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Preparation and Properties of Organic-Inorganic Hybrid Materials from Sodium Silicate

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Summary

In this study, organic-inorganic hybrid monomer, poly silicic acid urethane methacrylate (PSUMA), was prepared by reaction of poly silicic acid extracted from sodium silicate aqueous solution with THF and 2-(methacryloyloxy)ethyl isocyanate. The PSUMA was copolymerized with methyl methacrylate to obtain hybrid copolymers. The material properties such as mechanical properties, thermal properties, Vickers hardness, transparency and so on were evaluated. The PMMA-PSUMA hybrid copolymers kept high transparency and showed higher elastic modulus and Vickers hardness than those of raw PMMA. Moreover, in comparison with PMMA, the hybrid copolymers had greater heat-resistance and lower volume contraction.

Introduction

Organic-inorganic hybrid materials have been widely investigated in order to improve their matrix properties [1-5]. There have been many attempts to develop high performance organic-inorganic hybrid material which combines inorganic and organic features using various techniques. These organic-inorganic hybrid materials have been investigated in various stages from micro order to molecule order. The organic polymer materials exhibit excellent flexibility, toughness, moldability and adhesiveness, but their heat-resistance properties are inferior to those of inorganic materials. On the other hand, inorganic materials show high elastic modulus, heat resistance, corrosiveness, weather resistance, solvent resistance and mechanical strength. However, they are very brittle and their moldability is very poor. Organic-inorganic hybrid material obtained by combining organic polymers and inorganic compounds at nano or molecular order is expected to be an original material which exhibits high performance in all properties. In conventional organic - inorganic hybrid materials produced by mixing or dispersing inorganic material in organic polymer, their material properties are mainly determined by interfacial status between the organic and inorganic components, as well as the size and dispersibility of the inorganic material as filler. In order to obtain high performance hybrid materials, the inorganic component must be dispersed minutely and homogeneously in organic polymer matrix and the interface between inorganic and organic components must have good adhesion status. However, in conventional composite material obtained by mixing inorganic fillers with organic polymers, the lower physical properties of the composite material are often observed when minute inorganic fillers are used, due to the difficulty of homogeneous dispersion. Because of the shortcomings of conventional composite material, researches which obtains organic-inorganic hybrid materials dispersed with metal oxide such as silica, titania, zirconia at nano or molecular level in polymer matrix by the sol-gel method have been widely conducted [6-8]. The sol-gel method allows the reaction to occur at low temperature, and the high homogeneity is obtained. In addition, it is easy to prepare a thin film and is recognized as one of the suitable methods for preparing the organic-inorganic hybrid material [9, 10]. However, it is difficult to obtain thick film or bulky material with the sol-gel method, since water or alcohol produced by hydrolysis and condensation reaction generates cracks and voids. With bulky organic-inorganic hybrid materials, for example, several methods which introduce silica particles modified with silane coupling agents or condensate of alkoxysilane into polymer matrix have been reported [11, 12]. Although material properties such as elastic modulus and surface hardness have been improved by hybridization, control of the reaction and improvement of affinity in the organic-inorganic interface are required to produce materials with better performance.

In this study, original organic-inorganic hybrid materials composed of silica as the inorganic component and poly(methyl methacrylate) as the organic matrix were produced, and the mechanical and thermal properties were investigated. Poly silicic acid extracted from sodium silicate was used as the inorganic component in this investigation. Vinyl groups were introduced by the reaction of silanol group in poly silicic acid and 2-(methacryloyloxy)ethyl isocyanate. By this method, the introduction of polymerizable group into the inorganic component is possible without the generation of by-products such as alcohol and water, and the reaction is easily controlled.

The aim of this study is to develop an original bulky organic-inorganic hybrid material which has high mechanical performance.

