}]_8$ (T_8 -type) where R can be one of a number of organic groups (functional or inert). Properly selecting polymerizable R is a useful part of synthesizing various silsesquioxane-based materials, facilitating the tailoring of the hybrid polymer's properties at a molecular level, and preventing the problem of compatibility or phase separation that usually is present in an ordinary inorganic nanoparticle/polymer system. Several POSS-based hybrid polymers have been prepared [4–21]. These POSS-based polymers can be roughly classified into three categories. One category is the 'star-type' architecture in which the POSS cage contains multi-functional polymerizable groups (more than two). Although these functional groups can form three-dimensional network materials, few of these materials can be characterized in detail because nearly all of these

precursors are octafunctional, such as methacrylate and epoxy-functional $^R\text{T}_8$ [4,5]. Essentially none of these materials is soluble.

The second category is the 'bead-type' architecture in which the T_8 -type cage is incorporated into the backbone of polymer by two functional or active groups. The third category is the 'pendant-type' architecture, in which the single functional POSS can be polymerized using the standard method of polymerization as a monomer or a comonomer. These macromers or monomers, such as POSS-silanol [15], POSS-norbornadiene [16], POSS-acrylate [17], POSS-styrene [18], and POSS-bisphenol have been incorporated into polysiloxane [19], polyacrylate [17,20], polystyrene [18], polynorbornadiene [16] and polyurethane [21] to prepare their associated hybrid polymers. The POSS has effectively reinforced the thermal and mechanical properties of the hybrid polymers. However, the mechanism by which the POSS reinforces the polymers is not yet well understood. In this work, a series of POSS-based poly(hydroxystyrene-*co*-vinylpyrrolidone-*co*-isobutylstyryl polyhedral oligosilsesquioxanes) (PHS-PVP-POSS) hybrid polymers were synthesized. According to our results, only a very low POSS content can effectively improve thermal properties of poly(hydroxystyrene-*co*-vinylpyrrolidone) (PHS-PVP) copolymers. The reinforcement mechanism is studied.

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2. Experimental

2.1. Materials

Isobutylstyryl polyhedral oligosilsesquioxane (POSS) was purchased from the Hybrid plastic Co. Inc. of USA. Both vinylpyrrolidone (VP) and acetoxystyrene (AS), purchased from the Aldrich, were distilled from calcium hydride under reduced pressure and stored in sealed ampuls in a refrigerator. The high purity azobisisobutyronitrile (AIBN) (Aldrich) was also kept in the dry box and used as received. Spectroscopic grade THF and toluene (Aldrich) were predried over 4 Å molecular sieves and distilled from metal sodium immediately prior to use. All other solvents were purchased from Aldrich and used without further purification.

2.2. Instrumentation

Thermal properties were characterized on a DSC from Du-Pont (DSC-9000). The measurement was made using 5–10 mg sample on a DSC sample cell. Temperature and energy calibration were carried out with indium. The scan rate was 20 °C/min within the temperature range of 30–260 °C after the sample was quickly cooled to 0 °C using the liquid nitrogen from the melt for the first scan and then scanned from 20 to 280 °C at 20 °C/min. The glass transition temperature (T_g) is at the midpoint of the specific heat increment. FTIR spectra were measured with a spectral resolution 1 cm⁻¹ on a Nicolet Avatar 320 FTIR spectrophotometer using KBr disks or pellets at room temperature.

2.3. Polymerization

All polymerization reactions were carried out under nitrogen using a vacuum-line system. PHS–PVP–POSS copolymers were prepared by two-step reactions. The poly(acetoxystyrene-co-vinylpyrrolidone-co-isobutylstyryl polyhedral oligomeric silsesquioxanes) (PAS–PVP–POSS) was prepared by a free radical copolymerization method. The PHS–PVP–POSS hybrid polymer was then obtained by a selective deacetylation. For comparison purpose, poly(vinylpyrrolidone) (PVP), poly(acetoxystyrene) (PAS), poly(vinylpyrrolidone-co-isobutylstyrylPOSS) (PVP–POSS), poly(acetoxystyrene-co-vinylpyrrolidone) (PAS–PVP) and poly(acetoxystyrene-co-isobutylstyrylPOSS) (PAS–POSS), poly(hydroxystyrene) (PHS), poly(hydroxystyrene-co-isobutylstyrylPOSS) (PHS–POSS), poly(hydroxystyrene-co-vinylpyrrolidone) (PHS–PVP) and poly(hydroxystyrene-co-vinylpyrrolidone-co-isobutylstyrylPOSS) (PHS–PVP–POSS) were also synthesized. Typical example of experimental procedures to synthesize these polymers are given below.

