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SYNTHESIS OF POLY(METHYL METHACRYLATE)-SILICA NANO-COMPOSITE

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ABSTRACT

Transparent organic/pre-ceramic composite films of poly(methyl methacrylate) [PMMA] and perhydropolysilazane [PHPS] were synthesized by blending poly(methyl methacrylate-*co*-2-hydroxyethyl methacrylate) [P(MMA-*co*-HEMA)] random copolymers and PHPS. In the blend films, P(MMA-*graft*-PHPS) graft copolymers were formed, PMMA and PHPS were microscopically phase-separated in the solid state. Morphology of the microphase separation was investigated by transmission electron microscopy by changing HEMA content of the random copolymers and blend ratio of PHPS to HEMA. To convert PHPS to silica glass, the blend films were calcinated at 100°C. The morphology of the microphase separation of the films was not changed by the calcinations; the calcinated films were transparent. When the molar content of HEMA of P(MMA-*co*-HEMA) and the molar content of PHPS to HEMA in feed were 14.5% and 150%, respectively, the morphology was well ordered lamellae of PMMA and silica.

Key Words: PMMA; Silica; Perhydropolysilazane; Random copolymer; Lamellae

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INTRODUCTION

Strict control of morphology of microphase separation is important for development of novel highly functional materials. Many studies of organic (polymer)/inorganic (silica) nano-composites have been investigated as novel materials with new properties such as transparency, high mechanical strength, etc. [1–6]. A sol-gel reaction of alkoxysilanes is well used for synthesis of the organic polymer/silica nano-composites, since the reaction is carried out at room temperature with mild conditions [7–13]. Many transparent organic polymer/silica composites have been synthesized by the sol-gel reaction. Silica synthesized by the sol-gel reaction under 200°C contains a number of lattice defects. Strictly, properties of silica as synthesized by the sol-gel method under 200°C are different from silica glass. In order to obtain a silica glass phase by the sol-gel method, calcination should be carried out over 500°C. Thus, it is impossible to obtain organic polymer/silica glass composite by the sol-gel reaction.

On the other hand, silica can be synthesized with perhydropolysilazane [PHPS], which is well known as a pre-ceramic oligomer for Si_3N_4 [14–21], by calcination at low temperature (ca. 100°C) with specific condition [22]. Silica synthesized with PHPS is amorphous solid without pores, its properties, such as density, refractive index, etc., are close to silica glass [23]. Recently, PHPS is used as a good pre-ceramics for an insulator in semiconductor industry.

PHSP is highly reactive with hydroxyl groups. This suggests that a graft copolymer having PHPS sequence as branches can be synthesized by blending PHPS with the organic copolymer having hydroxyl group randomly. It is well known that graft copolymers with incompatible sequences form microphase separation [24]. As well as in block copolymers, the morphology of the microphase separation of the graft copolymer is governed by volume fraction of each sequence (Molau's law [25]). The microphase-separated films with organic polymer and PHPS phases will be prepared, if the graft copolymer with organic polymer and PHPS sequences is prepared. Additionally, if the glass transition temperature (T_g) of the organic polymer is higher than calcination temperature of PHPS (ca. 100°C), the microphase separation of the organic polymer/silica film will be kept after calcination. Then, the organic polymer/silica glass composites will be obtained. Advantages of this method are 1) properties of the silica phase are close to silica glass, 2) random copolymers having hydroxyl group can be used as raw materials. The random copolymers with hydroxyl group are easily synthesized by radical copolymerization.

The purpose of this study is to synthesize microphase separated polymer/silica glass nano-composite by blending of PHPS and the organic polymer with the hydroxyl groups, and the calcination of the blend films. For this purpose, poly(methylmethacrylate-*co*-2-hydroxyethyl methacrylate)



[P(MMA-*co*-HEMA)] random copolymers synthesized by radical co-polymerization of MMA and HEMA were chosen as the organic copolymers. Effects of the HEMA content in the P(MMA-*co*-HEMA) and blend ratio of PHPS to HEMA on the morphology of the microphase separation of the blend films and calcinated films were investigated by transmission electron microscopy. To clarify the details of the microphase separation, formation of the graft copolymers in the blend was also investigated.

