Effects of heat treatment on the properties of poly(methyl methacrylate)/ silica hybrid materials prepared by sol–gel process

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Abstract

In this research, hybrid materials based on poly(methyl methacrylate) and silica were synthesized via sol–gel process. Their glass transition behavior was investigated by differential scanning calorimeter. In DSC measurement, 180°C heat-treated hybrid materials exhibited higher miscibility as compared to untreated materials. Relationship between miscibility variation of hybrid materials and heat treatment was discussed with the data from thermogravimetric analysis and infrared spectra. It was found that degradation behavior and silica structure was affected by heat treatment. At the same time, content of hydrogen bonds were elevated at the organic–inorganic interface, which may enhance the phase miscibility. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

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 [1]. In addition, this technology has made great advances in ceramic or organic modified hybrid materials in the past two decades [2–4], which can produce homogeneous materials with higher thermal stability, density, and hardness [5–8]. Hence, 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 [4,9–11].

An approach for making hybrid materials by using covalent bonds connecting the organic and inorganic phases was carried out via synthesis of the alkoxysilyl-containing organic precursors. In the early years of 1990s, articles presented by Wei et al. illustrated that transparent materials can be obtained in the systems constructed from methyl methacrylate [5,6], styrene [7], or acrylonitrile [8] with silica. On the other hand, polymethacrylate/silica [12] and polyimides/silica [13] hybrid systems also formed homogeneous films without covalent bonds but with hydrogen

bonds as the main interaction at the organic–inorganic interface. With this strong bond interaction at the organic–inorganic interface, hybrid material forms homogeneous phase and becomes transparent, where hydrogen bonding binds the organic phase to the inorganic matrix and prevents the occurrence of macro-phase separation.

At the present time, sol–gel process has been widely used and investigated in industrial plants and laboratories, and developed for various applications of optical, electrical, and biochemical purposes [9,10,14–17]. The central issues of sol–gel technology are making transparent films and nano-scaled materials for suitable applications. The scale of phase separation in hybrid systems is thought to be most essential to the formation of transparent films or other gel forms. It is important to recognize that homogeneity and phase behavior of hybrid materials is related to the organic–inorganic interfacial interaction. Heat effect is also a focal point for sol–gel synthesized hybrid system, which may cause further condensation or structure deformation, and has to be investigated in more detail.

In this study, poly(methyl methacrylate)/silica hybrid materials with various organic–inorganic ratios were synthesized via sol–gel process. Effect of heat treatment was studied by the physical properties investigation in terms of glass transition temperature variation and phase behavior. More evidence from thermogravimetric analysis and infrared spectra would also be discussed.

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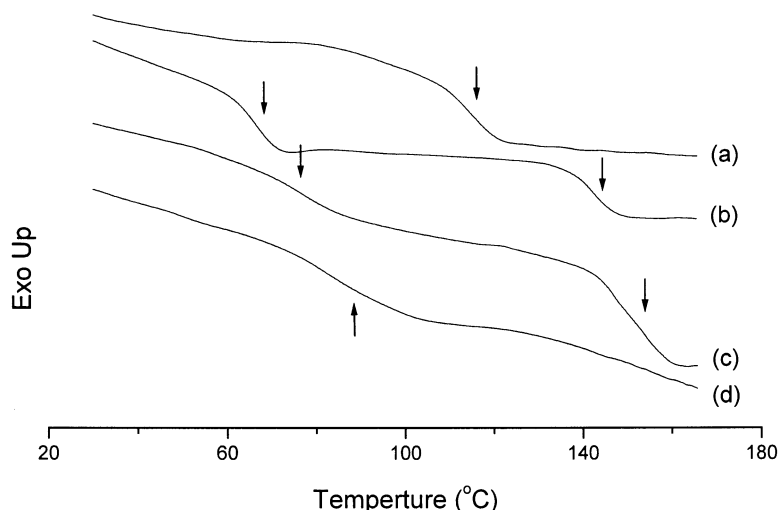*E-mail address:* imchu@che.nthu.edu.tw (I.-M. Chu).

Fig. 1. DSC thermogram curves of hybrid materials without heat treatment: (a) neat PMMA; (b) TEOS/PMMA (20/80); (c) TEOS/PMMA (40/60); and (d) TEOS/PMMA (80/20). The glass transition temperatures (T_gs) are denoted by arrows.