The polymerization of the PAS–PVP–POSS copolymer was carried out by adding 200 mg of *p*-acetoxystyrene,

800 mg of VP and 50 mg of isobutylstyryl polyhedral oligosilsesquioxane (POSS) monomers in 7 ml of toluene solvent using the AIBN initiator (10 mg) (1 wt% based on monomer) at 80 °C under nitrogen atmosphere for 24 h. The product then was poured into excess cyclohexane under vigorous agitation to precipitate the copolymer, then purified in THF/cyclohexane and dried in a vacuum oven. Product yield of 52% was obtained through this procedure.

The synthesis of PHS–PVP–POSS copolymer was carried out by dispersing 100 mg of PAS–PVP–POSS copolymer in a mixture of aqueous sodium carbonate and dioxane for 2 h at 40 °C under nitrogen atmosphere. The product was then poured into an excess hydrochloric acid solution under vigorous agitation to precipitate the copolymer, then rinsed with water, dried in a vacuum oven and the yield was almost 100%.

2.4. Determination of component content [22,23]

IR analysis was used to determine the respective contents of components of the polymer. Poly(acetoxystyrene) (PAS), poly(vinylpyrrolidone) (PVP) and poly(isobutylstyryl polyhedral oligosilsesquioxane) (POSS) were also prepared according to the above procedures. A series of POSS/PVP and PAS/PVP mixture with known quantities of POSS and PAS were prepared to plot a calibration curve. PVP, PAS, and POSS were first dissolved in a solvent, cast into a thin film, and then thoroughly ground with KBr powder in a smooth agate mortar to ensure intimate mixing. The carbonyl stretching vibration of the PVP is at 1680 cm⁻¹. The POSS moiety exhibit an antisymmetric Si–O–Si (siloxane) absorption band centered at 1109 cm⁻¹. The carbonyl absorption band of PAS is at 1760 cm⁻¹. The carbonyl band at 1680 cm⁻¹ was taken as the internal standard. The ratios of area of the absorption band at 1109 cm⁻¹ versus that at 1680 cm⁻¹ (I_{1109}/I_{1680}), and the area of the band at 1760 cm⁻¹ versus that at 1680 cm⁻¹ (I_{1760}/I_{1680}) are plotted against the mole concentration ratios of POSS/PAS and PAS/PVP, respectively. The plot gave a linear calibration, as shown in Fig. 1(a) and (b). The PVP molar concentration is assumed to be equal to one, and the relative mole concentrations of POSS (Y_{POSS}) and PAS (Y_{PAS}) are as follows:

$$Y_{\text{PAS}} = 2.882(I_{1760}/I_{1680}) + 0.039 \quad (1)$$

$$Y_{\text{POSS}} = 0.083(I_{1109}/I_{1680}) + 0.0028 \quad (2)$$

Hereafter, we calculate the respective component molar concentrations of these hybrid polymers by the following equations:

$$\text{POSS content (mol\%)} = Y_{\text{POSS}}/(1 + Y_{\text{POSS}} + Y_{\text{PAS}}) \quad (3)$$

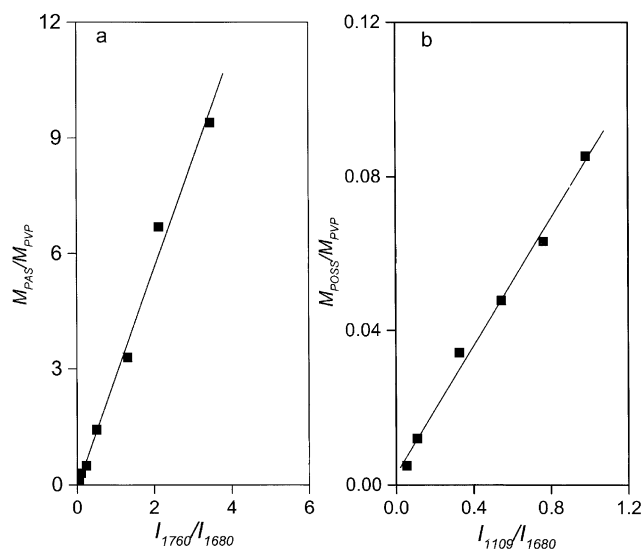


Fig. 1. Calibration curve for determining component contents of POSS based hybrid polymers using the intensity ratios of absorption bands of POSS at 1109 cm^{-1} , PAS at 1760 cm^{-1} and PVP at 1680 cm^{-1} , respectively.

$$\text{PAS content (mol\%)} = Y_{\text{PAS}} / (1 + Y_{\text{POSS}} + Y_{\text{PAS}}) \quad (4)$$

$$\text{PVP content (mol\%)} = 1 / (1 + Y_{\text{POSS}} + Y_{\text{PAS}}) \quad (5)$$

