

Preparation and Morphology of Transparent Poly(methyl methacrylate)–Poly(dimethylsiloxane) Hybrid Materials Using Multifunctional Silicone Macromonomer

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ABSTRACT: In this study, transparent poly(methylmethacrylate) (PMMA)–silicone hybrid materials, P(MMA-*co*-SigUMAx), were prepared with methylmethacrylate (MMA) and multifunctional silicone macromonomer introduced methacryl groups. The transmittance of hybrid materials improved with increase of methacryl groups of silicone macromonomer and reached around 90% T. Atomic force microscopic analysis, scanning electron microscope examinations, and copolymerization kinetics estimation by proton nuclear magnetic resonance revealed that the silicone macromonomer randomly incorporated in the copolymer with MMA by the increase of methacryl groups and suppresses

the aggregation of the silicone segment. The hybrid materials introduced over 10 wt % of silicone component had water-shedding surface and the water contact angle was elevated from 65 to 95°. Though the mechanical properties of hybrid materials were lowered by introduction of flexible silicone component, thermal property such as 5 wt % weight loss temperature were improved. © 2011 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 124: 1316–1322, 2012

Key words: methacrylate; multifunctional silicone macromonomer; transparency; morphology; water-shedding quality

INTRODUCTION

Poly(dimethylsiloxane) (PDMS) consisting siloxane bond for main chain and methyl group for side chain, and shows very excellent properties arising from the unique structure. Pure PDMS and PDMS copolymer have various useful properties, in particular water-repellent performance, and are mainly used in paints and coating agents.^{1–4} In application such as coatings, it is difficult to keep water-repellent effect because the adhesive property between substrate and PDMS is low and peeling of the coating layer is generated. To improve the lower adhesive property, polymer blend, block copolymer, and graft copolymer including PDMS moiety have been widely investigated.^{5–14} Kim et al. reported that graft copolymer of styrene (St) and PDMS macromonomer, which introduced polymerizable vinyl group at a terminal of PDMS indicated high water contact angle around 90° at 20 wt % of PDMS macromonomer content.¹⁴ Inoue et al. prepared polymer blend of poly(methylmethacrylate) (PMMA) and its block copolymer

with PDMS, and found that the water contact angle of the polymer blend reached to 85° and the water-repellent property was improved by addition of only 4 wt % of block copolymer.⁵ McGrath and coworkers prepared graft copolymer PMMA-*g*-PDMS films, and the domain size of PDMS in the polymer matrix and water contact angle were found to increase with increasing PDMS content or molecular weight.⁶ However, many reported materials containing PDMS are opaque because the solubility parameter of PDMS differs considerably from those of matrix polymers as major component, and there have been few reports which mentioned the transparency and the surface properties or microphase-separated structure of bulk materials containing PDMS.

In our previous paper, we have reported that the transparency of bulk materials consisting of styrene (St) and PDMS macromonomer with methacryl group (SiUMA) affected by the presence of ethylene glycol dimethacrylate (EGDMA) as cross-link component, and cross-linked structure formed by EGDMA and the copolymerization rate had a significant influence on the transparency of the product.¹⁵ Moreover, the contact angle of bulk copolymer material with EGDMA, P(St-*co*-SiUMA-*co*-EGDMA) with 10 wt % of SiUMA, was greater than 90°, which was a 10° improvement compared to pure poly(St).

The aim of this study was to prepare novel PMMA based transparent bulk hybrid materials

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including PDMS macromonomer without EGDMA as cross-linker. PMMA is used in various fields such as lens and tail lamp cover of the car, aquarium for fish, signboard and so on, because PMMA is excellent in mechanical strength, modulus and workability with the high transparency. The increasing applicable fields of PMMA can be expected by giving water repellency, although the transparency was retained. In this study, new PDMS macromonomers introduced methacryl groups at side chain were synthesized with carbinol-modified PDMS and 2-(methacryloyloxy)ethyl isocyanate (MOI), and we tried that the preparation of high transparency PMMA-PDMS hybrid materials by the immobilization of the silicone part in matrix polymer. The PDMS macromonomers introduced methacryl groups at side chain were polymerized with MMA to obtain bulk materials whose physical properties, morphology and copolymerization rate were subsequently investigated.

