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Effect of hydrogen bonding on the glass transition behavior of poly(acrylic acid)/silica hybrid materials prepared by sol–gel process

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Abstract

Poly(acrylic acid) is a water soluble polymer, which has a high glass transition temperature of ca. 102°C. However, when silica (20% of TEOS) was incorporated via sol–gel process, it was found that glass transition temperature of the hybrid material decreased drastically. From the analysis of infrared spectra, this phenomenon can be attributed to the decreasing of hydrogen bonding between carboxyl and carbonyl groups of the poly(acrylic acid). Furthermore, with the TEOS content of 40–60%, silica matrix was formed and resulted in the occurrence of phase separation. With TEOS content further increased to 80%, molecular chains of PAA were aggregated together to form poly(acrylic acid) matrix. Hence, the chain segments of PAA were no more confined by the silica matrix and only single T_g was observed during DSC thermoscan. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Glass transition temperature; Infrared spectra; Hydrogen bonding

1. Introduction

Poly(acrylic acid) and poly(methacrylic acid) are both water soluble polymers, which may be prepared by direct polymerization of acrylic acid by free radical technique. These polymers can be easily modified and applied diversely to adhesives, release agents, dispersants, thickeners, and flocculants [1,2]. These uses are directly attributed to the varied physical properties and the high reactivity of these acrylic polymers. Therefore, many of the applications depend on the ability of these polymers to form complexes or to react to the desired substrates. The origin of the interfacial interaction between organic polymer chain segments and inorganic surface is thus an important aspect of these polymers.

Lately, review of silica film preparation was provided by Nishimori and Hasegawa et al. [3,4], in which the thick silica films were fabricated by electrophoretic sol–gel deposition technique on silica particles in the presence of poly(acrylic acid). Furthermore, particle size distribution of silica and morphology of film surfaces were discussed in terms of various amount of poly(acrylic acid). However, these works focus on the application of processing technique to obtain crack-free films, but the interfacial interaction between poly(acrylic acid) and silica was not fully discussed.

In the other literature on poly(acrylic acid)/alumina system [5], it is known that there is a strong interaction between the polymer and the inorganic surface, in which the acidic groups of poly(acrylic acid) play an important role for the binding force to prevent the incompatibility between organic molecular chain segments and inorganic matrix. This interaction is manifested in the physical and mechanical properties of the composite in the absence of intramolecular or intermolecular anhydride cross-linking. Such interaction has been reported in the literature of nylon 66/graphite fiber systems [6]. This strong interfacial bonding between the fiber and matrix provides an excellent adherence force and can be maintained after subsequent polymerization of the monomer. However, with only thermogravimetric data or photos of scanning electric microscope in these studies, direct evidence of the origin of the interfacial interaction is still lacking, hence, it is the objective of this study to investigate this phenomenon.

Sol–gel process is a convenient method for the preparation of oxide films from alkoxysilyl group containing materials via continuous reaction steps of hydrolysis and condensation catalyzed by acidic or basic catalysts [7]. In addition, for the time being, sol–gel is not only a manufacturing process for the homogeneous inorganic glasses but also a technique for the synthesis of various kinds of organic-inorganic hybrid materials [8–12]. In this research,

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this technique was used to prepare the desired PAA/silica hybrid materials with PAA as catalyst. As indicated in review [1], PAA is a strong acid with the pK_a value of 4.75, which was only slightly greater than its monomer (pK_a of acrylic acid is 4.26). Therefore, this material not only acts as one component of hybrid materials but also can be used as acid catalyst in sol–gel process.

2. Experimental

2.1. Materials

Poly(acrylic acid) (PAA, MW = 450,000, Scientific Polymer Products) and tetraethoxysilane (TEOS, tetraethyl orthosilicate, Merck) were used as received. Hydrochloric acid (HCl, Union Chemical Works) was applied as catalyst and deionized water used was generated from the Milli-Q plus water purification system (Millipore). The solvent, 1,4-dioxane (Fisher Scientific), was of ACS grade.