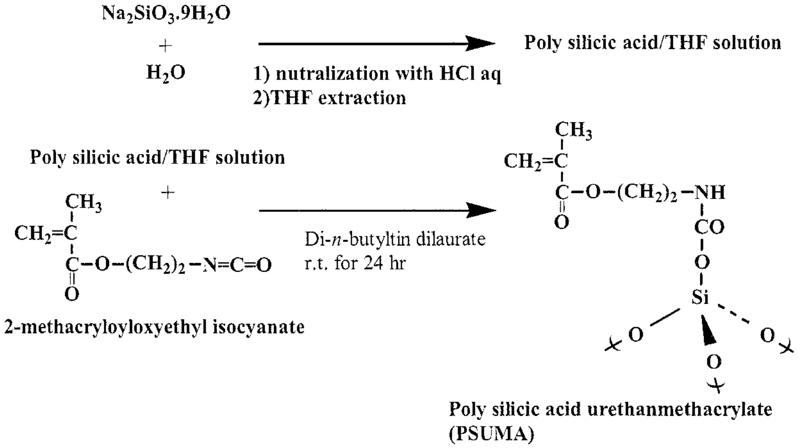
Experimental

Material

2-(methacryloyloxy)ethyl isocyanate (MOI) was supplied from the Showa Denko K.K. All other solvents and reagents were used the commercial product without further purification.

Preparation of poly silicic acid urethane methacrylate

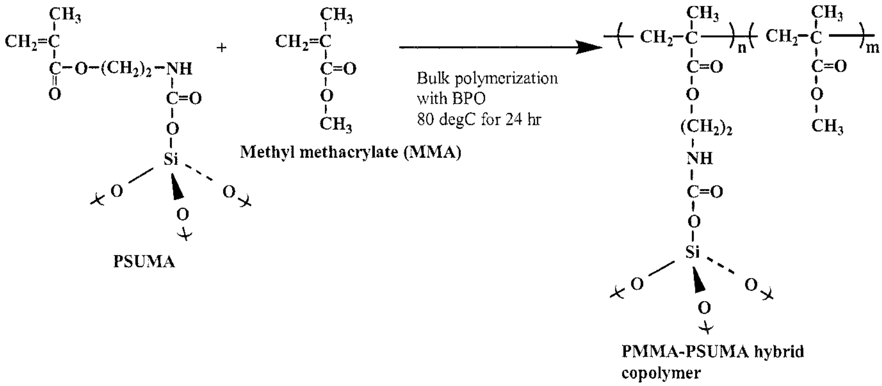
Scheme 1 indicates synthetic scheme of silicic acid urethane methacrylate (PSUMA). $Na_2SiO_3.9H_2O$ (15.35g) was dissolved in distilled water (50ml). This aqueous solution was added dropwise to 2.4mol/l HCl aqueous solution (50ml) for 15 minutes and then the solution was stirred for 10 minutes. After 10 min, NaCl (27.5g) and THF (100ml) were added to the solution, and stirring was continued for 30 minutes. THF layer was extracted with a separating funnel, and dehydrated using anhydrous sodium sulfate. To introduce vinyl group to silica surface, MOI (silicic acid-to-MOI molar rate of 2.2) and di-*n*-butyltin dilaurate (DBTL) (250~500ppm) as a catalyst were added to the silicic acid/THF solution. The reaction was carried out at the room temperature for 24 hours. The reacted solution was evaporated to remove the solvent. The viscous residues were added to toluene to precipitate and then the precipitates were filtrated to separate unreacted MOI. The precipitates were dissolved in acetone, and this solution was filtrated. Poly silicic acid urethane methacrylate, PSUMA, was obtained by evaporation of the filtrate.



Scheme 1. Synthetic scheme of poly silicic acid urethane methacrylate (PSUMA).

Preparation of PMMA-PSUMA hybrid copolymers

PSUMA was dissolved to MMA at various contents with heating at 60 °C. Bulk polymerization was carried out at 80 °C for 24 hours as illustrated in Scheme 2. Benzoyl peroxide (BPO) was used as a free radical initiator.



Scheme 2. Preparation scheme of PMMA-PSUMA hybrid copolymer.