EXPERIMENTAL

Materials

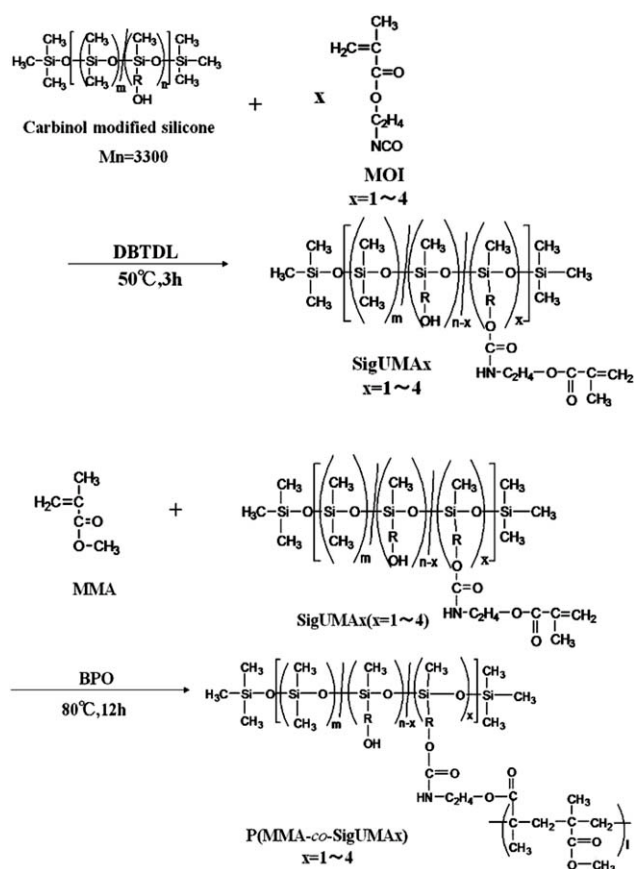
2-(methacryloyloxy)ethyl isocyanate (MOI) was supplied by Showa Denko K.K. and was used as received. Carbinol-modified PDMS (product name: X-22-4039, $M_n = 3300$, mgKOH/g = 58) was provided by Shin-Etsu Chemical. All other solvents and reagents were purchased from Nacalai Tesque, and were used without further purification.

Preparation of PDMS macro monomers introduced methacryl groups at side chain

PDMS macro monomers introduced methacryl groups at side chain, SigUMAx ($x = 1, 2, 3$), were synthesized with carbinol-modified PDMS with OH groups at side chain and MOI. The reaction scheme is depicted in Scheme 1. A given amounts of MOI and di-*n*-butyltin dilaurate (DBTL) (ca. 250-500 ppm) as catalyst were added to carbinol-modified PDMS, and the reaction was carried out at 50°C for 4 h with stirring. The reaction molar ratio of MOI to carbinol-modified PDMS was varied from 1 to 4. The end of reaction between MOI and OH group of carbinol-modified PDMS was confirmed by the disappearance of the peak attributed to the isocyanate (NCO) moiety (at 2272 cm^{-1}) in IR measurements. The x in sample code (SigUMAx) denotes reaction molar ratio of MOI, for example, SigUMA₁ presents reaction molar ratio MOI to carbinol-modified PDMS is 1.

Preparation of PMMA-PDMS copolymers with SigUMAx

To prepare PMAA-PDMS copolymer hybrid materials, bulk polymerization of MMA and SigUMAx was car-



Scheme 1 Preparation scheme of SigUMAx and P(MMA-co-SigUMAx) hybrid materials.

ried out (see Scheme 1). A given amount of MMA and SigUMAx were mixed and then 0.3 wt % of benzoyl peroxide (BPO) was added as radical initiator. The mixture was poured into a mold made from aluminum plates clamped together and sealed with 2 mm thick Teflon[®] gasket. The mold was heated in an oven at 80°C for 12 hrs to obtain bulk copolymer materials. A copolymer hybrid material obtained from mixture of 90 wt % of MMA and 10 wt % of SigUMAx, for example, will be noted P(MMA-co-SigUMAx) = 90/10.