2.2. Preparation of desired hybrid films

PAA was thoroughly dissolved in appropriate amount of dioxane first, and TEOS solution was prepared with reagent mole ratio of $H_2O/TEOS = 15/1$. Subsequently, PAA solution was added into TEOS solution in various organic–inorganic ratios with thorough mixing. The sol–gel process was carried out at room temperature. After 5 h, homogeneous solution can be obtained. These solutions were then heated at 60°C under vacuum for 6 h. Post-reaction was conducted at 70°C under vacuum for 24 h to remove residual solvent and by-products (water and alcohol). In addition, neat-silica was prepared with reagent mole ratio of $HCl/H_2O/TEOS = 0.025/15/1$ and $PAA/H_2O/TEOS = 0.025/15/1$ (calculated by monomer units of acrylic acid) under the same heat treatment procedure for the comparison of two acidic catalysts.

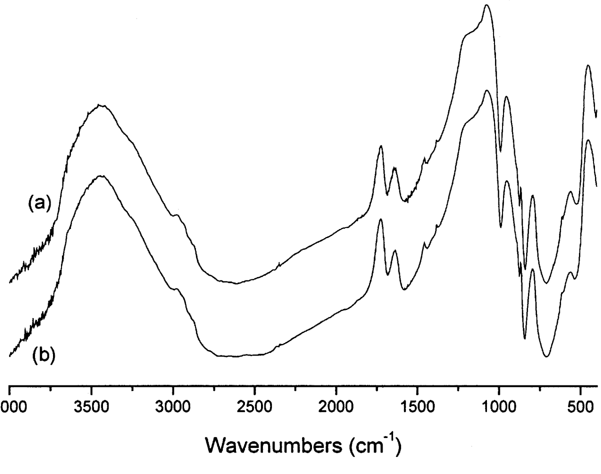

Fig. 1. Infrared absorption of neat silica that synthesized via sol–gel process using (a) hydrochloric acid and (b) poly(acrylic acid) as acid catalyst.

2.3. Methods and measurements

Differential scanning calorimeter (DSC, TA 2010) was used for the investigation of glass transition temperature variation of synthesized hybrid materials. Appropriate amount of samples (ca. 5 mg) were sealed in aluminum sample pans. DSC analyses of these hybrid materials were then conducted under a dry nitrogen at a heating rate of 20°C/min. Besides, infrared spectra of the hybrid materials were obtained from Fourier transform infrared spectrophotometer (FTIR, Nicolet Avatar 320) in spectral range of 4000–400 cm^{-1}.

3. Results and discussion

3.1. Sol–gel process via PAA catalyzed

In this research, PAA/silica hybrid materials were prepared by PAA catalyzed process. The neat silica film was also made with same procedure and compared to hydrochloric acid catalyzed system to study the characteristic of silica structure. The infrared spectra of PAA catalyzed and hydrochloric acid catalyzed silica were showed in Fig. 1.

In this figure, with such small amount of PAA added, there was no obvious absorption peak of organic species observed. In addition, absorption peaks of silica structure (O–H str. (silanol group) at 3440 cm^{-1}, Si–OH str. at 951 cm^{-1}, Si–O–Si asym. str., sym. str., and bending at 1073, 793, and 451 cm^{-1}, respectively) were all well resolved. The absorption peaks of distinct groups in the silica film of PAA catalyzed were entirely conformed the infrared absorption of hydrochloric acid catalyzed silica without any difference of intensity or peak position. It means that PAA catalyzed silica film has the same silica structure as hydrochloric acid catalyzed system and can be used as acid catalyst for the execution of sol–gel process and obtains desired silica structure.