Measurements

The characterization of PSUMA was performed by ^{1}H-NMR (BRUKER model AVANCE 200FT-NMR spectrometer) and FT-IR (Nicolet model AVATAR 320 spectrophotometer) measurements. Chemical shifts in ^{1}H-NMR spectra were reported as δ values (ppm) relative to tetramethylsilane (TMS) as an internal standard. $CDCl_3$ was used for the measurement. FT-IR spectra were measured in the region of 4000-400 cm^{-1} by the KBr method and liquid film method with KRS cell. To evaluate the content of inorganic component in PSUMA, thermogravimetric analysis (TGA) (Seiko Instrument model TG 30) was carried out in the region of 25-700 °C with platinum pan, and the programming rate was 10 °C/min. Alumina powder was used as a reference material. In order to detect SiO_2 component in combusted residuals by TGA measurement, fluorescent X-ray analysis was performed with Seiko Instruments Industry Model SEA2010L fluorescent X-ray spectrometer. Gel permeation chromatography (THOSO model HLC-8020) was measured with tetrahydrofurane as eluent to determine molecular weight of poly silicic acid and PSUMA. Elemental analysis of PSUMA was carried out with Yanaco CHN recorder model MT-3. VIS spectrometry was performed with JASCO model V-520 spectrophotometer in the region from 380 to 800 nm to evaluate transparency of PMMA-PSUMA hybrid copolymer. Scanning electron microscopic analysis of PMMA-PSUMA hybrid copolymer was performed. The sample was sputtered-coated with platinum and Hitachi Model S-4500 scanning electron micrograph was used to take the micrograph. Dynamic mechanical analysis (DMA) measurement of PMMA-PSUMA hybrid copolymer was carried out using SEIKO INSTRUMENT INDUSTRY model DMS-200 viscoelastometer. DMA of the hybrid copolymer was measured in the region from 25 to 250 °C at 1Hz, 2°C/min programming rate. The mechanical properties of PMMA-PSUMA hybrid copolymers were evaluated by three-point bending test using TOYO BALDWIN Tensilon model UTM-4LH at 25 °C. The size of specimen was 50mm × 10mm × 2mm. To evaluate surface hardness of PMMA-PSUMA hybrid copolymer, Vickers hardness (AKASHI model AVK-A Vickers hardness scale) was measured at room temperature. The 1kgf load was loaded on the sample for 15 seconds using the diamond indenter and then the cross-section area of the indentation which remained in the sample was measured.

Volume contraction

The volume contraction of PMMA-PSUMA hybrid copolymer was calculated using monomer density and hybrid copolymer. The density of PSUMA was measured by sink-and-float test using Kyoto electronics model DA-130 densimeter. The density of PMMA-PSUMA hybrid copolymer was evaluated by Archimedes method using METTLER TOLEDO solid densimeter. The volume contraction (*V. C.*) was calculated by the following equation.

$$V.\ C.\ (\%) = 100 \times (1 - \rho_m / \rho_p)$$
$$\rho_m = \rho_{MMA} \times \varphi_{MMA} + \rho_{PSUMA} \times \varphi_{PSUMA}$$

where, ρ_m is the density before polymerization. ρ_p is the density after polymerization. ρ_{MMA} and ρ_{PSUMA} are the densities of MMA and PSUMA, respectively. φ_{MMA} and φ_{PSUMA} are weight fractions of MMA and PSUMA.

Results and Discussion

Characterization of PSUMA

Figure 1 shows time dependence of IR spectra of PSUMA. The reaction of MOI and silicic acid was confirmed by the disappearance of the peak attributed to the -NCO unit (at 2270 cm^{-1}) and the generation of the new peaks attributed to C=O and N-H of the urethane bond (at 1640cm^{-1} and 1560 cm^{-1} respectively) as the reaction proceeded. Moreover, in IR spectrum of PSUMA after purification, the strong peaks, due to ester unit of MOI and Si-O-Si, were observed at 1719cm^{-1} and 1065 cm^{-1} respectively. Figure 2 indicates ^{1}H-NMR of purified PSUMA in $CDCl_3$. The assignment of each peak is also shown in the Figure 2. As can be seen from the figure, all peaks originated for MOI unit were confirmed. From these results, it can be considered that the NCO group of MOI reacted with OH group of silicic acid. The results of GPC measurement of silicic acid and PSUMA are summarized in Table 1.

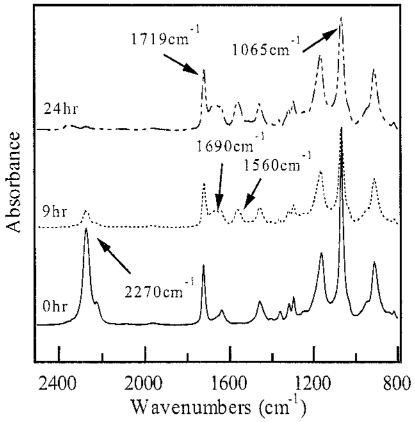


Figure 1. Time dependence of IR spectra of PSUMA.