2. Experimental

2.1. Materials

Poly(methyl methacrylate) (PMMA, MW = 77,000, Chi-Mei Co. Ltd) and tetraethoxysilane (TEOS, tetraethyl orthosilicate, Merck) were used as received. Hydrochloric acid (HCl, Union Chemical Works Ltd) was applied as the catalyst and the water used was generated from the Milli-Q plus water purification system (Millipore). The solvents: ethanol (Showa) and tetrahydrofuran (THF, BDH) were all of reagent grade.

2.2. Preparation of desired hybrid films

PMMA was thoroughly dissolved in appropriate amount of THF first. TEOS solution was then prepared with reagent ratio of $H^+/H_2O/ethanol/TEOS = 0.025/25/5/1$. Subse-quently, the TEOS solution was added into PMMA solution in various organic–inorganic ratios, namely 20/80, 40/60, 60/40, 80/20, and 100/0 (w/w) for TEOS/PMMA, and well mixed. The sol–gel process was carried out at 30°C. The samples were covered to reduce evaporation loss of the solvent. After 30 min, homogeneous solution can be obtained. These solutions were then heated at 70°C under vacuum for 3 h to remove residual solvent and by-products (water and alcohol). Post-reaction was conducted below 180°C for heat treatment. In addition, neat PMMA was under the same heat treatment procedure for comparison.

2.3. Methods and measurements

Differential scanning calorimeter (DSC, TA 2010) was used for the investigation of glass transition temperature
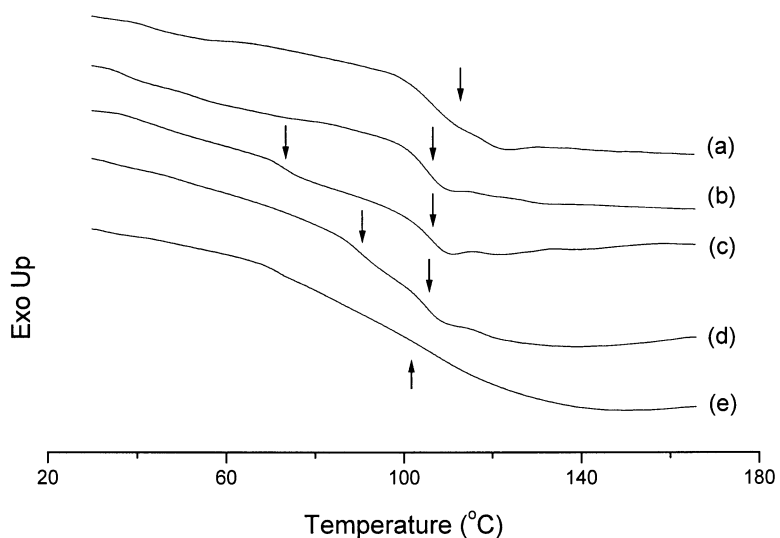

Fig. 2. DSC thermogram curves of 180°C heat-treated hybrid materials: (a) neat PMMA; (b) TEOS/PMMA (20/80); (c) TEOS/PMMA (40/60); (d) TEOS/PMMA (60/40); and (e) TEOS/PMMA (80/20). The glass transition temperatures (T_gs) are denoted by arrows.

Table 1
Glass transition temperatures of PMMA/silica hybrid materials

Hybrid materials	Glass transition temperatures (°C)	
	Without heat treatment	With 180°C heat treatment
Neat PMMA	116.1	112.9
TEOS/PMMA (20/80)	68.2, 144.4	106.7
TEOS/PMMA (40/60)	76.5, 154.0	73.6, 106.7
TEOS/PMMA (60/40)	81.2[a]	90.7, 105.9
TEOS/PMMA (80/20)	88.8[a]	101.6[b]

[a] Only single T_g was found in these two hybrid materials over the testing temperature range.
[b] With 180°C heat treatment, TEOS/PMMA (80/20) showed only single but extremely wide glass transition profile.

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 from 10 to 165°C. The thermogravimetric data was obtained from thermogravimetry analyzer (TGA, TA 951) performed under dry nitrogen atmosphere over a temperature range of 50–800°C 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 2000–400 cm^{-1}.