EXPERIMENTAL

Materials

Methylmethacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA) were purified by distillation under vacuum. Benzene, tetrahydrofuran (THF) and n-hexane were dried with sodium metal and distilled under vacuum. Copper (I) bromide (CuBr, Wako Pure Chemical Industries, Ltd.), methyl-2-bromopropionate (Tokyo Chemical Industry Co., Ltd.), 1,1,4,7,10,10-hexamethyltriethylenetetramine (Aldrich), 2-butanone, 1-propanol and perhydropolysilazane [PHPS]/xylene solution (N-110, Tonen Co., PHPS concentration = 20 wt%, Mw of PHPS = 700) were used without purification.

Synthesis of poly(methylmethacrylate-*co*-2-hydroxyethyl methacrylate) [P(MMA-*co*-HEMA)]: P(MMA-*co*-HEMA) was synthesized by atom transfer radical polymerization. A typical run of the polymerization was as follows: 10 mL of monomer, 7 mL of 2-butanone, 3 mL of 1-propanol, certain amounts of methyl-2-bromopropionate, 1,1,4,7,10,10-hexamethyltriethylenetetramine and CuBr were added to a tube. Molar ratios of methyl-2-bromopropionate to monomer, 1,1,4,7,10,10-hexamethyltriethylenetetramine and CuBr were set to 1/100, 1/1 and 1/1, respectively. Then the tube was sealed under vacuum and kept at 20°C for 16 hours for polymerization. After 16 hours, polymerization was stopped by cooling the tube. The solution was diluted with benzene and precipitated with n-hexane. Polymer was purified by re-precipitation with benzene and n-hexane, and freeze-dried with benzene under vacuum.

Characterization

Number-average molecular weight (M_n) and molecular weight distribution index (M_w/M_n) were measured by gel permeation chromatography (GPC). For GPC measurements, hydroxyl group in P(MMA-*co*-HEMA) was modified with phenyl isocyanate in THF. Then, the polymer was precipitated in n-hexane, collected, dried and dissolved in THF. The GPC measurement was carried out with a gel permeation chromatograph (Tosoh, HPLC-8020) with THF as an eluent at 35°C. Flow rate was 1.0 mL min⁻¹.



The content of HEMA was measured with $^1\text{H-NMR}$ (JEOL, GLX-500, 500 MHz) with deuterized chloroform as a solvent by using peaks at 3.6 ppm and 3.8 ppm originated from hydrogen in methyl ester of MMA and in methylene next to hydroxyl group of HEMA, respectively.

Preparation and calcination of blend films of P(MMA-*co*-HEMA) and PHPS: 1 wt% of P(MMA-*co*-HEMA)/THF solution and N-110 were added under nitrogen atmosphere. The solution was stirred at 20°C for 24 hours. A small amount of the solution was sampled for the investigation of graft formation. The remaining solution was cast on a Teflon dish and gradually dried under dried nitrogen atmosphere. Obtained blend film of P(MMA-*co*-HEMA) and N-110 was heated at 100°C for 4 hours under steam.

Characterization of graft copolymer: Graft copolymers were recovered by precipitation of the sampled solutions with *n*-hexane and dried. Content of PHPS in the polymer was measured with a Fourier-transfer infrared spectrometer (Jasco, FT/IR-410) by using absorption at 835 and 1730 cm^{-1} originated Si-N bonding in PHPS and carbonyl group in PMMA, respectively.

Morphological observation by transmission electron microscopy: To observe morphology of phase separation of the films, ultra thin specimens of the films before and after calcination were microtomed with cryo-microtome (Reichert-Nissei, Ultracut-N) with diamond knives. Morphology of the specimens was observed with a transition electron microscope (JEOL, JEM-200CX) with 80 kV without staining.

Measurement of differential scanning Calorimetry: 20 mg of the blend film was sealed in an aluminum pan and measured with a differential scanning calorimeter (Perkin-Elmer, Pyris 1) in a temperature range from 50–200°C with ramping rate 20 K min^{-1} .

