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Interaction of PMMA–silica in PMMA–silica hybrids under acid catalyst and catalyst-less conditions

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Abstract

PMMA–silica hybrids were prepared by the sol–gel process polymerization from methyl methacrylate (MMA) and tetraethyl orthosilicate (TEOS) and hydroxypropyl acrylate (HPA). The mechanisms of interaction between the organic PMMA and inorganic silica in the PMMA–silica hybrids prepared under acid catalyst and catalyst-less conditions were analyzed by Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS). By FTIR absorption spectra, and XPS spectrum analyses, it was found that the covalent bond (Si–O–C) between the organic component and the inorganic component was formed even under catalyst-less condition. The catalyst had a great influence on yielding Si–O–C bonds.The ratio of the covalent bond, Si–O–C, between the organic component and the inorganic component under the acid catalyst condition was higher than that under the catalyst-less condition. With the results of FTIR and XPS analyses, a chemical reaction process was made clear and with this process the differences of the recation vecocitry, the formation of Si–O–Si bonds and Si–O–C bonds and their amount under the acid catalyst condition and/or catalyst-less condition could be predicted quantatively.

PACS: 81.20.Fw; 78.30.Er; 79.60.Jv

1. Introduction

Organic–inorganic hybrid materials prepared by the sol–gel process have been extensively studied due to their valuable applications such as photochromic, contact lenses, and active wave-guides. One of the widely studied hybrid materials is PMMA–silica hybrid material [1–8]. Wei et al. [4] examined monolithic PMMA–silica hybrid under an acid catalyst, and Huang and Qiu [5,6] used an in situ sol–gel process to prepare the acrylic-silica hybrid materials. Coltrain et al. [7] studied the morphologies and properties of the hybrid materials prepared by various acrylic polymers and tetraethoxysilane (TEOS) or tetramethoxysiliane (TMOS). In these researches, it was reported that the transparent PMMA–silica hybrid materials could be prepared under acid catalyst condition [4–8], but it was hard to be obtained for PH > 6 [8]. However, recently, we have successfully synthesized monolithic and transparent PMMA–silica hybrid under catalyst-less condition [9]. Two hybrid material systems under acid catalyst and catalyst-less conditions were prepared by in situ polymerization from methyl methacrylate (MMA + 5%PMMA powder), tetraethyl orthosilicate (TEOS) and hydroxypropyl acrylate (HPA). It is found that the mechanical behavior and thermal properties of the obtained PMMA–silica hybrid materials deeply depend on the situation with or without a catalyst. Thus, it is important to clarify the interaction between organic PMMA and inorganic silica in nanohybrids with and/or without an acid catalyst because the performance of

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organic–inorganic hybrid materials is determined by its interaction.

Fourier transform infrared (FTIR) spectra and X-ray photoelectroscopy spectroscopy (XPS) are widely used as analytical methods for investigating the functional group and elemental and chemical composition of solids (organic, mineral or metallic) [10,11]. Unlike other techniques, XPS detects all the elements in the periodic table, except hydrogen and helium, which have no core electrons. The photoelectron spectrum provides much information on electron binding energy, shift in binding energy (chemical shift), and concentration on electrons. XPS is thus extensively applied to research in solid-state physics and to solve the problems related to interaction [12–15].

In the present paper, the mechanisms of interaction between the organic PMMA and inorganic silica of the PMMA–silica hybrids prepared under acid catalyst and catalyst-less conditions were analyzed by FTIR and XPS.

2. Experiment

2.1. Preparation of the samples

The precursor materials used were methyl methacrylate (MMA, 99%), PMMA powder tetraethyl orthosilicate (TEOS, 99.9%), tetrahydrofuran (THF, 99.5%) and hydrochloric acid (HCl), hydroxypropyl acrylate (HPA) and benzoyl peroxide (BPO). All of these materials were reagent grade.