3. Results and discussion

3.1. Variation of glass transition temperatures

Glass transition temperatures (T_gs) of these organic–inorganic hybrid materials were investigated by DSC. The thermo-scan profiles were sketched in Figs. 1 and 2 for hybrid materials with or without 180°C heat treatment. All the T_g values were tabulated in Table 1. It can be found that neat PMMA has an obvious single T_g at 116.1°C. However, synthesized PMMA/silica hybrid materials of TEOS/PMMA (20/80) and TEOS/PMMA (40/60) exhibited two T_gs before heat treatment. The second T_g (lower one) of these two hybrid materials was lower than that of neat PMMA, while the first T_g (higher one) was higher than that of neat PMMA. These T_gs of hybrid materials were also increased with inorganic silica content. The second T_g was 68.2°C for TEOS/PMMA (20/80) and increased to 88.8°C for TEOS/PMMA (80/20). Similarly, the first T_g was 144.4°C for TEOS/PMMA (20/80) and increased to 154.0°C for TEOS/PMMA (40/60). Due to DSC instrument's limitation and degradation of the materials, possible higher T_gs were not measured for TEOS/PMMA (60/40) and TEOS/PMMA (80/20).

On the other hand, hybrid materials that had undergone 24 h of 180°C heat treatment showed entirely different behavior. It was found that neat PMMA has a T_g value of 112.9°C. In addition, hybrid material of TEOS/PMMA (20/80) also has a single T_g value of 106.7°C. However, both TEOS/PMMA (40/60) and TEOS/PMMA (60/40)
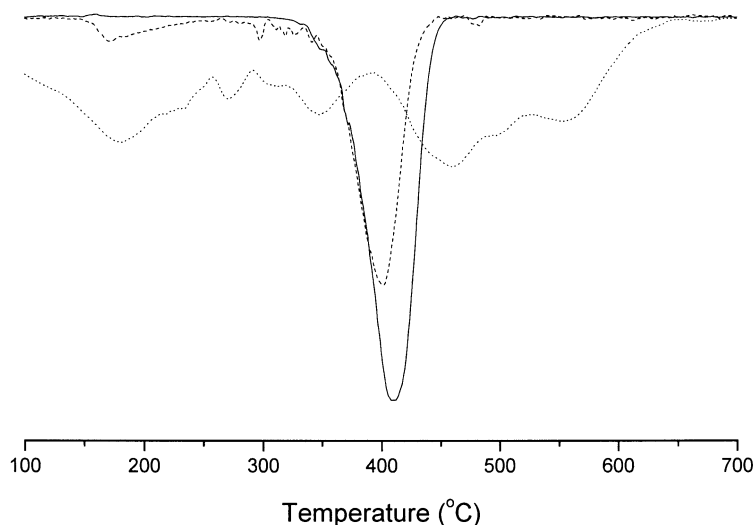

Fig. 3. Differential thermogravimetric data of hybrid materials without heat treatment: solid line for neat-PMMA; dashed line for TEOS/PMMA (60/40); and dotted line for silica.
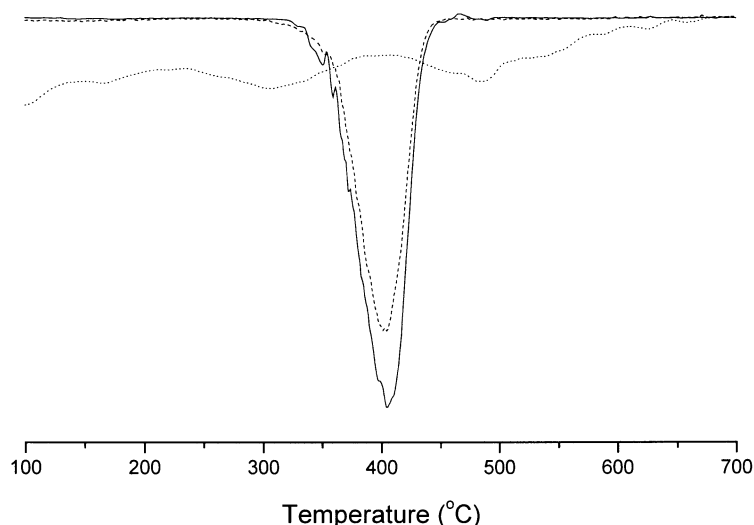
Fig. 4. Differential thermogravimetric data of 180°C heat-treated hybrid materials: solid line for neat-PMMA; dashed line for TEOS/PMMA (60/40); and dotted line for silica.