Measurements

Fourier-transform infrared spectroscopic (FTIR) measurements were performed with Nicolet model AVATAR 320 spectrophotometer. FTIR spectra were recorded in the 4000–400 cm^{-1} region by the attenuated total reflection method and the liquid film method with a Zn-Se crystal cell. To estimate copolymerization rate between MMA and SigUMAx, proton nuclear magnetic resonance (¹H-NMR) measurements in CDCl₃ were carried out with BRUKER ADVANCE 2000 FT-NMR spectrometer. Visible spectrometry was performed with a Hitachi High-Technologies, model U-3310 spectrophotometer from 380 to 800 nm to evaluate the transparency of obtained materials. X-ray photoelectron spectroscopy

(XPS) measurement (incident angle: 30°) with Surface Science Instruments, model X-probe SSK-100 was employed to analyze Si content in obtained material surface. Dynamic mechanical analysis (DMA) measurements were carried out using a SII NanoTechnology, model DMS-6100 viscoelastometer from -130 to 180°C at 1 Hz, at a heating rate of 2°C/min. To evaluate thermal decomposition temperature of prepared copolymers, thermogravimetric analysis (TGA) (SII NanoTechnology model TG/DTA-6200) was carried out over the range 30–600°C with a platinum pan, at a heating rate of 10°C/min. Alumina powder was used as a reference material. The mechanical properties of PMMA-PDMS copolymers were evaluated by three-point bending test using Tensilon mechanical tester (ORIENTEC, model RTC-1250A) at 25°C. The size of specimen was 50 mm × 10 mm × 2 mm. Atomic force microscopic (AFM) analysis in force-modulation mode was carried out to evaluate morphology of PMMA-PDMS copolymer with NanoScope[®] IIIa from Veeco Instruments. The morphology of PMMA-PDMS copolymer was also evaluated by scanning electron microscopy (SEM) with JOEL model JSM-7001F. SEM images were acquired at ambient temperature with platinum sputtering and an operating voltage of 5 kV. Water contact angles on PMMA-PDMS copolymer surface were measured with Drop Master 300 (Kyowa Interface). The drop method using distilled water in dry condition was employed.

Evaluation of copolymerization kinetics

Reaction kinetics between MMA and SigUMAx was estimated as follows:

One gram of respective monomers (MMA or SigUMAx) or MMA/SigUMAx mixture blended at various ratios was bottled in Pyrex vial and then heated at 80°C in oil bath to start copolymerization. After predetermined time, a small sample was transferred from the reaction vial to different vial and quenched in ice bath to stop the copolymerization. Subsequently, unreacted monomers in quenched vial were extracted with 1 mL of *n*-hexane and a given amount of CDCl₃ was added to the extract in order to analyze by ¹H-NMR. Monomer conversion was calculated based on the integral ratio of CH₃ (3.75 ppm) in -COOCH₃ for MMA and C₂H₄ (4.22 ppm) in -COOC₂H₄- for SigUMAx. The peak originated from CDCl₃ was used as primary standard in the analysis.

$$\text{Conversion (\%)} = 100 \times (M_f - M_r) / M_f$$

where, M_f is feed molar quantity and M_r is residual molar quantity

Moreover, copolymer composition and copolymerization curves were calculated from monomer conver-