3.2. Glass transition temperature of PAA/silica hybrid system

It is well known that PAA is a kind of acrylic polymer, which can be applied as adhesives and has a glass transition temperature of ca. 106°C [13]. However, with small amount of silica introduced to the system, it was found that these materials were obvious softer that neat PAA and did not exhibited glassy but amorphous condition at room temperature. Hence, DSC was introduced in order to investigate the certain glass transition temperatures (T_gs) of these hybrid materials in detail.

Fig. 2 shows the DSC thermogram curves of neat PAA and hybrid materials. All the T_gs were denoted by arrows, which were 129.5°C for neat PAA, −7.4°C for PAA/TEOS (80/20), 136.4 and 4.3°C for PAA/TEOS (60/40), 117.4 and 27.3°C for PAA/TEOS (40/60), and 102.8°C for PAA/TEOS (20/80), respectively. The T_g value of PAA was shown

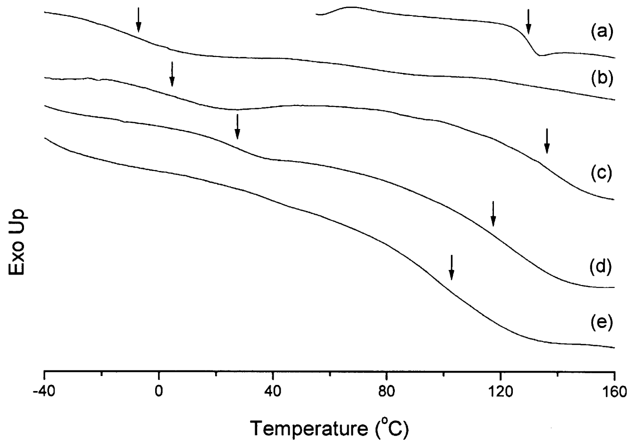

Fig. 2. DSC thermogram curves of hybrid material: (a) neat PAA, (b) PAA/TEOS (80/20), (c) PAA/TEOS (60/40), (d) PAA/TEOS (40/60), and PAA/TEOS (20/80). The glass transition temperatures (T_gs) were denoted by arrows.

higher than commercial products, which was due to the high molecular weight of the material used. Furthermore, it is interesting to notice that with 20% of TEOS added into, the hybrid system exhibited single glass transition behavior and the T_g decreased to extreme low value of −7.4°C. In general, with silica blended into the hybrid system prepared via sol–gel process and mixed in molecular level (only single phase were found), materials showed higher T_g value than neat polymers, which was due to the enhancement of silica structure [14,15]. However, in this hybrid system, hydrogen bonding interaction of PAA chain segments was strong and important for its physical behavior. Hence, the collapse of intra-phase interaction of PAA has to be taking into account.

In 1950s, Gordon and Taylor illustrated an equation to predict the T_g value of blended system from distinct components [16]

$$T_g = \frac{\omega_1 T_{g1} + k\omega_2 T_{g2}}{\omega_1 + k\omega_2}, \tag{1}$$

where ω_i is the weight fraction of individual species and k is an index of similar degree of molecular structure and properties

$$k = \frac{\rho_1 \Delta\alpha_2}{\rho_2 \Delta\alpha_1} = \frac{\nu_2 \Delta\alpha_2}{\nu_1 \Delta\alpha_1}, \tag{2}$$

where ρ_i is the density of the component i, ν_i the specific volume of the component i, and $\Delta\alpha_i$ is the difference of the thermal expansion coefficient between the glassy and amorphous state of the component i. This equation counted both free volume and the thermal expansion coefficient for the glass transition behavior of polymer blends. Moreover, take hydrogen bonding strength into account, Kwei proposed other equation that added the specific interaction term, $q\omega_1\omega_2$, into Gordon–Taylor equation in 1980s [17]

$$T_g = \frac{\omega_1 T_{g1} + k\omega_2 T_{g2}}{\omega_1 + k\omega_2} + q\omega_1\omega_2, \tag{3}$$

where q is a parameter corresponded to the strength of hydrogen bonding, which can be considered as the equilibrium between breaking of hydrogen bonding of PAA and formation of the interfacial interaction between organic and inorganic phases in this hybrid system. It also means that the T_g deviation depends on the change of entropy, which corresponds to the variation of the hydrogen bonding interaction within the hybrid system. From the decreasing of T_gs from 129.5°C for PAA to −7.4°C for 20% of TEOS in the system, an inference can be made that high strength hydrogen bonding of PAA was collapsed with the addition of small amount of silica and formed much weaker interaction between organic and inorganic phases even through the actual value of q in this system cannot be determined from these information.