showed two T_gs. These T_g values were 73.6, 106.7°C for TEOS/PMMA (40/60) and 90.7, 105.9°C for TEOS/PMMA (40/60), respectively. For higher silica content, TEOS/PMMA (80/20) exhibited only single but tremendous wide profile of glass transition in DSC measurement (101.6°C). These results indicate that phase separation still existed in the hybrid materials with more than 20% TEOS content after 180°C heat treatment. Nevertheless, from the result of T_g measurements that two T_gs were combined or become closer, it can be recognized that hybrid materials of TEOS/PMMA (20/80) and TEOS/PMMA (40/60) have obvious higher miscibility of organic and inorganic phases with 180°C heat treatment [18]. It can be referred to higher interfacial interaction acquired during the heat treatment. More evidences and possible explanation would be presented and discussed with the data of thermogravimetric analysis and infrared spectra.

3.2. Differential thermogravimetric analysis

Figs. 3 and 4 show the results of differential thermo-gravimetric analysis of neat PMMA, synthesized hybrid materials, and silica before and after the heat treatment, respectively. Furthermore, degradation temperatures of all the synthesized hybrid materials were tabulated explicitly in Table 2. There were only single degradation stage found on TGA measurement, which were at 409 and 405°C, for neat PMMA of untreated and 180°C heat-treated, respectively. Besides, degradation of both untreated and heat-treated silica was proceeded continuously from testing temperature to 680°C with TGA measurement. It is interesting to notice that an obvious difference was found between untreated and heat-treated hybrid materials. The pre-degradation stage of all the untreated organic–inorganic hybrid materials started at 150°C and ended at 260°C. It was close to the temperature of maximum degradation rate of untreated silica. Subsequently, main degradation occurred from 300 to 460°C with tremendous weight loss. However, following 180°C heat treatment, hybrid materials did not exhibit two steps degradation but only single degradation stage from 300 to 460°C according to TGA measurements. It

Table 2
Degradation temperatures of PMMA/silica hybrid materials

Hybrid materials	Without heat treatment		With 180°C heat treatment	
	Pre-degradation stage	Main degradation stage	Pre-degradation stage[a]	Main degradation stage
Neat PMMA	–	409	–	405
TEOS/PMMA (20/80)	198	400	–	399
TEOS/PMMA (40/60)	156	400	–	400
TEOS/PMMA (60/40)	171	401	–	403
TEOS/PMMA (80/20)	181	399	–	400
Silica[b]	179	460	306	485

[a] All the PMMA/silica hybrid materials showed single stage degradation after 180°C heat treatment.
[b] The degradation temperatures were sketched with maximum degradation rate on the figures of differential thermogravity analysis, although synthesized silica degraded continuously with increasing temperatures during TGA thermo-scan.
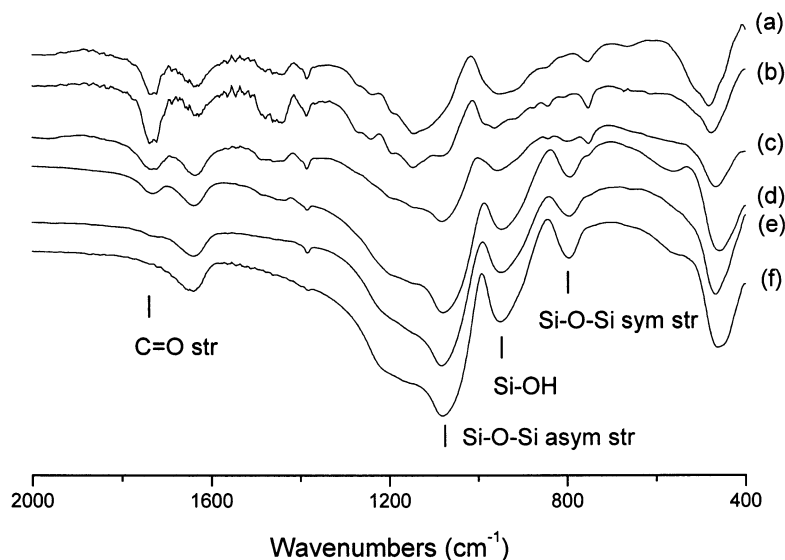
Fig. 5. Infrared spectra of hybrid materials without heat treatment: (a) neat PMMA; (b) TEOS/PMMA (20/80); (c) TEOS/PMMA (40/60); (d) TEOS/PMMA (60/40); (e) TEOS/PMMA (80/20); and (f) silica.