3. Results and discussion

3.1. Thermal properties

The detailed synthesis and characterization of these POSS-based hybrid polymers will be described elsewhere. The POSS contents of the relative hybrid polymers are determined from Eqs. (1)–(5), and are summarized in Table 1. The PHS–PVP copolymer with 50 mol% PVP is selected as the organic polymer matrix in the preparation of the POSS based hybrid polymers, because this composite has the optimum hydrogen bonding interaction between

Table 1
Thermal properties of POSS based hybrid polymers and parent polymers

Homopolymers without POSS			POSS based polymers			
No.	Polymer	T_g (°C)	No.	Hybrid polymer	POSS content (mol%)	T_g (°C)
1	PAS	122.3	6	PAS–POSS	2.4	106.3
2	PVP	148.4	7	PVP–POSS	2.0	138.9
3	PHS	149.1	8	PHS–POSS	2.4	191.5
4	PAS–PVP	122.5	9	PAS–PVP–POSS	0.8	84.4
5	PHS–PVP	194.9	10	PAS–PVP–POSS	2.2	98.5
			11	PAS–PVP–POSS	3.2	123.9
			12	PHS–PVP–POSS	0.8	205.8
			13	PHS–PVP–POSS	2.2	235.5
			14	PHS–PVP–POSS	3.2	245.3

hydroxyl groups of PHS and carbonyl groups of PVP [24,25].

The POSS-based PAS–POSS, PVP–POSS and PAS–PVP–POSS hybrid polymers were also synthesized and characterized for comparison. Table 1 reveals that the PAS–POSS_{2.4} hybrid polymer (2.4 mol% POSS) has a single T_g (Table 1, No. 6) which is 16 °C lower than that of pure PAS (Table 1, No. 1). The PVP–POSS hybrid polymer (2.0 mol% POSS) has a single T_g at 138.9 °C , which is 9.5 °C lower than that of pure PVP (Table 1, No. 2). The observed lower T_g of these two hybrid polymers suggest that certain forms of association reduce the original dipole–dipole interaction within pure PAS and pure PVP polymer chains. A similar result was also found for the hybrid PAS–PVP–POSS hybrid, relative to the PAS–PVP copolymer, as shown in Table 1. The PAS–PVP–POSS_{2.2} has a T_g of 98.5 °C , which is lower than that of the pure PAS by 23.8 °C , and that of the pure PVP by 49.9 °C , and that of the corresponding PAS–PVP copolymer (Table 1, No. 4) by 24.0 °C . The T_g of the PAS–PVP–POSS hybrid polymer increases as the POSS content is increased (Table 1, Nos. 9–11). In conclusion, when a smaller POSS moiety is incorporated into the hybrid copolymer or polymer, its T_g value does not increase as would be expected, it actually decreases relative to the non-POSS based polymer or copolymer. Haddad and Lichtenhan [18] found a similar result for the hybrid polystyrene with a low POSS content. When the POSS content in the hybrid polymer is quite low, the POSS acts as an inert diluent and reduces the self-association of the homopolymer molecules, resulting in lower T_g . However, at a higher POSS content, T_g of the hybrid polymer increases with POSS content due to the rigid nature of the POSS. The POSS monomer is more rigid and dimensionally larger. The diameter of the POSS moiety is about $25\text{--}30\text{ Å}$ while a typical polymer chain segment from a vinyl type monomer is about $2\text{--}5\text{ Å}$, implying that the POSS moiety may dominate the local chain motion of the polymer. Table 1 summarizes all glass transition temperatures of these polymers and hybrids.

Fig. 2 displays the expanded FTIR spectra from 1800 to 1620 cm^{-1} for PAS, PAS–POSS hybrid, PVP, PVP–POSS hybrid, PVP–PAS and PVP–PAS–POSS hybrid, respectively. The absorptions at 1760 cm^{-1} (Fig. 2(a)) and 1680 cm^{-1} (Fig. 2(b)) are assigned to the free carbonyls of PAS and PVP. These carbonyl bands clearly widen and shift toward a higher frequency when the POSS is attached to these polymers (Fig. 2(a) and (b)). The carbonyl absorption peak of the PAS–POSS_{2.4} hybrid polymer containing 2.4 mol% POSS is at 1764 cm^{-1} , higher than that of the PAS (1760 cm^{-1}). The carbonyl absorption peak of the PVP–POSS_{2.0} hybrid polymer with 2.0 mol% POSS is at 1682 cm^{-1} , slightly higher than that of the PVP at 1680 cm^{-1} . These results further verify that the POSS acts as an inert diluent to reduce the self-association interaction of these homopolymers. Fig. 2(c) shows that the carbonyl vibration band from the PAS component of