In addition, with higher ratio of TEOS content (40–60%), two T_gs were found in DSC thermo-scan, furthermore, the higher T_g was diminished and the lower T_g was raised with the increasing of the content of inorganic silica. While TEOS content increased to 80%, the lower T_g was vanished and hybrid material showed only single T_g of 102.8°C. From this T_g variation and the hindrance effect to hydrogen bonding from inorganic structure, which may decrease the T_g of PAA, it is convinced that PAA chain segments were lie into two different molecular environments; one is silica matrix (for lower T_g segments) and the other is PAA-rich phase (for higher T_g segments) with TEOS content of 40–60%. Moreover, with TEOS content of 80%, only single but broad glass transition behavior at ca. 102.8°C was found in DSC thermo-scan, which was approached to the T_g of neat PAA and may due to entirely macrophase separation of PAA and silica matrix, which made molecular chains of PAA (in silica matrix) to aggregate together to form a neat PAA matrix in this hybrid material. These viewpoints from DSC thermo-scan would be further discussed with infrared spectra later.

3.3. FTIR spectroscopy analysis

Fig. 3 shows the infrared absorption of carbonyl group. It is obvious that a shoulder exists on the side of lower wavenumbers in all the materials, which may due to the formation of hydrogen bonds from carboxyl and silanol groups. A recent review provided by Ma et al. [18] described the hydrogen bonding analysis in novolak-type phenolic resin/aliphatic polyester blends. It was reported that the interaction between two phases can be analyzed from the infrared absorption of carbonyl stretching by curve fitting. Furthermore, the contribution to the interfacial interaction by hydrogen bonds in blending systems can be observed. The analysis of hydrogen bonding has also been reported in the literatures of polyamide/phenolic resin [19] and phenolic resin/phenoxy resin systems [20]. By using

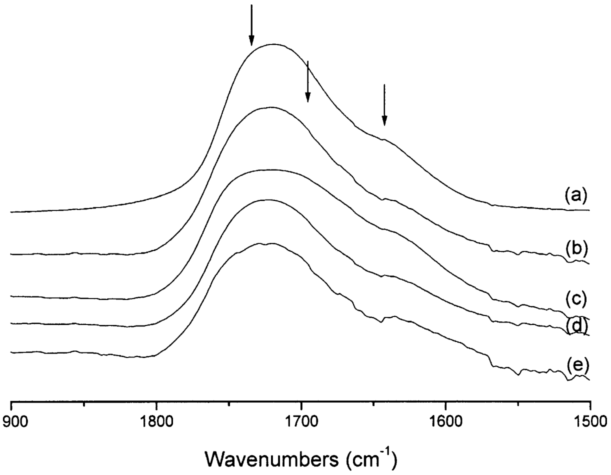

Fig. 3. Infrared analysis of carbonyl groups on hybrid materials: (a) neat PAA, (b) PAA/TEOS (80/20), (c) PAA/TEOS (60/40), (d) PAA/TEOS (40/60), and (e) PAA/TEOS (20/80). Absorption peaks of free carbonyl (1733 cm^{-1}), silanol bonded (1695 cm^{-1}), and carboxyl bonded carbonyl groups (1644 cm^{-1}) were denoted by arrows.

an appropriate baseline, the absorption band of carbonyl groups may be readily separated into two peaks by Gaussian curve fitting. The fraction of hydrogen bonded carbonyl can be calculated from the following equation suggested by Coleman et al. [21]

$$f_{\text{free}} = \frac{A_{\text{free}}}{(A_{\text{bonded}}/1.5) + A_{\text{free}}}, \qquad (4)$$

where A_{bonded} is the area of hydrogen bonded carbonyl absorption, A_{free} the area of free carbonyl absorption, and f_{free} is the fraction of unbonded carbonyl group. In addition, the conversion coefficient 1.5 in Eq. (4) is the ratio of absorptive coefficients of two bands for hydrogen bonded and free carbonyl in ester groups.