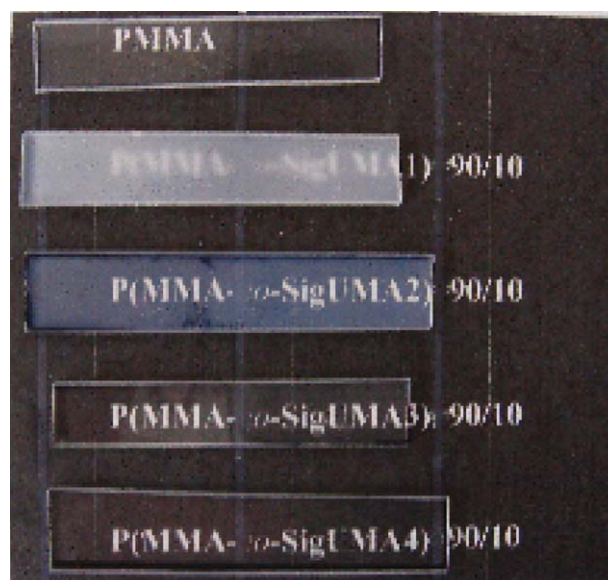


Figure 1 Photograph of P(MMA-*co*-SigUMAx)=90/10 hybrid materials.

sions in ¹H-NMR measurement at various SigUMAx content and initial feed molar ratios of monomers.

RESULTS AND DISCUSSION

Transparency of P(MMA-*co*-SigUMAx) hybrid materials

Figure 1 shows photographs of P(MMA-*co*-SigUMAx) = 90/10 and transmittance (at 600 nm) of P(MMA-*co*-SigUMAx) at various SigUMAx content is listed in Table I. As can be seen from Figure 1 and Table I, P(MMA-*co*-SigUMA₂) indicated higher transmittance than that of P(MMA-*co*-SigUMA₁) but both samples were opaque materials. On the other hands, transparency hybrid materials which showed around 90% T could be prepared by using SigUMA₃ and SigUMA₄. The transparency of copolymer hybrid materials was affected by MOI molar ratio (x) in SigUMAx (not concentration of SigUMAx) and the silicone macromonomer with MOI molar ratio over 3 was required to prepare the transparent hybridized material.

Morphology and copolymerization kinetics of P(MMA-*co*-SigUMAx)

Figure 2 depicts SEM image of P(MMA-*co*-SigUMA₁) = 90/10 and P(MMA-*co*-SigUMA₃) = 90/10. As can be seen from SEM image of P(MMA-*co*-SigUMA₁) = 90/10, asperity surface and several hundred nanometer domains originated from phase separation were observed. On the contrary, P(MMA-*co*-SigUMA₃) = 90/10 had smoother surface than that of P(MMA-*co*-SigUMA₁) = 90/10 and distinct irregularity was not observed.

TABLE I
Transmittance at 600 nm of P(MMA-*co*-SigUMAx) Hybrid Materials at Various SigUMAx Content

Sample code	Transmittance (%T at 600 nm)
P(MMA- <i>co</i> -SigUMA ₁) = 90/10	0.8
P(MMA- <i>co</i> -SigUMA ₁) = 80/20	0.5
P(MMA- <i>co</i> -SigUMA ₁) = 70/30	0.3
P(MMA- <i>co</i> -SigUMA ₂) = 90/10	78.7
P(MMA- <i>co</i> -SigUMA ₂) = 80/20	78.4
P(MMA- <i>co</i> -SigUMA ₂) = 70/30	78.0
P(MMA- <i>co</i> -SigUMA ₃) = 90/10	90.3
P(MMA- <i>co</i> -SigUMA ₃) = 80/20	89.8
P(MMA- <i>co</i> -SigUMA ₃) = 70/30	90.4
P(MMA- <i>co</i> -SigUMA ₄) = 90/10	90.6
P(MMA- <i>co</i> -SigUMA ₄) = 80/20	90.1
P(MMA- <i>co</i> -SigUMA ₄) = 70/30	90.3

Figure 3 illustrates AFM images of P(MMA-*co*-SigUMA₁) = 90/10 and P(MMA-*co*-SigUMA₃) = 90/10. In force-modulation employed in this study, high brightness part denotes low modulus part, that is, the silicone part is brightly observed, and the PMMA part is darkly detected. In AFM image of P(MMA-*co*-SigUMA₁) = 90/10, which was opaque one, the numerous high brightness parts were observed and it was considered that silicone components became massed together on material surface. As for P(MMA-*co*-SigUMA₃) = 90/10, which showed high transmittance, the high brightness part is sparsely dispersed, and the macrophase separation of the silicone component seems to have not been generated.