Prescribed amount of TEOS and HPA was added into a three-neck flask and stirred at 45 °C for 4 h. Then, MMA (5% PMMA powder), the initiator (BPO) for MMA and HPA were added and the mixtures were stirred at 70 °C for 3 h, followed by the addition of H_2O or H_2O + HCl and THF. The resulting mixture was stirred at 40 °C for 20 min. Finally, a homogeneous solution was obtained. The obtained homogeneous solution was poured into a teflon vat, and then cured from the room temperature to 160 °C. Starting composition of PMMA–silica hybrid materials is listed in Table 1. Poly (MMA-co-HPA) was referred to as PMHA. PMMA–silica hybrids prepared under the catalyst-less and acid catalyst conditions were referred to as PMHS-1a and PMHS-2a, respectively.

Table 1
Starting composition in PMMA–silica hybrid materials

Sample code	MMA (5%PMMA) (mol)	TEOS (mol)	HPA (mol)	HCl (mol)	H_2O (mol)	THF (mol)
PMMA	1	0	0	0	0	0
PMHA	1	0	0.5	0	0	0
PMHS-1a	1	0.5	0.5	0	1.5	5
PMHS-2a	1	0.5	0.5	0.005	1.5	5

2.2. FTIR and XPS spectra measurements

FTIR spectra of the samples were obtained using KBr pellets.

XPS spectra of the samples were analyzed using an ESCA (JPS-9010MC, JEOL). Unmonochromatized MgKα (Photon energy equal to 1253.6 eV) radiation was used as the excitation source. The analyzed area was about 6 mm^2 for obtaining a global response from irradiation. The power of the X-ray was limited to 100 W (10 mA, 10 kV) and pass energy was fixed at 10 eV. Energy calibration was effected with reference to aliphatic carbon C1s at binding energy (BE) = 284.00 eV. The Gussian component peaks were fitted by the peak maximum position, the full-width at half-maximum, and the peak area.

3. Results and discussion

3.1. FTIR spectrum

The FTIR absorption spectra of PMHA, PMHS-1a and PMHS-2a were shown in Fig. 1(a)–(c), respectively. For comparison, the absorption spectrum of the pure silica was also presented in Fig. 1(d). The weight percents of silica content of PMHS-1a and PMHS-2a are 18.9% and 18.7%, respectively. From Fig. 1(a)–(c), it is clear that the absorption peak at 1639–1650 cm^{-1} attributed to C=C double carbon bond, which existed in both MMA and HPA, has disappeared in these three materials indicating the polymerization of MMA and HPA.

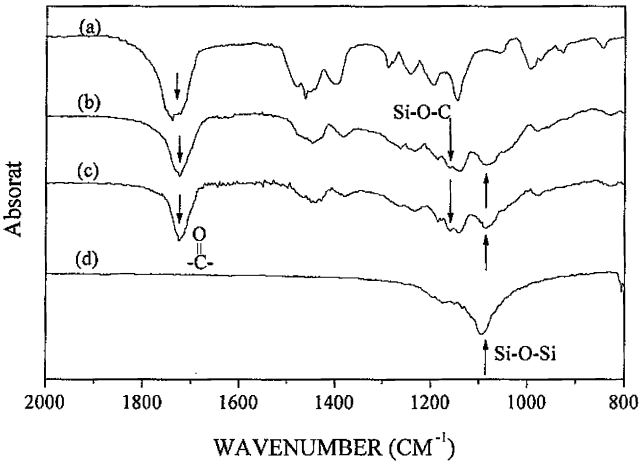


Fig. 1. FTIR absorption spectra for (a) PMHA, (b) PMHS-1a, (c) PMHS-2a and (d) silica.

The absorption peak at 1000–1100 cm^{-1} in Fig. 1(d) can be assigned to the Si–O–Si asymmetric stretching [16]. The corresponding bands at 1000–1100 cm^{-1} are also observed in PMMA–silica hybrids (see Fig. 1(b) and (c)), which were due to the formation of silica structure via a sol–gel process with TEOS added.

Observing the FTIR absorption spectra of both Fig. 1(b) and (c), we could find an absorption peak existed at 1153–1159 cm^{-1} and this has been reported as Si–O–C [16]. It was found that the covalent bonds (Si–O–C) between the organic component and the inorganic component were formed under the acid catalyst and/or catalyst conditions.