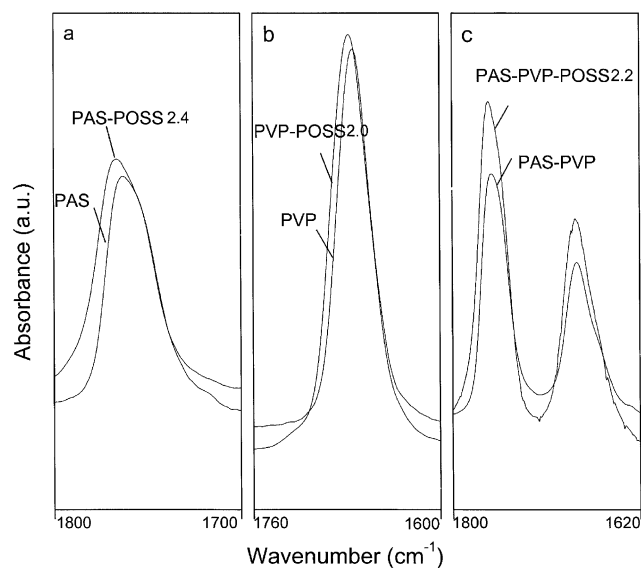


Fig. 2. FTIR spectra in the regions 1800–1600 cm^{-1} recorded at room temperature of (a), pure PAS and PAS–POSS hybrid polymer; (b), pure PVP and PVP–POSS_{2.0} hybrid polymer; (c), PAS–PVP copolymer and PAS–PVP–POSS_{2.2} hybrid polymer.

the PAS–PVP–POSS_{2.2} hybrid polymer shifts upward to 1765 cm^{-1} and the band is widened. These FTIR results further confirm that the POSS acts as a diluent of the polymer, reducing the self-association and yielding a T_g lower than that of the corresponding parent polymers. However, the carbonyl absorption band from the PVP component of the PAS–PVP–POSS_{2.2} remains at 1680 cm^{-1} , which value is virtually the same as for the PAS–PVP.

These PHS–PVP–POSS hybrid polymers were obtained by selective deacetylation of corresponding PAS–PVP–POSS hybrid polymers. Here, mole fractions of components are assumed to remain unchanged because the reaction involves only complete deacetylation of PAS–PVP–POSS. Fig. 3 presents the differential scanning calorimetry thermograms of pure PHS, parent PHS–PVP copolymer, PHS–POSS_{2.4} and various PHS–PVP–POSS hybrid polymers. It is quite interesting to notice that the T_g of the PHS–POSS_{2.4} hybrid polymer is dramatically higher than that of its parent PHS. The PHS–POSS_{2.4} has a T_g of 191.5 °C, 85.2 °C higher than that of the PAS–POSS_{2.4} hybrid polymer with the same POSS content (Table 1, No. 6) before deacetylation, and 42.4 °C higher than that of pure PHS (Table 1, No. 3). Although the POSS content in the hybrid PHS–POSS polymer is only 2.4 mol%, its presence can markedly increase the T_g of the PHS. On the other hand, the PAS–POSS_{2.4} hybrid polymer actually has a lower T_g than the PAS homopolymer. The significant T_g increase of the PHS–POSS_{2.4} indicates that new and strong specific interactions must occur between POSS and PHS in these hybrid polymers. The hydroxyl group of the PHS is well known to be an efficient proton donor, offering excellent potential to form a hydrogen bonding interaction with

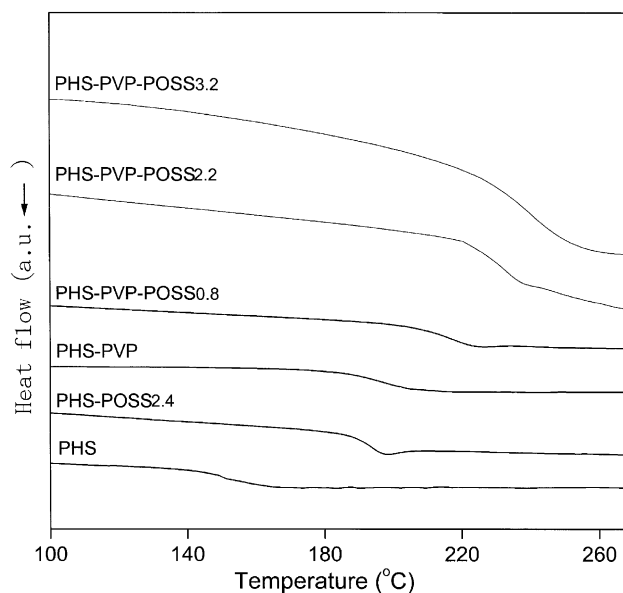


Fig. 3. The differential scanning calorimetry thermograms of PHS, PHS–POSS_{2.4}, PHS–VP (Table 1, No. 5), PHS–PVP–POSS_{0.8}, PHS–PVP–POSS_{2.2} and PHS–PVP–POSS_{3.2}.

proton-acceptor polymers, such as the siloxane group of POSS. The formation of hydrogen bonds between POSS siloxane and PHS hydroxyl tends to cause physical cross-linking in PHS–POSS because every POSS has 12 siloxane groups. Therefore, more than one hydrogen bonds is anticipated on each POSS cube, effectively restricting molecular chain motion and significantly increasing T_g . This effect may be the main reason for the PHS–POSS copolymer possessing significantly higher glass transition temperature than that of PHS, even though the POSS content is small. The PAS–POSS has a lower T_g than PAS because of the lack of formation of hydrogen bond. In addition, these inorganic POSS cores tend to reduce the self-association of PAS chains, and thus cause lower T_g than the parent PAS.