From these results, the aggregation of the silicone was prevented with increasing of the methacryl unit in SigUMAx and the silicone chains were isolated so that SigUMAx acts as cross-linking agent¹⁵

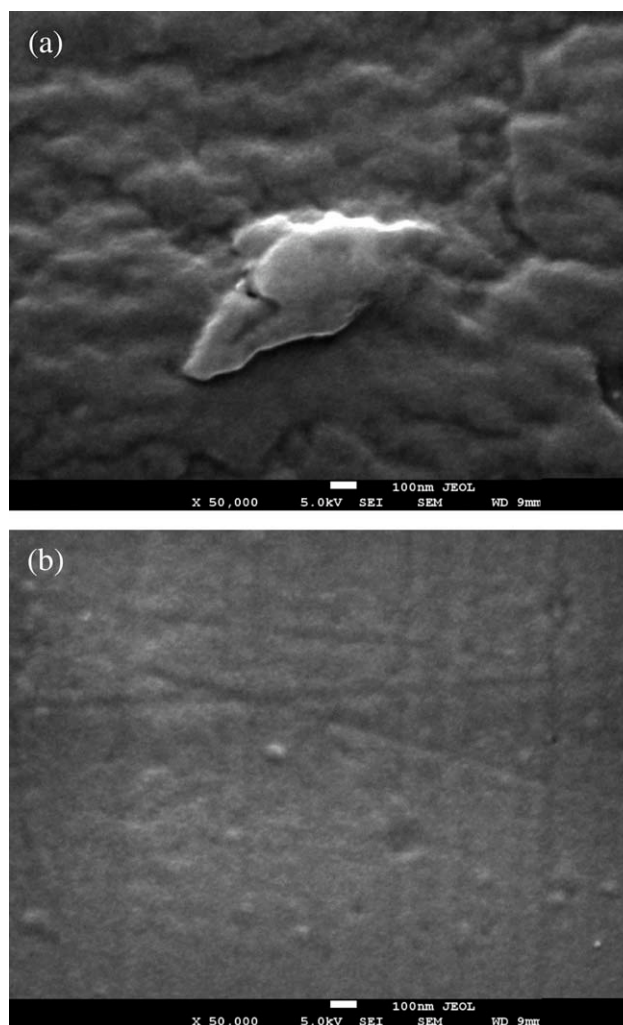


Figure 2 SEM images of P(MMA-*co*-SigUMAx) hybrid materials, (a) P(MMA-*co*-SigUMA₁)=90/10 and (b) P(MMA-*co*-SigUMA₃)=90/10