3.2. Si2p XPS spectrum

The formation of covalent bonds, Si–O–C, was also evidenced by XPS spectra. The general XPS spectra (0–1000 eV) for PMHS-1a and PMHS-2a are shown in Fig. 2(a) and (b), respectively, and they present the peak of major element and its intensity of a composition. The peaks in Fig. 2(a) and (b) suggested that major elements were carbon, oxygen, and silicon, and the intensity of each element between both materials are almost the same.

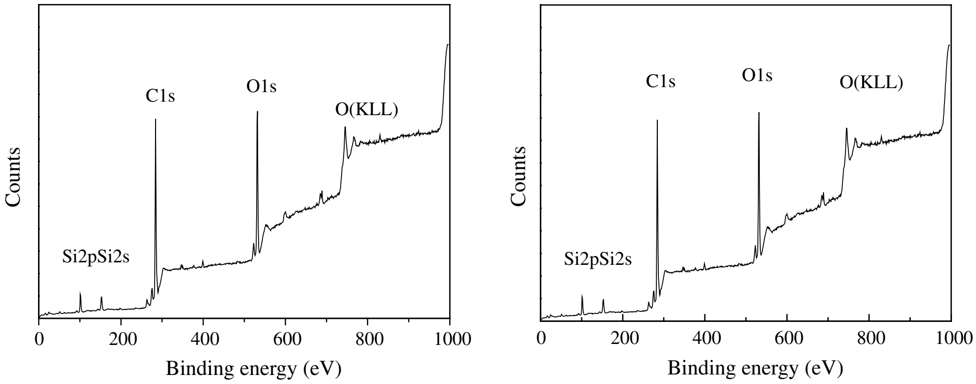
Fig. 3 shows the high-resolution Si2p spectra of pure silica (Fig. 3(a)), PMHS-1a (Fig. 3(b)) and PMHS-2a (Fig. 3(c)). Striking difference between these peaks is observed. The peaks of PMHS-1a and PMHS-2a can be decomposed into two component peaks, (A) and (B), while the spectrum of pure silica shows only one single peak (A) at binding energy (BE) of 103.38 eV.

The binding energy of 103.38 eV at peak (A) is a typical value for Si–O–Si bonds in materials [10,17]. The binding energy of the second component peak (B) is 102.00 eV, shifted by approximately 1.38 eV to a low binding energy side. This second component peak (B) may indicate the presence of covalent Si–O–C bonds between silica and polymer [10,13]. The relative peak intensity of the first component peak to the second component peak for the hybrids, PMHS-1a and PMHS-2a, is different. The peak intensity ratio of the Si2p [Si–O–C]/Si2p {[Si–O–Si] + [Si–O–C]}, i.e., [B]/([A] + [B]), in PMHS-2a is larger than that in PMHS-1a. Table 2 listed the peak intensity ratio, [B]/([A] + [B]), for PMHS-1a without a catalyst and PMHS-2a hybrids with an acid catalyst. It is found that the amount of Si–O–C bonds in PMHS-2a was more than three times as large as that in PMHS-1a. Based on above results, it is clear that the catalyst has a great influence on yielding Si–O–C bonds. The acid catalyst condition makes Si–O–C bonds easier to be formed than the catalytic-less condition.

3.3. O1s XPS spectrum

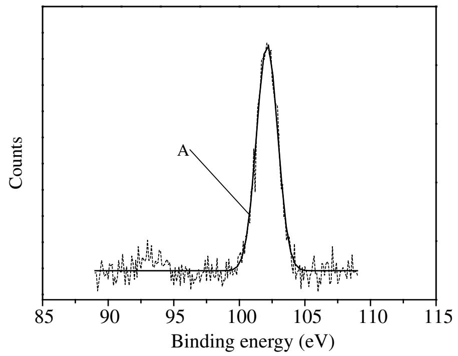
The formation of covalent Si–O–C bonds was further evidenced by O1s XPS spectra. Fig. 4 shows the O1s spectra for pure silica (Fig. 4(a)), PMHA (Fig. 4(b)), PMHS-1a (Fig. 4(c)) and PMHS-2a (Fig. 4(d)), respectively. Based on decomposition analyses of component peaks, Fig. 4(a) has only one single peak (C) and it was attributed to the Si–O–Si bond. The peak of O1s spectrum in the PMHA can be decomposed into two component peaks. The first component peak (D) is the C=O bond, and the second component peak (E) is the C–O–C(C–O–H) bond [14]. The second component peak (E) was shifted by approximate 1.63 eV to the high binding energy side.