RESULTS AND DISCUSSION

First, poly(methyl methacrylate-*co*-2-hydroxyethyl methacrylate) [P(MMA-*co*-HEMA)] random copolymers with different 2-hydroxyethyl methacrylate [HEMA] contents were synthesized as pre-polymers of poly(methyl methacrylate-*graft*-perhydropolysilazane) [P(MMA-*graft*-PHPS)] graft copolymers. Because of a strong tendency of radical transfer to hydroxyl group of HEMA during the polymerization, it is difficult to obtain linear P(MMA-*co*-HEMA) by traditional radical polymerization. On the other hand, linear poly(2-hydroxyethyl methacrylate) [PHEMA] was obtained by atom transfer radical polymerization (ATRP) [26]. Thus, in this work, P(MMA-*co*-HEMA) copolymers were synthesized by ATRP at 20°C.

Table 1 shows characteristics of P(MMA-*co*-HEMA) copolymers. Three types of P(MMA-*co*-HEMA) random copolymers were synthesized. Since these polymers were synthesized by ATRP, distribution indices of



Table 1. Characteristics of P(MMA-*co*-HEMA) Random Copolymers

| Code | $M_n \times 10^4$ ^a | M_w/M_n ^a | HEMA Content (mol%) ^b |
|------|--------------------------------|------------------------|----------------------------------|
| RA1 | 6.36 | 1.34 | 2.1 |
| RA2 | 4.50 | 1.31 | 14.5 |
| RA3 | 6.96 | 1.38 | 29.5 |

^a M_n and M_w/M_n are number-average molecular weight and disparity index of molecular weight determined by GPC.

^bDetermined by ¹H-NMR.

molecular weight (M_w/M_n) were relatively narrow. Increasing the HEMA content decreases the solubility of the random copolymers in hydrophobic solvents that are good solvents for PHPS. Therefore, in this work, the HEMA contents were set to be less than 30 mol%. Here, localization of HEMA in MMA was neglected, since values of r_1 and r_2 , where monomer 1 = MMA and monomer 2 = HEMA, are 0.29 and 1.054, respectively at 60°C [27]. Consequently, three types of homogeneous random copolymers with different HEMA contents were obtained.

Next, perhydropolysilazane [PHPS] was reacted with P(MMA-*co*-HEMA) copolymers in benzene. RA1 and 0.5 in code RA1-0.5 indicate polymer type (RA1) and molar ratio of PHPS to HMEA in feed, respectively. A PHPS molecule can react with several hydroxyl groups. This indicates that PHPS acts as a crosslinker of P(MMA-*co*-HEMA), when the polymer concentration of P(MMA-*co*-HEMA) is high. The largest value of the molecular weight of P(MMA-*co*-HEMA) was 6.96×10^4 for RA3. The end-to-end distance of RA3 in THF was 19.6 nm. Therefore, the overlap concentration of RA3 in THF was 2.92 wt/vol%. To prevent gelation, the polymer concentration of P(MMA-*co*-HEMA) was set to 1 wt% that was lower than the overlap concentration of P(MMA-*co*-HEMA). As a result, all solutions were not macro-gelated by blending.

The formation of graft copolymer in the blend was investigated. To collect the graft copolymer formed in the blend solutions, sampled solution was poured to n-hexane that was a poor solvent for P(MMA-*co*-HEMA) and a good solvent for PHPS. PHPS content in the precipitated polymer, the graft copolymer, was analyzed by FT-IR. Figure 1 shows the typical time conversion curves of PHPS content of the graft copolymers. The PHPS content in the graft copolymer drastically increased with the reaction time till up to 12 hours. After 12 hours, the PHPS contents in all graft copolymers were saturated. Thus, the blend solutions were cast after 12 hours. The PHPS content in the graft copolymer was increased with the increasing of the HEMA content of P(MMA-*co*-HEMA) and the blend ratio of PHPS to HEMA in the feed.