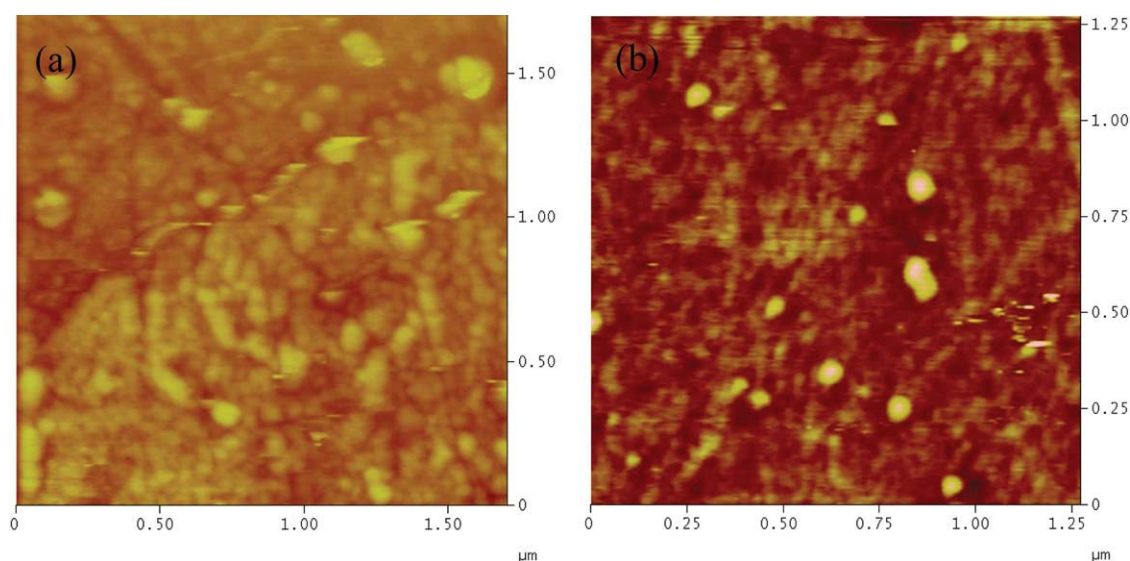


Figure 3 AFM images of P(MMA-*co*-SigUMAx) hybrid materials, (a) P(MMA-*co*-SigUMA₁)=90/10 and (b) P(MMA-*co*-SigUMA₃)=90/10. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

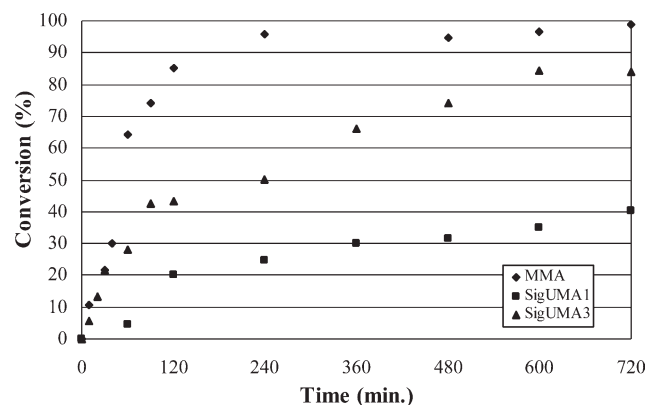


Figure 4 Time vs. conversion curves of MMA, SigUMA₁ and SigUMA₃ in single polymerization

Copolymerization kinetics of MMA and SigUMAx was investigated by ¹H-NMR measurements. Figure 4 indicates conversion curves of MMA, SigUMA₁ and SigUMA₃ obtained from individual single polymerization experiments, respectively. The SigUMA₁ showed very low reactivity and the conversion remained about 40% after 720 min. On the contrary, SigUMA₃ exhibits higher reactivity and the conversion reached about 80% after 720 min. The SigUMA₁ showed poor reactivity in single polymerization because SigUMA₁ have high molecular weight and less polymerizable units, while SigUMA₃ have more polymerizable units and indicated improved reactivity in single polymerization. This difference in reactivity was greatly concerned in the transparency of the final product.

Figure 5 graphs copolymerization curves of P(MMA-co-SigUMA₁) and P(MMA-co-SigUMA₃). In the series of P(MMA-co-SigUMA₁), obtained copolymerization curve greatly detached from the ideal copolymerization curve and the difference from ideal copolymerization curve also increased with increasing SigUMA₁ feed molar ratio. The opaqueness of final hybrid materials with SigUMA₁ was caused by this less reactivity for MMA and aggregation of SigUMA₁. Whereas in series of P(MMA-co-SigUMA₃) obtaining transparency hybrid materials, the copolymerization curve neared the ideal copolymerization curve in comparison with SigUMA₁ and it is considered that SigUMA₃ is randomly incorporated in the copolymer. These results support the results in transparency, SEM, and AFM described above and it was confirmed that the improvement of reactivity for MMA and isolation of the silicone component by increase of methacryl units in silicone macromonomer contributed the transparency and morphology of final hybrid materials. The number of methacryl units also play important role in copolymerization with MMA as same as single polymerization.

In the next section, the physical properties of P(MMA-co-SigUMA₃) with the good transparency will be described.