The PHS–PVP–POSS hybrid polymer yields similar results as the PHS–POSS system. T_g of PHS–PVP–POSS_{0.8} (Table 1, No. 12) is 205.8 °C (Table 1, No. 12) which is 121.4 °C higher than that of the corresponding PAS–PVP–POSS_{0.8} hybrid (Table 1, No. 9). The PHS–PVP–POSS_{0.8} has a T_g , 11 °C higher than that of the corresponding non-POSS PHS–PVP copolymer (Table 1, No. 5). Again, the T_g of PAS–PVP–POSS_{0.8} (84.4 °C) is significantly lower than that of the corresponding PAS–PVP copolymer (122.5 °C). These findings further verify that certain interactions must occur between POSS and PHS–PVP when the POSS moiety is incorporated into the PHS–PVP copolymer chain.

T_g of the PHS–PVP–POSS hybrid polymer was found to increase with POSS content. For example, the T_g of PHS–PVP–POSS_{2.2} (Table 1, No. 13) was at 235.5 °C, significantly higher than that of the PHS–PAS (194.9 °C) without POSS and that of the PHS–PVP–POSS_{0.8} (205.8 °C).

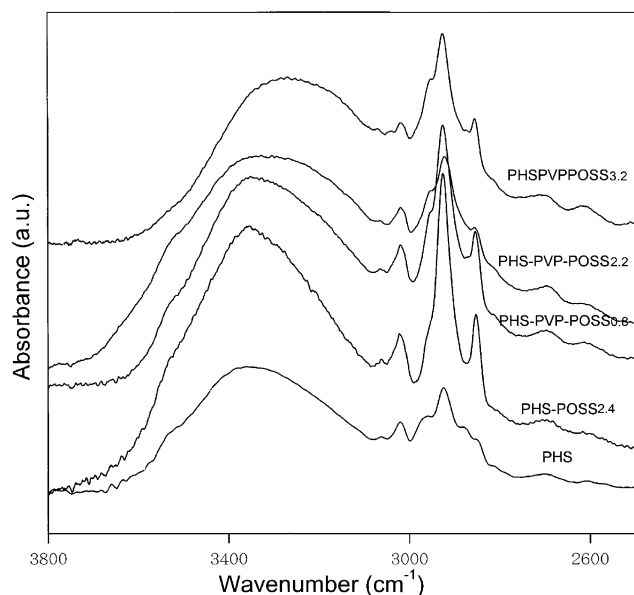


Fig. 4. FTIR spectra in the regions 3800–3000 cm^{-1} recorded at room temperature for pure PHS, PHS-POSS_{2.0}, PHS-PVP-POSS_{0.8}, PHS-PVP-POSS_{2.2}, and PHS-PVP-POSS_{3.2}.

3.2. FTIR spectra and enhancement mechanism

FTIR spectroscopy is a suitable technique for investigating particular intermolecular interactions. FTIR absorption changes, in terms of strength and positions of characteristic functional groups, are attributable to the existence of specific intermolecular and/or intramolecular interactions. FTIR spectra of these PHS-PVP-POSS hybrid polymers were carefully compared to elucidate the enhancement effect of POSS on PHS and PHS-PVP polymers.

In the PHS-PVP-POSS hybrid, the monomeric unit of the PVP contains a carbonyl group with a $\nu_{\text{C=O}}$ stretching mode at 1680 cm^{-1} . The POSS as a pendant, yielding a $\nu_{\text{Si-O-Si}}$ vibration mode at 1109 cm^{-1} , attached to the polymer chain. The repeating unit of the PHS has no functional group to generate an absorption in the regions, 1600–1850 and 1050–1150 cm^{-1} . The PHS has a strong characteristic absorption band in the region of 3200–3600 cm^{-1} , attributed to the hydroxyl vibration mode. Therefore, any change of the FTIR spectra in these regions is attributed to the change in the chemical environments of the carbonyl, siloxane, and hydroxyl groups, especially the formation of hydrogen bonds. Fig. 4 shows the expanded infrared spectra recorded in the region, 2500–3800 cm^{-1} , for various PHS-PVP-POSSs, PHS-POSS_{2.4} hybrid polymers, and pure PHS at room temperature. The hydroxyl stretching vibration of the pure PHS occurs at higher frequency between 3100 and 3600 cm^{-1} . A broad band centered at 3350 cm^{-1} is attributable to the wide distribution of hydrogen-bonded hydroxyls of the PHS. A relatively narrower shoulder peak at 3525 cm^{-1} is associated with the free (non-hydrogen bonded) hydroxyl. When