means that possible reactions, which may occur at predegradation stage, took place at the time of 180°C heat treatment. In a recent review presented by Yano et al. [19], it was pointed out that the pre-degradation stage occurred in this temperature range during TGA measurement, which was resulted from the elimination of ethanol and water generated from further condensation process. Hence, an inference can be draw that further condensation of the hybrid materials with heat treatment was proceeded in the 180°C oven, and showed only single degradation stage instead of two steps degradation.

3.3. Analysis of silica structure development with infrared spectra

Infrared spectra of neat PMMA, synthesized hybrid materials, and silica were sketched in Figs. 5 and 6 for untreated and 180°C heat-treated materials, respectively. In these two figures, all the materials showed distinct infrared absorptions for PMMA functional groups and silica structure. These infrared absorption peaks were all well resolved and can be used in order to investigate the development of material structure with increasing silica content.
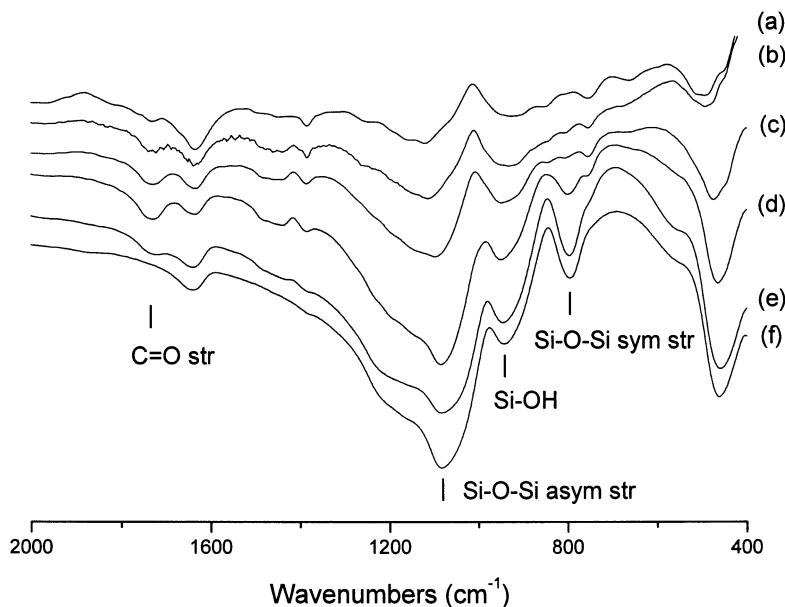