The peak of O1s XPS spectral in the PMHS-1a can also be decomposed into two component peaks (D and F) although the second comonent peak (F) in the PMHS-1a was shifted by approximately 1.16 eV to the high binding energy side. It could be considered that the second comonent peak (F) is not contributed only

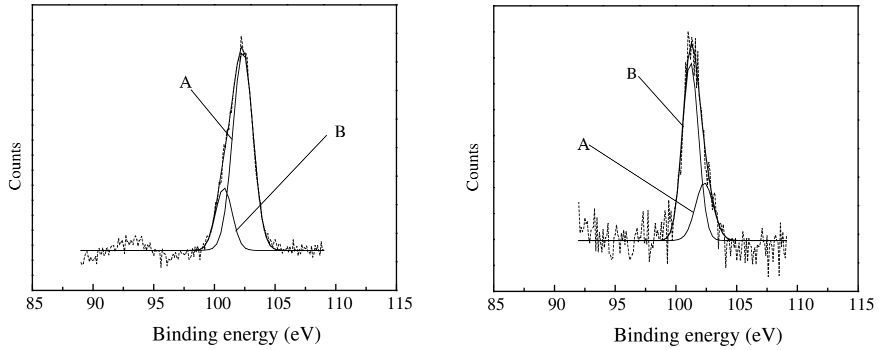


(a) PMHS-1a **(b)** PMHS-2a

Fig. 2. XPS spectra of PMMA–silica hybrids.



(a) Silica



(b) PMHS-1a **(c)** PMHS-2a

Fig. 3. Si2p spectra of samples.

Table 2
The peak intensity ratio of Si2p [B]/Si2p ([B] + [A]) for PMHS-1a and PMHS-2a

Intensity ratio	PMHS-1a	PMHS-2a
$\frac{[B]}{[[A]+[B]]}$	0.2060	0.7361

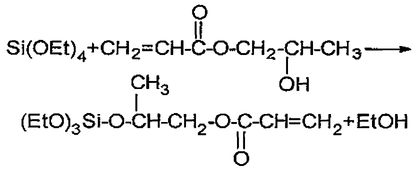
by the C–O–C(C–O–H) bond. On the other hand, since silicon element existed in this material, the component peak (F) position may indicate the presence of three types of bonds, i.e., Si–O–Si, Si–O–C and C–O–C(C–O–H) bonds.

The peak of O1s spectral in the PMHS-2a can be decomposed into two component peaks (D and G) as did above. The second component peak (G) in the PMHS-2a was only shifted by approximate 0.97 eV to the high binding energy side. Thus this resulted in that the peak F is not only contributed by the C–O–C(C–O–H) bond, but also by the combination of three types of bonds, Si–O–Si, Si–O–C and C–O–C(C–O–H). On the other hand, the binding energy of Si–O–C bond is the lowest in these three types of bonds [10], and this means that when the Si–O–C bond exists the binding energy of the peak F will shift to the low binding energy side. The silica content in PMHS-1a and PMHS-2a is almost the same. This means that the amount of Si–O–C bonds in PMHS-2a is larger than that in PMHS-1a since the binding energy of F component peak in PMHS-1a is lower than the G component peak in the PMHS-2a.

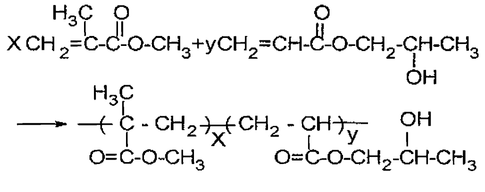
This result agrees well with that from Si2p spectral, in which the ratio of the covalent bond, Si–O–C, between the organic component and the inorganic component under acid catalyst is larger than that under the catalyst-less condition.