Physical properties of P(MMA-co-SigUMA₃)

Figure 6 indicates the relationship between water contact angle and Si content on P(MMA-co-SigUMA₃) surface. Water contact angle of P(MMA-co-SigUMA₃) surface greatly increased from 65 to 83° by addition of only 3 wt % of SigUMA₃, since much Si component exists on the surface. Afterwards, the water contact angle also increased with increase of the silicone content and reached to 95°, the water repellent property of P(MMA-co-SigUMA₃) was improved. However, the additional effect of SigUMA₃ was leveled off at about 10 wt % added. This blunting process of water contact angle seems to be caused by saturation of silicone amount which exists on the material surface.¹⁶

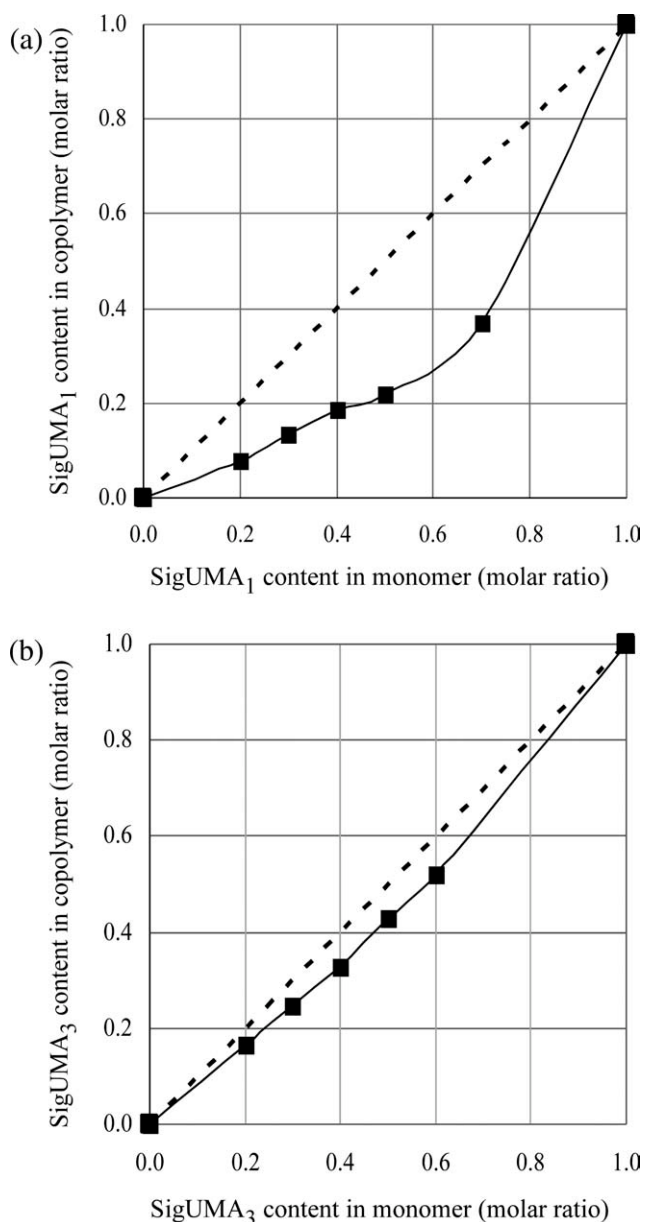


Figure 5 Copolymerization curves of SigUMA₁ and SigUMA₃ with MMA

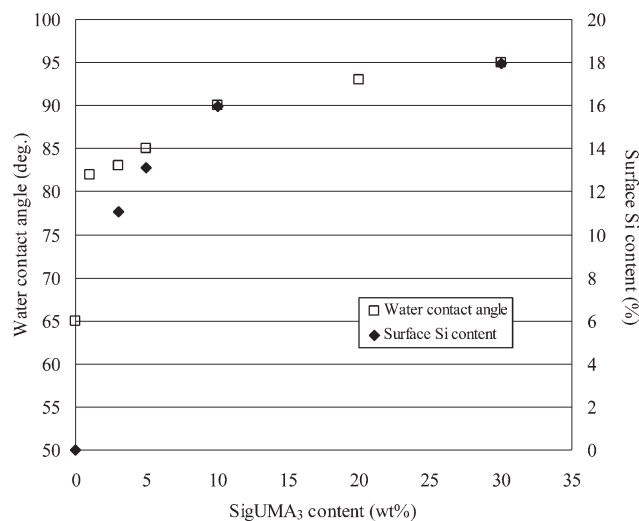


Figure 6 Relationship between water contact angle (deg.) and surface Si content (%).