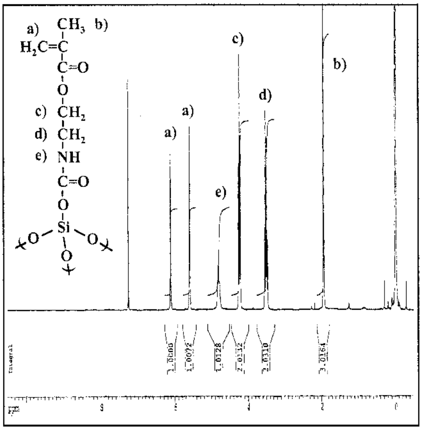


Figure 2. ^{1}H-NMR spectrum of PSUA.

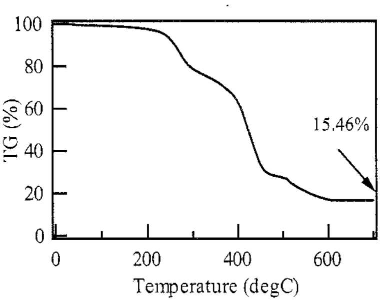


Figure 3. TGA curve of PSUMA.

Table 1. Molecular weight data and result of elementary analysis of PSUMA.

	Mn	C (%)	H (%)	N (%)
Poly silicic acid	434	---	---	---
PSUMA	3,060	45.54	6.19	7.80

The result of elementary analysis of PSUMA is also listed in Table 1. The molecular weight of silicic acid obtained by GPC measurement (polystyrene standard) was 434, which is equivalent to 7.2 units of SiO_2, while that of PSUMA was 3,060. From the GPC measurements, 16.9 units of MOI reacted with one molecule of silicic acid. This indicates that NCO group of MOI reacts with OH group of silicic acid. Therefore, this chemical formula of PSUMA can be represented as $[CH_2C(CH_3)COO(CH_2)_2NHCO]_x[SiO_2]_y$, where x and y are molar ratio of each component in PSUMA. The x and y values were calculated at 7.84 and 16.6 from the results of elementary analysis and the molecular weight of PSUMA. These values agree with almost all the results obtained by GPC measurement. Figure 3 indicates TGA curve of PSUMA. As can be seen from the figure, PSUMA contained silica component of 15.46 wt%, and this value also agrees closely with the theoretical value (15.37 wt%) calculated using x and y in the chemical formula. Moreover, from the result of fluorescent X-ray analysis, it was confirmed that major component in combusted residuals by TGA measurement is silicon. It is generally reported that the reaction rate of polycondensation reaction of silica is mostly affected by the pH value of the solution [13]. In this study, extraction of the silicic acid was performed in acidic region. Therefore, it can be assumed that the rate of the polycondensation reaction of the silica was slow and siloxane oligomer having low molecular weight was formed [14]. Though such siloxane oligomer grows linearly under the acidic condition, the cyclic structure is formed when it grows over the tetramer [15]. In IR spectrum of PSUMA, the peak which originates from cyclic siloxane structure larger than the tetramer was observed at $1065 cm^{-1}$ (see Figure 1). Figure 4 shows some presumed structures of PSUMA, assuming that the PSUMA consisted of silica octamer and 16 units of MOI. As illustrated in Figure 4, several structures of cyclic siloxane oligomer larger than tetramer seem to exist in the PSUMA. PSUMA can be considered a hybrid monomer at the molecular order.

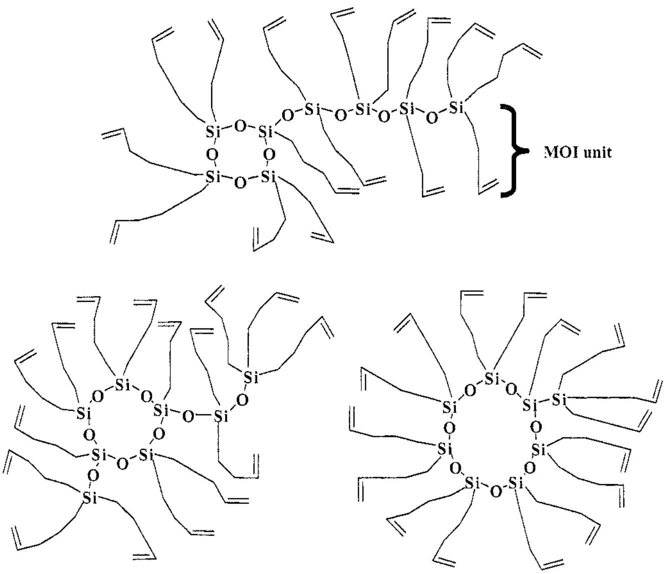


Figure 4. Presumed structures of PSUMA.