Fig. 6. Infrared spectra of 180°C heat-treated hybrid materials: (a) neat PMMA; (b) TEOS/PMMA (20/80); (c) TEOS/PMMA (40/60); (d) TEOS/PMMA (60/40); (e) TEOS/PMMA (80/20); and (f) silica.
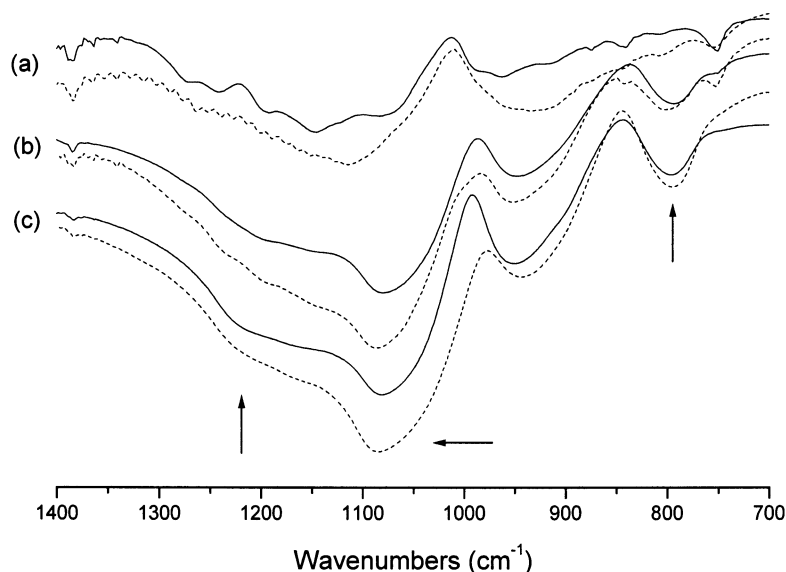
Fig. 7. Infrared analysis of silane group and silica structure on hybrid materials: (a) TEOS/PMMA (20/80); (b) TEOS/PMMA (60/40); and (c) silica, in which solid lines and dashed lines indicate untreated and heat-treated materials, respectively. Absorption peaks of Si–OC$_2$H$_5$ (1220 cm^{-1}), Si–O–Si asym. str. (1081 cm^{-1}), and Si–O–Si sym. str. (796 cm^{-1}) are denoted by arrows.

In these two figures of infrared spectra, it can be easily found that the absorption peak of Si–O–Si asymmetric stretching at ca. 1081 cm^{-1} was found, which was due to the formation of silica structure via sol–gel process with TEOS added. This adsorption peak was increased with TEOS content. Simultaneously, absorption peak of silanol group (Si–OH) at 948 cm^{-1} was also found. Furthermore, with the TEOS content increased to 60%, two absorption peaks located at 1205 and 796 cm^{-1} were detected, which resulted from the exis-

tence of unreacted silane group on TEOS and the formation of silica network [20,21], respectively. With these variations of peak intensity, the formation of silanol group and silica structures from silane group (TEOS) can be determined qualitatively. However, with more detailed observation, there are still some differences about infrared analysis between hybrid materials with and without heat treatment, i.e. infrared absorption peaks of silane group and silica structure still varied with heat treatment. It is believed that influence of heat
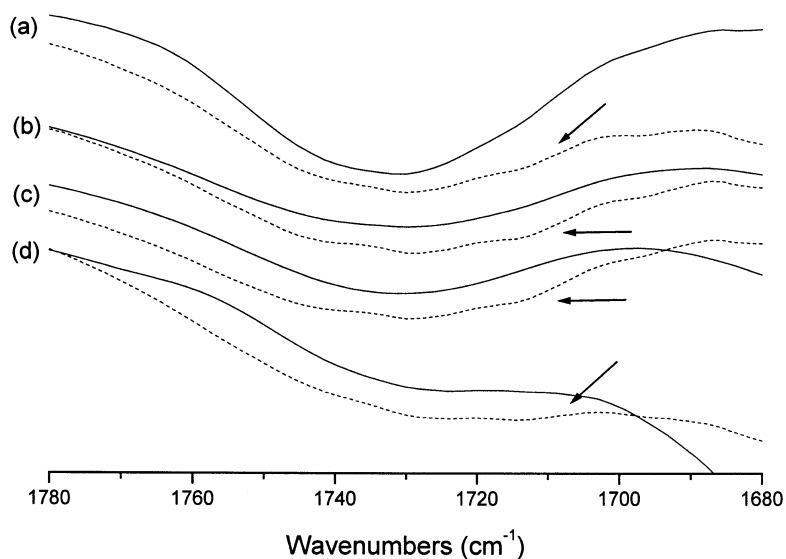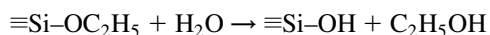

Fig. 8. Infrared analysis of carbonyl groups on hybrid materials: (a) TEOS/PMMA (20/80); (b) TEOS/PMMA (40/60); (c) TEOS/PMMA (60/40); and (d) TEOS/PMMA (80/20), in which solid lines and dashed lines indicate untreated and heat-treated materials, respectively. Absorption peaks of hydrogen-bonded carbonyl groups (ca. 1708 cm^{-1}) are denoted by arrows.