By using this method, carbonyl stretching absorption of neat PAA can be easily separated into two Gaussian peaks at 1730 and 1642 cm^{-1}, which were absorptions of free carbonyl and carboxyl bonded carbonyl groups, respectively. However, curve fitting for carbonyl absorption of hybrid materials were more complicated and cannot be divided into two peaks. In the previous work [22], it indicated that silanol bonded carbonyl groups in acrylic copolymer/silica hybrid system has an absorption at ca. 1700 cm^{-1}. This value is far away from the infrared absorption of carboxyl bonded carbonyl group on PAA, hence, it should be attempted to analyze all the hybrid materials for the partition of carbonyl absorptions into three Gaussian peaks. These fitting peaks were at ca. 1736, 1695, and 1637 cm^{-1} (with max. error of 5 cm^{-1}) for free, silanol bonded, and carboxyl bonded carbonyl groups, respectively, and were tabulated in Table 1. In addition, these areas of specific fitting peaks were calculated with Eq. (4) to acquire the proportion of distinct carbonyl groups and were plotted on Fig. 4. From this figure, it was found that fraction of free carbonyl group was decreased to lowest value of 39%, in which TEOS content was 40%. Then, the value was elevated to high proportion of 73% with the increasing of TEOS content. Variation of fraction of silanol-bonded carbonyl group was more simplified, which was diminished continuously from 32 to 4% with TEOS content. In addition, fraction of carboxyl-bonded carbonyl group was ca. 22% in neat PAA and in the hybrid materials with more than 60% of TEOS. It is interesting that fraction of carboxyl bonded carbonyl group has a lower value of 14% and higher value of 30% with 20 and 40% TEOS in the system. Moreover, these two compositions of PAA/silica hybrid materials also showed drastic change in their glass transition behavior as it was discussed in the last section of DSC results. It means that physical properties of these hybrid materials surely have a relationship with the interaction of hydrogen bonding.

It is well known that molecular structure of poly(methyl acrylate) is similar to that of PAA. The only difference between these two polymers is that PAA contains carboxyl group, which may result the formation of hydrogen bonding in bulk polymer. The absence of hydrogen bonds is also the reason of lower T_g for poly(methyl acrylate) than PAA. However, in this study, it was found that T_g of the system was decreased to extreme low value with 20% of TEOS in hybrid system although the ratio of free carbonyl group was decreased in infrared analysis. As described in previous reports presented by Drago et al. [23]and Wu et al. [24], the value of association enthalpy, Δh was increased with the tendency of frequency shift. It also means that greater shifting of the distinct absorption frequency was resulted from the increasing of the hydrogen bond strength. According to the frequency shifting of hydrogen bonded carbonyl group, which were 41 cm^{-1} for silanol bonded and 99 cm^{-1} for

Table 1
The curve fitting results from the infrared spectra of the hybrid materials

Hybrid materials	Free C=O		Silanol bonded C=O		Carboxyl bonded C=O	
	ν (cm^{-1})	f_{free}[a]	ν (cm^{-1})	$f_{\text{s-bonded}}$	ν (cm^{-1})	$f_{\text{c-bonded}}$
Neat PAA	1730.1	74.9	–	–	1641.8	25.1
PAA/TEOS (80/20)	1739.2	54.4	1695.2	31.6	1633.1	14.0
PAA/TEOS (60/40)	1740.6	39.3	1695.9	30.5	1634.8	30.1
PAA/TEOS (40/60)	1737.7	58.1	1695.7	22.9	1638.6	19.0
PAA/TEOS (20/80)	1731.1	73.2	1691.2	4.1	1637.5	22.7

[a] Fractions of free, silanol bonded, and carboxyl bonded carbonyl groups were calculated from the areas of distinct fitting peaks with Eq. (4).