Characterization of PMMA-PSUMA hybrid copolymers

Mechanical properties and Vickers hardness of PMMA-PSUMA hybrid copolymers

The mechanical properties of PMMA-PSUMA hybrid copolymer were evaluated by three-point bending tests. These results are summarized in Table 2. With the increase of the SiO_2 content, the bending strength and deflection of the PMAM-PSUMA hybrid copolymer decreased slightly. Elastic modulus increased drastically with increasing SiO_2 content, as the elastic modulus of PMMA-PSUMA hybrid copolymer containing SiO_2 at 12.4 wt% became 1.67 times of raw PMMA. The variation of Vickers hardness (*Hv*) as a function of SiO_2 content in the hybrid copolymer is also listed in Table 2. Vickers hardness of PMMA-PSUMA hybrid copolymer also increased with increasing SiO_2 content in the same way the result of elastic modulus indicates, and became 1.88 times of raw PMMA. It is considered that hydrogen bond attributed to urethane bond and dispersion of silica component at molecular order play important roles in the improvement of elastic modulus and surface hardness.

Table 2. Mechanical properties and Vickers hardness (Hv) of PMMA-PSUMA hybrid copolymers.

PSUMA content (wt%)	Modulus (GPa)	Strength (MPa)	Deflection (mm)	*Hv* (MPa)
0	3.1	135	5.4	192
10	3.3	141	9.0	192
20	3.5	156	7.8	211
30	3.7	145	6.4	224
40	3.7	136	3.9	230
50	3.6	144	3.5	254
60	3.9	130	3.1	262
70	4.2	125	3.0	281
80	5.2	131	2.7	360

Size stability of PMMA-PSUMA hybrid copolymers

Acrylic monomer shows large volume contraction when polymerized. In the hybrid material with acrylic unit, lower material property is anticipated at the void in the interface between organic and inorganic phase which arises by contraction. Therefore, a smaller volume contraction is desired in order to produce a superior excellent hybrid material. Table 3 shows the density before and after polymerization and volume contraction at various SiO_2 contents. The densities before polymerization increased with increasing SiO_2 content. The densities of PMMA-PSUMA hybrid copolymers demonstrated the same behavior. However, it was confirmed that the increase in the densities after polymerization was insignificant compared with that of PMMA. This does not affect the lightness which is an advantage of the organic material. Alternatively, the volume contractions of PMMA-PSUMA hybrid copolymers calculated from these values (ρ_m and ρ_p) decreased with the increase in the SiO_2 content, and it was confirmed that the hybrid copolymer density is much smaller (3.5% at 12.4 wt% of SiO_2) than that of raw PMMA (20.7%). For this reason, hybrid copolymers have excellent size stability. The hydrogen bond of urethane groups in

PSUMA seems to greatly contribute to the improvement of size stability in addition to the effect of silica as filler. The ρ_m increases so the packing of intermolecules may be improve as a result of the hydrogen bond of introduced PSUMA. The volume contraction is calculated by the ratio of ρ_m and ρ_p as described in previous experimental section. Therefore, it is considered that the size stability of the hybrid copolymer was improved since the difference between the values of ρ_p and ρ_m decreased as PSUMA content increased.

Table 3. The density before polymerization (ρ_m), the density after polymerization (ρ_p) and volume contraction (*V.C.*) calculated from ρ_m and ρ_p.