POSS moieties are incorporated to the PHS to produce the PHS-POSS_{2.4} (Table 1, No. 8), the position of the major peak associated with the hydrogen-bonded hydroxyl in the PHS-POSS_{2.4} shifts markedly toward lower wavenumber, from 3350 to 3325 cm^{-1} . The difference ($\Delta\nu = 200 \text{ cm}^{-1}$) between the frequency of the minor free hydroxyl stretching vibration band and the major hydrogen-bonded hydroxyl vibration mode in the PHS-POSS hybrid polymer exceeds the corresponding difference ($\Delta\nu = 175 \text{ cm}^{-1}$) for the pure PHS, reflecting a strengthened interaction in the hybrid polymer perhaps due to the increase in the average strength of intermolecular and/or intramolecular hydrogen bonding. PHS-PVP-POSS hybrid polymers exhibit a similar trend when POSS was incorporated into PHS-PVP to yield the PHS-PVP-POSS hybrid polymer. Fig. 4 reveals that the PHS-PVP-POSS_{0.8} yield a broader hydrogen bonded hydroxyl band centered at 3320 cm^{-1} and a narrower free hydroxyl absorption peak at 3525 cm^{-1} . The frequency difference ($\Delta\nu$) between the hydrogen bonded hydroxyl group and the free hydroxyl group absorption band of the PHS-PVP-POSS_{0.8} is 205 cm^{-1} . The frequency difference ($\Delta\nu$) further increases with the increase of the POSS content while the peak position of the free hydroxyl group remains unchanged. The frequency differences ($\Delta\nu$) in the PHS-PVP-POSS_{2.2} hybrid polymer that contains 2.2 mol% POSS is 220 cm^{-1} and increases to 250 cm^{-1} as the POSS content is increased to 3.2 mol%, indicating that the average intensity of the hydrogen bonding interaction of the PHS-PVP-POSS hybrid polymer increases with increasing POSS content. These results are consistent with the T_g behaviors of the PHS-PVP-POSS hybrid polymers. However, the frequency difference for the PHS-PVP-POSS is still less than the difference for the corresponding parent PHS-PVP copolymer ($\Delta\nu = 320 \text{ cm}^{-1}$), [24,25] implying that the increase in T_g depends not only on the strength of the formed hydrogen bonds. The POSS moiety in PVP-PAS-POSS_{2.2} does not increase T_g of its parent PVP-PAS, although the nanosized POSS is expected to hinder physically the molecular chain motion, implying that only the nanosized physical effect alone fails to induce a T_g increase in the PVP-PAS-POSS_{2.2}. The formation of the physical cross-linking structure of the PHS-PVP-POSS hybrid containing large and rigid POSS is responsible for hindering the motion of the polymer chain and results in T_g increase of the hybrid, even though the hydrogen bonding between the POSS siloxane and the hydroxyl is still relatively weaker than that between the PVP carbonyl and PHS hydroxyl. The formation of hydrogen bonds between the POSS siloxane and the PHS hydroxyl tends to increase the distance between molecular chains in the PHS-PVP-POSS and hinder the formation of hydrogen bonds between the PHS hydroxyl and the PVP carbonyl, thereby reducing overall hydrogen bonding intensity. These hydroxyl groups of the PHS near the POSS group are able to form multi-hydrogen bonds with POSS siloxanes and yield the rigid physically cross-linked POSS.

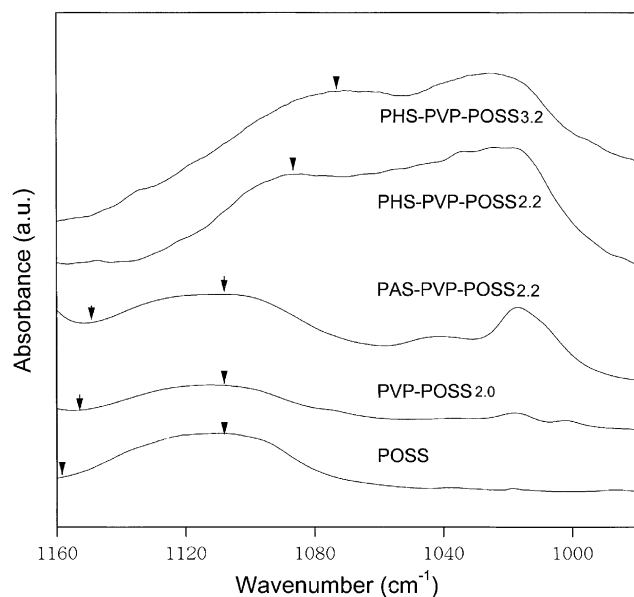


Fig. 5. FTIR spectra between 1160 and 9060 cm^{-1} recorded at room temperature for pure POSS, PVP-POSS_{2.0}, PAS-PVP-POSS_{2.2}, PHS-PVP-POSS_{2.2} and PHS-PVP-POSS_{3.2}.