treatment to silica structure of this hybrid system is truly important and cannot to be neglected.
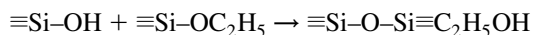
3.4. Mechanism of the heat treatment effect

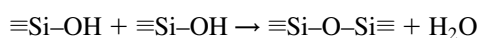Sol–gel process is well known to comprise the hydrolysis and condensation steps as shown below [22,23]:

1. Hydrolysis

$$\equiv Si\text{–}OC_2H_5 + H_2O \rightarrow \equiv Si\text{–}OH + C_2H_5OH$$

2. Alcohol condensation

$$\equiv Si\text{–}OH + \equiv Si\text{–}OC_2H_5 \rightarrow \equiv Si\text{–}O\text{–}Si \equiv C_2H_5OH$$

3. Water condensation

$$\equiv Si\text{–}OH + \equiv Si\text{–}OH \rightarrow \equiv Si\text{–}O\text{–}Si \equiv + H_2O$$

Undoubtedly, there are two types of condensation. One is from silanol and silane groups and generates molecules of ethanol; the other is from two silanol groups and water is the product. In Fig. 7, more explicit comparison of infrared spectra has been made with spectral range of 1400–700 cm^{-1}, which can describe the development of silica structure more definitely. In the figure, absorption peak of silane group (1205 cm^{-1}) was apparently diminished with heat treatment; furthermore, absorption of silica symmetric stretching (796 cm^{-1}) was also elevated. It means that alcohol condensation was proceeded with 180°C heat treatment and formed silica network. Consequently, the origin of the pre-degradation during thermogravimetric analysis from further reaction of alcohol condensation can be determined.

In addition, it seems that heat treatment effect may also have certain relation to the T_g variation. Hence, infrared spectra were examined again to interpret the relationship between heat treatment and glass transition behavior of materials. Absorption peaks of carbonyl group in hybrid materials were sketched in Fig. 8 with a spectral range of 1780–1680 cm^{-1}. In this figure, all the organic–inorganic hybrid materials with 180°C heat-treated display small shoulder at ca. 1708 cm^{-1}, which was due to the formation of hydrogen bonds between carbonyl group (organic phase) and silanol group (inorganic phase). The formation of hydrogen bonds may induce the organic–inorganic interfacial interaction. In this hybrid system, increase of hydrogen bonds content may result from the increasing of carbonyl group or silanol group content. However, from the infrared absorption of silanol group in Fig. 7, it was found that absorption intensity of silanol group did not increase with further hydrolysis or condensation. In addition, carbonyl group content either cannot elevate with heat treatment. Thus, the formation of hydrogen bonding between organic–inorganic phases may result from the other cause: diminish of the hindrance.

With infrared analysis in Fig. 7, it has been mentioned

that silane group was consumed with further condensation to form more complete silica structure during heat treatment. This may reduce the hindrance effect from ethyl group of unreacted silane. Although the content of silanol group was not increased, interfacial interaction was raised with the formation of hydrogen bonds between carbonyl group and silanol group. Consequently, hybrid materials of TEOS/PMMA (20/80) and TEOS/PMMA (40/60) acquired higher miscibility with heat treatment and exhibited only single T_g. With the same effect of heat treatment, a speculation can be made that TEOS/PMMA (60/40) and TEOS/PMMA (80/20) also gained higher miscibility with heat treatment, hence, before heat treatment, these materials may have another T_g value, which were greater than the testing temperature of 165°C. However, more information is needed from other instruments to validate the above hypothesis.

4. Conclusions

In this PMMA/silica hybrid system, it is observed from infrared spectra and thermogravimetric analysis that 180°C heat treatment causes further condensation and diminishes the content of silane group. Further condensation reaction consumes silane group and diminishes the hindrance effect from ethyl group of unreacted silane. Thus, hydrogen bonds can be formed from carbonyl group and silanol group between organic–inorganic phases. With the higher interfacial interaction from hydrogen bonding, heat treated hybrid materials acquire higher miscibility. Hence, TEOS/PMMA (20/80) and TEOS/PMMA (40/60) hybrid materials exhibit two closer glass transition temperatures or only single glass transition temperature after heat treatment.

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