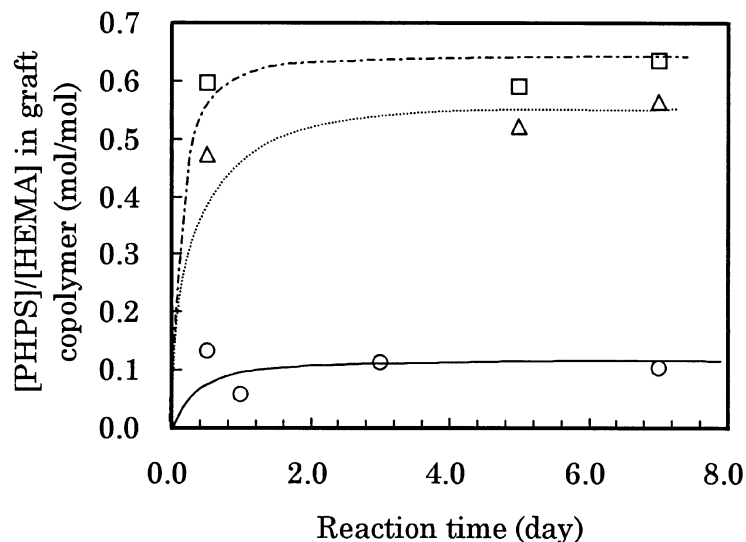


Figure 1. Time conversion of the PHPS content in P(MMA-*graft*-PHPS). (□): RA1-0.5, (Δ): RA3-1.0, (○): RA3-1.5.

Figure 2 shows the relation of the PHPS content in the graft copolymer at 12 hours to the feed conditions. For all polymers, the content of PHPS in the graft copolymer was increased with the feed ratio of PHPS to HEMA. However, the reaction was not quantitative. Especially, the PHPS contents of RA2 series were saturated when the feed ratio of PHPS to HEMA was larger than 1.5. Theoretically, a PHPS molecule can react with several hydroxyl groups. When the HEMA content is increased, the distance between hydroxyl groups is closer. The average distances between hydroxyl groups of RA 2 and RA 3 calculated from Kuhn's length of MMA are 1.6 and 1.1 nm, respectively. On the other hand, the diameter of the PHPS molecule was calculated to be 1.2 nm with the density and molecular weight of PHPS. This value is close to the average distances of the hydroxyl groups of RA 2 and RA 3. Thus, several HEMA units would be reacted with a same PHPS molecule. As a result, the PHPS content was lower than the quantitative value, when the HEMA content was high.

Next, the morphology of the microphase separation of the blend film was investigated by transmission electron microscopy (TEM). As described above, P(MMA-*graft*-PHPS) copolymers were formed in the blend film. Thus, not macroscopic but microscopic phase separation of the PMMA and PHPS phases in the film was expected. Figure 3 shows TEM micrographs of RA2 series before calcination. Volume fractions of PHPS in the films were 16.7, 31.2, 47.7 and 58.3 vol% for RA2-0.2, RA2-0.5, RA2-1.0 and RA2-1.5, respectively. Dark and white regions in the micrographs correspond to



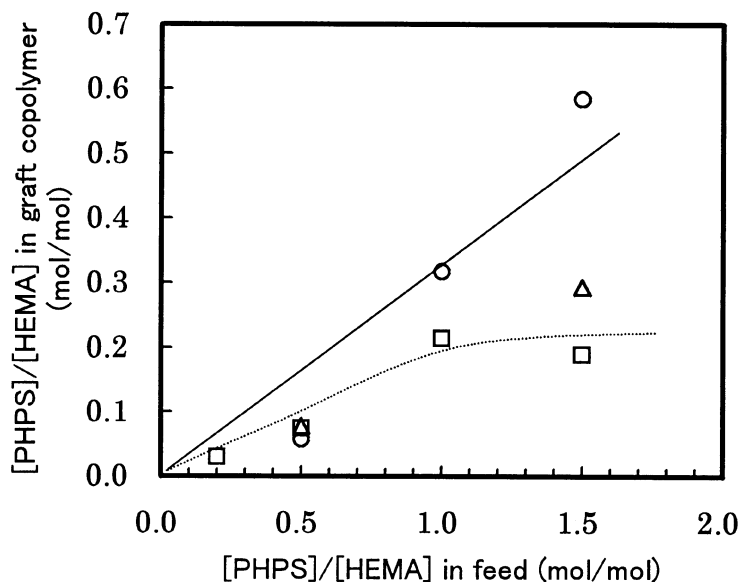


Figure 2. PHPS content in P(MMA-*graft*-PHPS) after 12 hours. (○): RA1 series, (□): RA2 series, (Δ): RA3 series.