Fig. 5 displays expanded FTIR spectra between 1160 and 950 cm^{-1} for pure POSS, PVP-POSS_{2.0}, PVP-PAS-POSS_{2.2} and PHS-PVP-POSS hybrid polymers. Pure POSS has a characteristic absorption band centered at 1109.4 cm^{-1} that corresponds to the siloxane vibration absorption. When POSS moieties are incorporated to the PVP, the siloxane broad absorption peak position remains essentially unchanged, and its absorption edge shifts only slightly towards a lower wavenumber. The PAS-PVP-POSS_{2.2} hybrid polymer yields similar results. Surprisingly, the maximum absorption band shifts considerably towards lower wavenumber when the POSS is attached to the PHS-PVP to form the PHS-PVP-POSS_{2.2} hybrid polymer. The maximum peak position of siloxane vibration band in PHS-PVP-POSS_{2.2} hybrid polymer shifts from 1109 to 1089 cm^{-1} ($\Delta\nu = 20 \text{ cm}^{-1}$) and shifts further to 1082 cm^{-1} for the PHS-PVP-POSS_{3.2} ($\Delta\nu = 27 \text{ cm}^{-1}$). These results indicate that the siloxane group of POSS must interact strongly with the hydroxyl group of the PHS. We think that the interaction caused by the formation of multi-hydrogen bonds between the POSS siloxane and the PHS hydroxyl is responsible for absorption shift of the siloxane vibration band. This result further supports our earlier assumption that is also consistent with T_g behaviors of these PHS-PVP-POSS hybrid materials.

Fig. 6 shows FTIR spectra between 1710 and 1620 cm^{-1} , obtained at room temperature for PVP (Table 1, No. 2), PHS-PVP copolymer (Table 1, No. 5) and various PHS-PVP-POSS hybrid polymers (Table 1, Nos. 12–14). Pure PVP has a strong carbonyl absorption band centered at 1680 cm^{-1} . This absorption band clearly shifts to a lower wavenumber when PVP is copolymerized with PHS. The central peak of the carbonyl band shifts to 1650 cm^{-1} when