3.4. Chemical reaction process

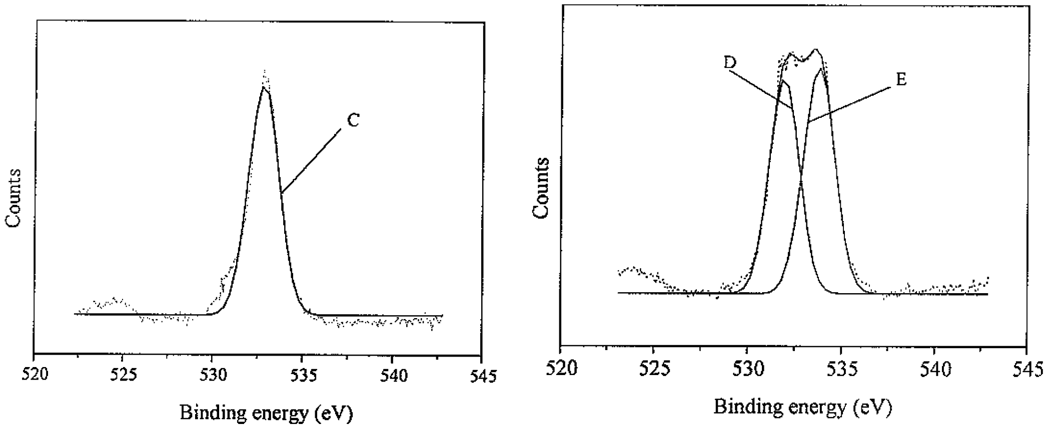
Based on the above peak position analyses, the following chemical reaction process may occur in the sol–gel process polymerization under an acid catalyst or catalyst-less condition.



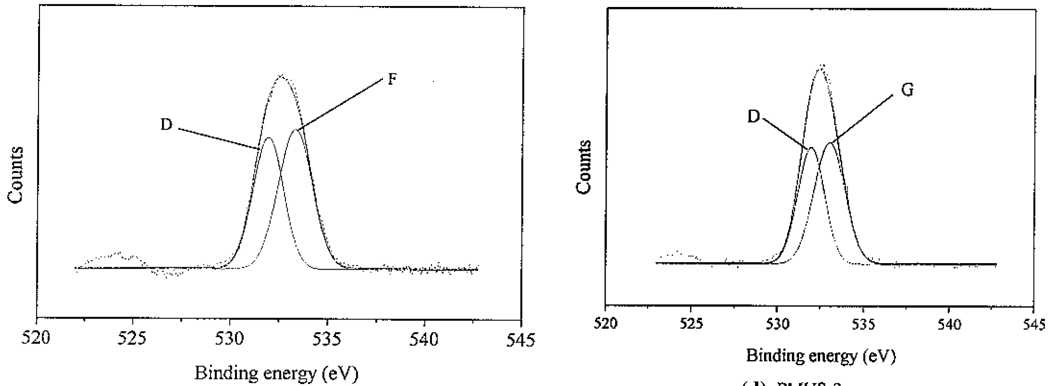
$$\mathrm{Si(OEt)_4 + CH_2{=}CH{-}\overset{\overset{O}{\|}}{C}{-}O{-}CH_2{-}\underset{\underset{OH}{|}}{C}H{-}CH_3 \longrightarrow (EtO)_3Si{-}O{-}\overset{\overset{CH_3}{|}}{C}H{-}CH_2{-}O{-}\underset{\underset{O}{\|}}{C}{-}CH{=}CH_2 + EtOH} \quad (1)$$



$$\mathrm{x\,CH_2{=}\overset{\overset{H_3C}{|}}{C}{-}\overset{\overset{O}{\|}}{C}{-}O{-}CH_3 + y\,CH_2{=}CH{-}\overset{\overset{O}{\|}}{C}{-}O{-}CH_2{-}\underset{\underset{OH}{|}}{C}H{-}CH_3 \longrightarrow {-}\!\left(\overset{\overset{H_3C}{|}}{\underset{\underset{O=C-O-CH_3}{|}}{C}}{-}CH_2\right)_{\!x}\!\left(CH_2{-}\underset{\underset{O=C-O-CH_2-\overset{\overset{OH}{|}}{C}H-CH_3}{|}}{C}H\right)_{\!y}{-}} \quad (2)$$