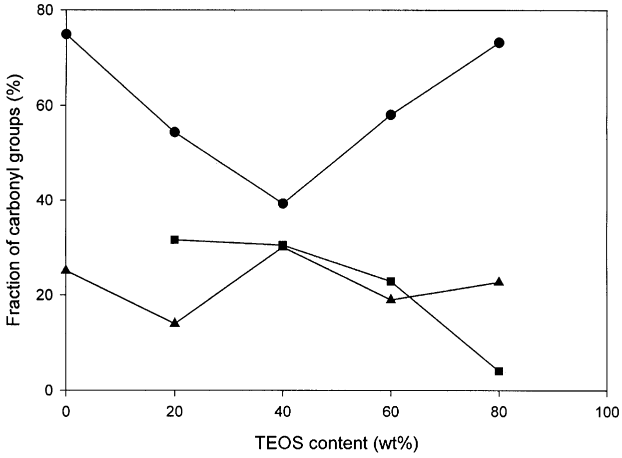

Fig. 4. Fraction of free (●), carboxyl bonded (▲), and silanol bonded (■) carbonyl groups at different TEOS content.

carboxyl bonded, it can be considered that carbonyl group formed much stronger hydrogen bonding with carboxyl group than silanol group. Therefore, with 20% of TEOS added, the content of stronger hydrogen bonding from carboxyl bonded carbonyl group was diminished and T_g decreased, although weaker hydrogen bonding from silanol bonded carbonyl group was formed in this homogeneous hybrid material. This is also the evidence of miscibility of organic and inorganic species. On the other hand, with the TEOS content of 40% in the hybrid system, first T_g (higher one) showed greater value than neat PAA may also due to the effect of hydrogen bonding, which the content of carboxyl bonded carbonyl group increased. Moreover, the content of free carbonyl group decreased to the lowest value and the content of silanol-bonded carbonyl group was still at high level. From the increase of carboxyl bonded carbonyl group, it can be judged that silica matrix was formed and a portion of the organic molecular chain segments in PAA-rich phase was no more hindered by silica structure and they aggregate together to form carboxyl bonded hydrogen bonding in this hybrid material. However, there is still a large amount of organic chain segment lay in silica matrix to form hydrogen bonding with silanol group. Hence, two T_gs were found in DSC investigation, and macrophase separation can be surely confirmed. In addition, with higher TEOS introduced to this system, the content of silanol-bonded carbonyl group was decreased continuous with the increasing of TEOS content. It means that the amount of organic chain segment lay in silica matrix was decreased. Furthermore, in hybrid materials with 80% TEOS content, there is no organic chain segments found in silica matrix, which the second T_g (lower one) was completely vanished and exhibited single and broad T_g at 102.8°C.

4. Conclusions

In this study, it was found that with TEOS content of 20%, hydrogen bonding between carboxyl and carbonyl groups in PAA was hindered by silica structure, which resulted in decreasing the T_g of homogeneous PAA/silica hybrid material to extreme low value of -7.4°C. While TEOS content increased, phase separation occurred as silica matrix was formed. The silica matrix was shown to confine some of organic molecular chain segments, but chain segments in PAA-rich phase was not hindered by silica structure and formed carboxyl bonded hydrogen bonding. Therefore, two T_gs were found in hybrid materials with TEOS content from 40 to 60%. With TEOS content increased to 80%, molecular chains of PAA were aggregated together from silica matrix. Hence, the chain segments of PAA were no more confined by the silica matrix, furthermore, only single T_g appeared during DSC thermo-scan.

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