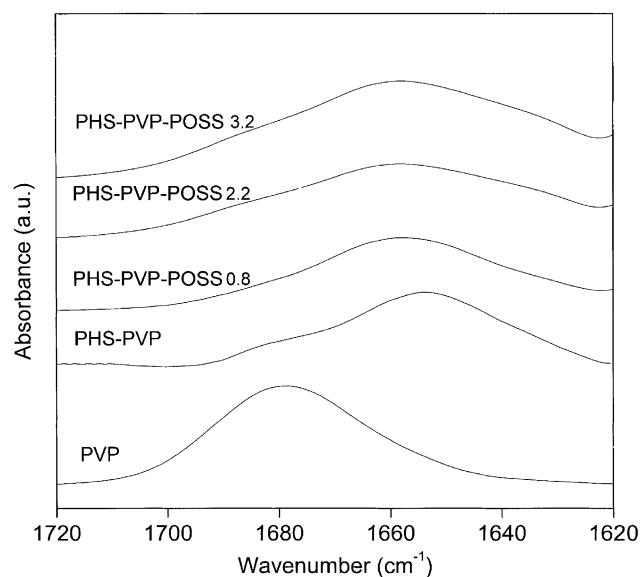
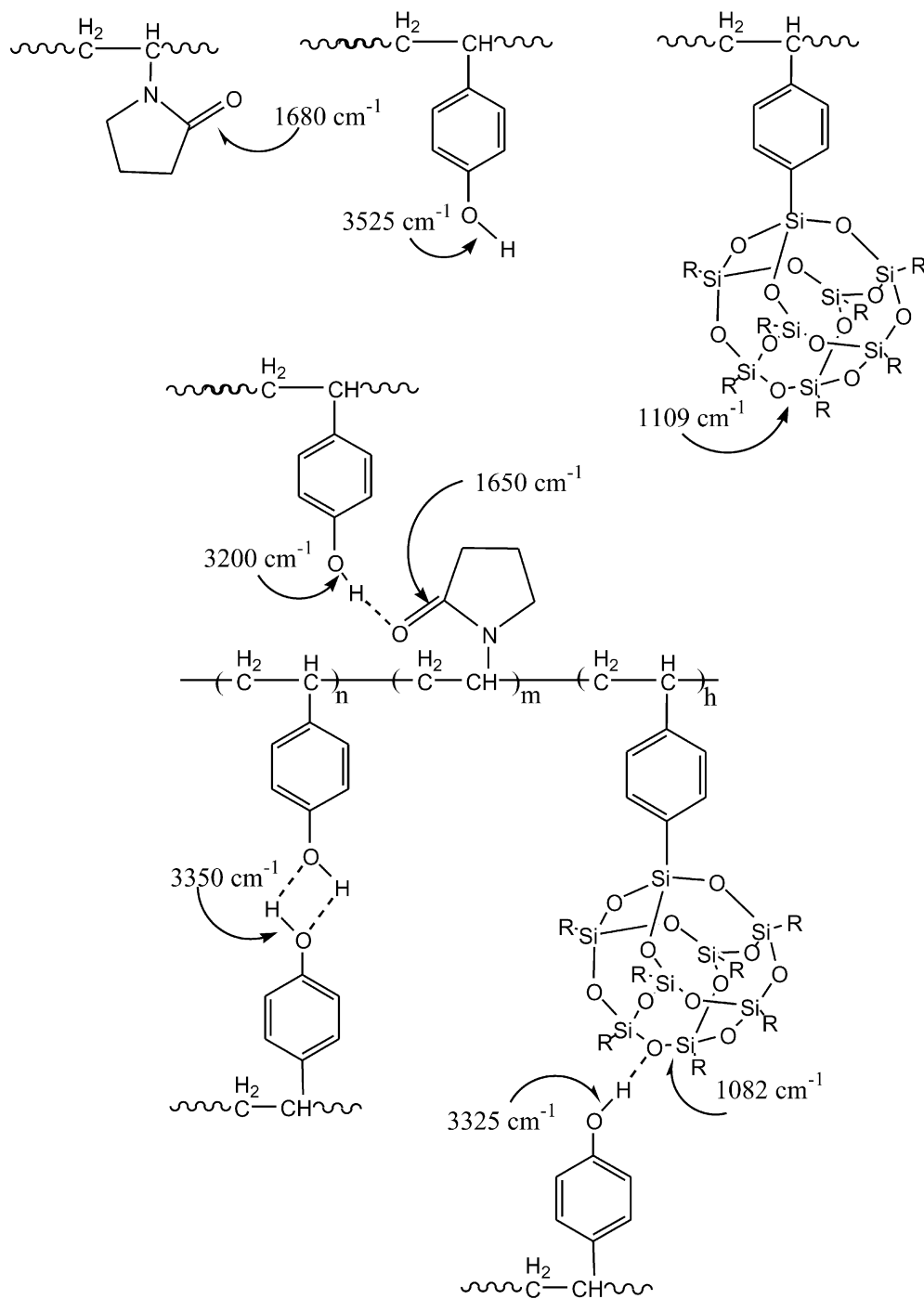


Fig. 6. FTIR spectra in the regions 1710–1620 cm^{-1} recorded at room temperature for PVP-PHS, PHS-PVP-POSS_{0.8}, PHS-PVP-POSS_{2.2} and PHS-PVP-POSS_{3.2}.

the PVP content is 50 mol%, because hydrogen bonds are formed between the PVP carbonyl and the PHS hydroxyl [25]. However, the carbonyl absorption band of the PVP moiety in the PHS-PVP-POSS hybrid polymer shift towards higher wavenumber as the POSS content is increased. Scheme 1 shows all the shifts and interactions of characteristic vibration bands. This result indicates that the intensity of hydrogen bonds between the PVP carbonyl and the PHS hydroxyl in the PHS-PVP-POSS hybrid polymer decreases declines as the POSS content increases. Portion of the PHS hydroxyl forms hydrogen bonds with the POSS siloxane and thus decreases the intensity of hydrogen bonds between the PHS hydroxyl and the PVP carbonyl, which is also consistent with the result observed for the hydrogen-bonded hydroxyl vibration band. This result indirectly confirms the formation of hydrogen bonds between the POSS siloxane and the PHS hydroxyl in the PHS-PVP-POSS hybrid polymer.

4. Conclusions

A series of hybrid polymers with various POSS contents was prepared and characterized. The large size and rigidity of the nanosized POSS alone does not cause T_g increase of POSS-based hybrid materials with low POSS content. Hydrogen bonds are formed between the POSS siloxane and the PHS hydroxyl in the PVP-PHS-POSS to form the physically cross-linked POSS structure, even though the hydrogen bonds between the POSS siloxane and the PHS hydroxyl are relatively weaker than those between the PVP carbonyl and the PHS hydroxyl. Such physically cross-linked POSS effectively restricts the polymer chain motion



Scheme 1.

and cause a significant increase in T_g of these hybrid polymers, even with small amount of POSS.

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