PHPS-rich and PMMA-rich phases, respectively. As expected, macro-phase separation was not observed in any of the films. This was due to the fact that P(MMA-*graft*-PHPS) copolymers were synthesized in all system. No phase separation was observed for RA2-0.2. The volume fraction of PHPS in the system RA2-0.2 was 16.7 vol%. According to Molau's law [25], the morphology of the microphase separation in the solid state should be PHPS spheres in a PMMA matrix. On the other hand, it is well known that organic polymers containing hydrophilic group/silica composites synthesized by the sol-gel method don't phase separate [7, 12, 28–32]. This is due to the fact that the silica molecule is surrounded and stabilized with several hydrophilic groups in the organic polymer. As described above, several HEMA units would be reacted with PHPS, all PHPS molecules in RA2-0.2 would be surrounded with P(MMA-*co*-HEMA). Therefore, RA2-0.2 was not phase-separated, like composites synthesized by the sol-gel method.

In contrast to the sol-gel method, the microphase separation became clearer by increasing of the PHPS feed. In other words, the segregation of PHPS occurred. This indicates that not all of the PHPS molecules were covered with P(MMA-*co*-HEMA). Especially, for RA2-1.5, a lamellar structure of PMMA and PHPS was obtained. Thickness of PMMA-rich phase and domain spacing were 10 and 110 nm, respectively. Even though the microphase separation was observed, the film RA2-1.5 was transparent, because the domain spacing was too short to scatter the light. Consequently,



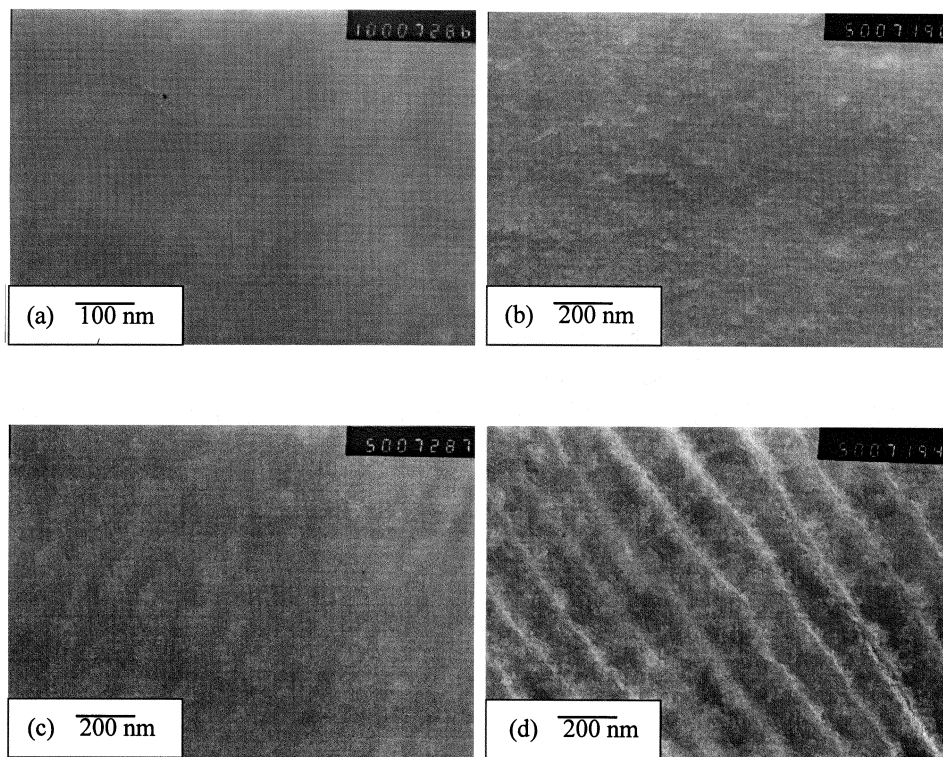


Figure 3. TEM micrographs of blend films of RA2 series. (a) RA2-0.2, (b) RA2-0.5, (c) RA2-1.0, (d) RA2-1.5.