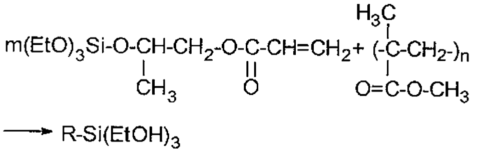


(a) Silica **(b)** PMHA



(c) PMHS-1a **(d)** PMHS-2a

Fig. 4. XPS spectra of O1s in samples.



$$m(\mathrm{EtO})_3\mathrm{Si{-}O{-}}\underset{\mathrm{CH_3}}{\mathrm{CH}}\mathrm{{-}CH_2{-}O{-}}\underset{\mathrm{O}}{\overset{}{\mathrm{C}}}\mathrm{{-}CH{=}CH_2} + (\mathrm{-}\underset{\mathrm{O{=}C{-}O{-}CH_3}}{\overset{\mathrm{H_3C}}{\mathrm{C}}}\mathrm{{-}CH_2{-}})_n \longrightarrow \mathrm{R{-}Si(EtOH)_3} \quad (3)$$

$$\mathrm{R\text{-}Si(OEt)_3 + H_2O \rightarrow R\text{-}Si(OH)_3 + EtOH} \quad (4)$$

$$\mathrm{Si(OEt)_4 + H_2O \rightarrow Si(OH)_4 + EtOH} \quad (5)$$

$$\equiv\mathrm{Si{-}OH + HO{-}Si}\equiv\ \rightarrow\ \equiv\mathrm{Si{-}O{-}Si}\equiv + \mathrm{H_2O} \quad (6)$$

$$\equiv\mathrm{Si{-}O{-}R + H_2O} \rightarrow\ \equiv\mathrm{Si{-}OH + HO{-}R} \quad (7)$$

$$\equiv\mathrm{Si{-}OH + HO{-}R} \rightarrow\ \equiv\mathrm{Si{-}O{-}R + H_2O} \quad (8)$$

From the above reaction formula, the reaction velocitry in the reaction formula (8) may be lower under catalyst-less condition than under a catalyst condition because the hydrolysis of the reaction formula (7) is harder and dehydration condensation of the reaction formula (6) is easier to occur under catalyst-less condition. The difference in the reaction speed has been confirmed in the experiments. Moreover, it is expected that many Si–O–Si bonds will be formed due to the reaction formula (6), and this will result in the decrement of the amount of Si–O–C bonds. This prediction has been proved by the results of Figs. 1, 3 and 4.

4. Conclusion

In the present paper, the interaction between the organic PMMA and inorganic silica in the PMMA–silica hybrids prepared under acid catalyst and catalyst-less conditions were analyzed by FTIR and XPS. Based on the spectral characteristics of FTIR and XPS, the results are remarked as follows.

By FTIR absorption spectra, the absorption peaks for C=C double carbon bond has disappeared in hybrid materials indicating the polymerization of MMA and HPA. The absorption peak for the Si–O–Si bond was observed due to the formation of silica structure via a sol–gel process. It was found that the covalent bonds (Si–O–C) formed even under the catalyst-less condition.

By both of Si2p and O1s XPS spectrum analyses, the covalent bonds, Si–O–C, formed under catalyst-less condition using the decomposition of the spectrum, it was clear that the catalyst had a great influence on yielding Si–O–C bonds.The ratio of the covalent bond, Si–O–C, between the organic component and the inorganic component under the acid catalyst condition was higher than that under the catalyst-less condition.

With the results of FTIR and XPS analyses, a chemical reaction process was made clear and with this process the differences of the reaction velocity, the formation of Si–O–Si bonds and Si–O–C bonds and their amount under the acid catalyst condition and/or catalyst-less condition could be predicted.

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