Table II summarizes mechanical properties estimated from three-point bending test and 5 wt % weight loss temperature of P(MMA-*co*-SigUMA₃). As can be seen from Table II, bending modulus and strength decreased with increasing of SigUMA₃ content. The lowering of the mechanical properties by the introduction of the flexible silicone chain seems to be more remarkable than the effect of cross-linking structure which formed by SigUMA₃ as multifunctional monomer. On the contrary, 5 wt % loss temperature was slightly improved by introducing —Si—O—Si— bond with larger binding energy than that of C—C bond. By replacing only 5 wt % of MMA with EGDMA as cross-linker in P(MMA-*co*-SigUMA₃) = 90/10, it was confirmed that the mechanical properties such as flexural strength and bending modulus were improved to same level with PMMA without affecting transparency (maintained 90.1%T), water contact angle (maintained 91°), and 5 wt % weight loss temperature.

TABLE II
Mechanical Properties and 5 wt % Loss Temperature of P(MMA-*co*-SigUMA₃) Hybrid Materials at Various SigUMA₃ Content

SigUMA ₃ content (wt %)	Flexural strength (MPa)	Bending modulus (GPa)	5 wt % loss temperature (°C)
0 (PMMA)	129	3.2	249
1	114	2.6	263
3	114	2.4	260
5	108	2.3	261
10	98	2.3	270
20	77	1.8	268
30	56	1.3	268
Add EGDMA sample ^a	120	2.9	269

^a Prepared in weight ratio of MMA/SigUMA₃/EGDMA = 85/10/5

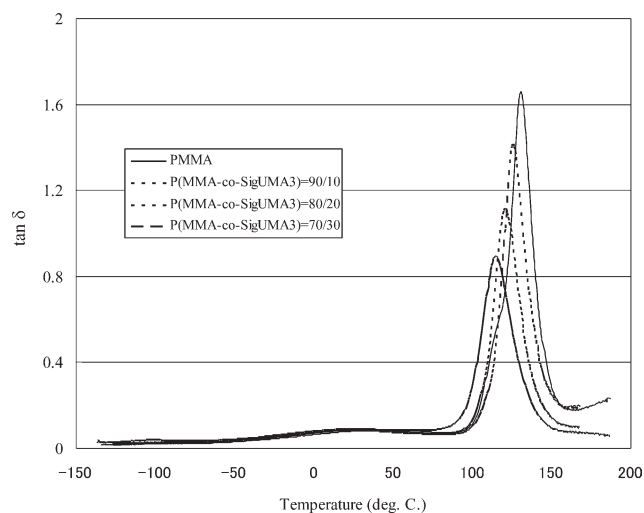


Figure 7 Temperature dependence of tan δ of P(MMA-*co*-SigUMA₃) hybrid materials

Figure 7 depicts temperature dependence of tan δ of P(MMA-*co*-SigUMA₃). The tan δ of PMMA was observed at 130°C. The peak temperature of tan δ was shifted to lower temperature side and the intensity was decreased. These results originated from introduction of the soft silicone segments and formation of the cross-linked structure by the copolymerization of MMA and SigUMA₃.¹⁷⁻¹⁹

CONCLUSION

In this study, transparent acryl-silicone hybrid materials, P(MMA-*co*-SigUMAx), were prepared. The transparency of final hybrid material depended on the number of methacryl groups introduced silicone chain and three methacryl groups were necessary in order to obtain the transparent hybrid material. It was confirmed that silicone macromonomer, SigUMAx, randomly incorporated in the copolymer with MMA by the increase of methacryl group and suppresses the aggregation of the silicone segment. Though the mechanical properties of final hybrid materials were lowered by flexible silicone component, water repellency and 5 wt % loss temperature were improved. The replacing of MMA with EGDMA as cross-linker was effective for the improvement on the mechanical properties of the hybrid material.

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