it was possible to obtain the transparent and microphase separated organic/PHPS composite film by changing the blend ratio of the PHPS to HEMA.

To convert the blend films to the organic polymer/ silica composite, the blend films were calcined at 100°C in steam. It should be notice that the glass transition temperature (T_g) of PMMA (110°C) was higher than the calcination temperature. Thus, the morphology of the microphase separation will be kept after the calcination. The calcination of the films was confirmed by vanishing of Si-N bonding observed by FT-IR measurements. Figure 4 shows TEM micrographs of the calcined blend films of RA2 series. Dark and white regions correspond to Silica-rich and PMMA-rich phases, respectively. The morphology became clearer by calcination. This can be explained from a view-point of solubility parameters of domains. Miscibility between polymers increased when the difference in the solubility parameters between the polymers is increased. The solubility parameter of PMMA is $9.08 \text{ (cal}^{1/2} \text{ cm}^{-3/2})$ [33]. The solubility parameters of silica and PHPS were calculated to be 3.73 and 8.44 ($\text{cal}^{1/2} \text{ cm}^{-3/2}$), respectively, with their den-



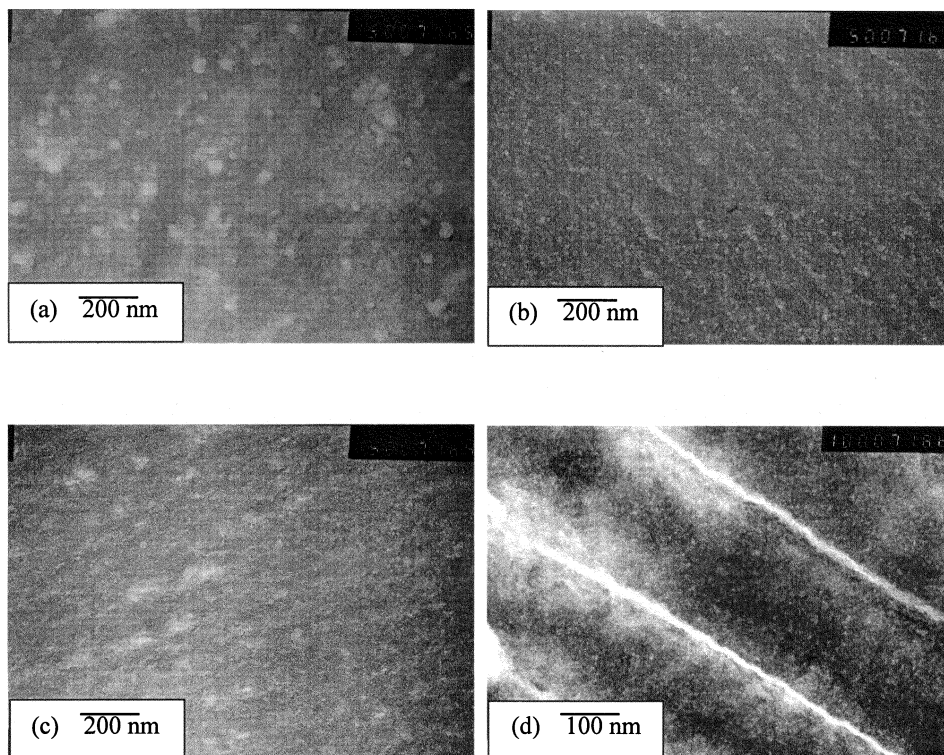


Figure 4. TEM micrographs of films of RA2 series calcinated at 100°C for 12 hours. (a) RA2-0.2; (b) RA2-0.5; (c) RA2-1.0; (d) RA2-1.5.

sities, molecular weights and molar attraction constants proposed by Small [34]. Since the solubility parameter of the inorganic phase decreased from 8.44 to 3.74 by the calcination, the difference in the solubility parameters between the PMMA phase and the inorganic phase increased from 0.64 ($=9.08 - 8.44$) to 5.35 ($=9.08 - 3.73$). As a result, the microphase separation became clearer by the calcination. However, for all films, the type of the morphology was not changed drastically by calcination. Thus, it was concluded that the microphase separation of PMMA and PHPS phases was kept by calcination at lower temperature than T_g of PMMA.

In order to investigate the stability of the microphase separation of the calcined films of the RA2 series, differential scanning calorimetry (DSC) measurements were carried out. Figure 5 shows the DSC curves of RA2, calcined RA2-0.2 and calcined RA2-1.5. A clear T_g peak due to PMMA was observed at 108°C for the organic polymer RA2. For RA2-0.2 that was a homogeneous composite of PMMA and silica glass, T_g increased to 140°C. This indicates that the thermal stability of PMMA was improved by composite formation with silica, while the macromolecularity remained



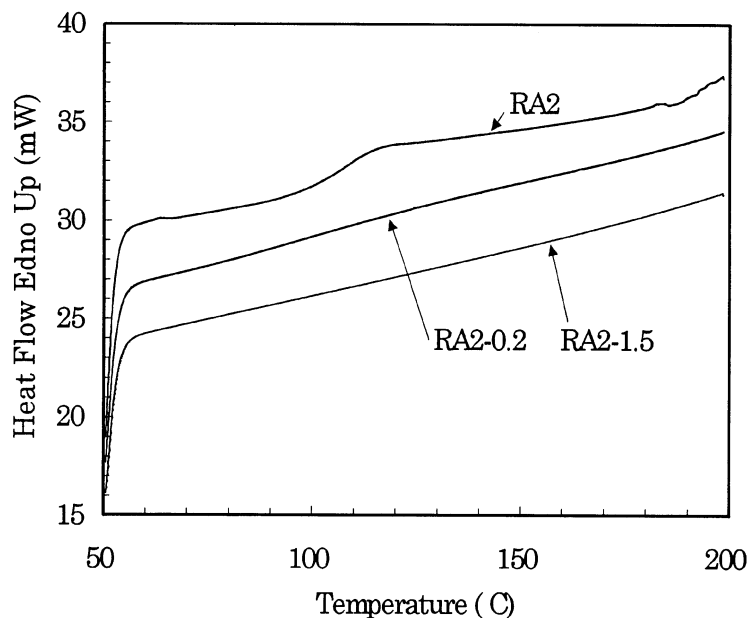


Figure 5. DSC curves of films of RA2 series. (a) RA2; (b) RA2-0.2 calcinated at 100°C for 12 hours; (c) RA2-1.5 calcinated at 100°C for 12 hours.

constant. For RA2-1.5 that consisted of lamellae of PMMA and silica glass, T_g was not detected, probably because silica glass formed a continuous phase in the film. Consequently, it was possible to control the macromolecularity of the film by changing the blend ratio of silica glass.

CONCLUSION

Transparent organic/pre-ceramic composite films of PMMA and PHPS were obtained by blending of P(MMA-*co*-HEMA) copolymers and PHPS. In the blend films, P(MMA-*graft*-PHPS) copolymers were formed. When the blend ratio of PHPS to HEMA was low, not only macroscopic but also microscopic phase separation of organic and pre-ceramic phases was observed. This was due to the lack that all PHPS molecules were surrounded with P(MMA-*co*-HEMA). When the blend ratio of PHPS to HEMA was high, microphase separation of PMMA and PHPS was observed. By calcination of the blend films at a temperature of 100°C that was lower than T_g of PMMA, the morphology of the microphase separation of the blend films was not changed but became clearer, because the solubility parameters of inorganic phases were decreased by the calcination.



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