PSUMA content (wt%)	ρ_m (g/cm^3)	ρ_p (g/cm^3)	*V.C.* (%)
0	0.94	1.18	20.7
10	0.97	1.20	18.7
20	1.01	1.20	15.9
30	1.05	1.21	13.5
40	1.08	1.22	11.1
50	1.12	1.23	9.1
60	1.15	1.24	6.9
70	1.19	1.25	4.8
80	1.23	1.27	3.5

Thermal properties of PMMA-PSUMA hybrid copolymers

In comparison with metal or inorganic materials, the physical properties of organic materials changed at a relatively low temperature. So organic materials are inferior in terms of heat-resistance. It is considered that the nano-composite is a useful method for improving such properties. Therefore, thermal properties of PMMA-PSUMA hybrids were evaluated by DMA measurement. The temperature dependence of storage modulus for some typical PMMA-PSUMA hybrid copolymers are shown in Figure 5 and tanδ peak temperature obtained from DMA measurements is listed in Table 4. The storage modulus of PMMA-PSUMA hybrid in lower temperature region (below 100 °C) increased with increases in SiO_2 content. Moreover, the temperature at which storage modulus greatly decreased was shifted to higher temperatures, and the decrease of the storage modulus was also controlled. As for tanδ, it was confirmed that the peak temperature shifted with the increase in SiO_2 content to higher temperatures, tanδ peak temperature rose from 126 °C (raw PMMA) to 217 °C (12.4 wt% of SiO_2). These results indicate that the mobility of the polymer network was reduced by hybridization. This improvement of thermal properties seems to originate from the formation of chemical bonds and high compatibility between organic and inorganic interfaces. The glass transition temperature of PMMA-PSUMA hybrid copolymer is approximately 100 °C higher than that of PMMA. The hybrid copolymer seems to be usable at higher temperatures than can be applied PMMA.

Table 4. Tanδ peak temperature of PMMA-PSUMA hybrid copolymers at various PSUMA content.

PSUMA content (wt%)	tanδ peak temperature (degC)
0	126
10	144
20	156
30	176
40	188
50	196
60	201
70	211
80	217

Table 5. Variation of transmittance of PMMA-PSUMA hybrid copolymers.

PSUMA content (wt%)	T%@500nm	T%@600nm
0	89.6	90.6
10	89.9	90.5
20	89.9	91.2
30	88.5	89.7
40	85.3	86.9
50	85.8	87.0
60	85.3	86.6
70	82.3	84.4
80	80.4	83.4

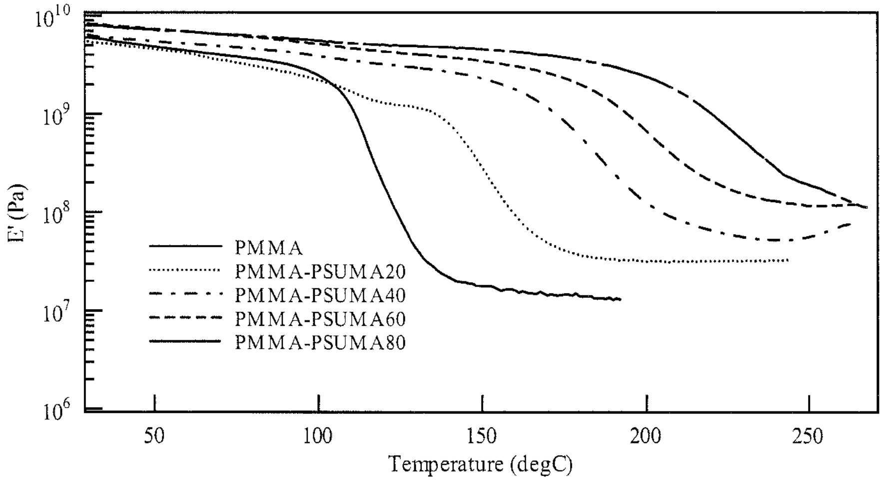


Figure 5. Temperature dependence of storage modulus of PMMA-PSUMA hybrid copolymers (the Arabic figures in the sample names mean the contents of PSUMA in hybrid copolymer).

Optical properties of PMMA-PSUMA hybrid copolymers

The transparency of PMMA is high compared to other general organic polymer materials, and it is one its important features. Table 5 summarizes visible light transmittance of PMMA-PSUMA hybrid copolymer and PMMA at 500nm and 600nm. Although the visible light transmittance of PMMA-PSUMA hybrid copolymer at each wavelength decreased slightly with increasing PSUMA content, all hybrid copolymers which were evaluated in this study showed visible light transmittance over 80 %T. This high transparency is also due to the dispersion of silica at molecular order. It is difficult to keep transparency when improving mechanical properties by the conventional method, where the inorganic filler is only mixed in the organic matrix. This hybrid method is thought to be an effective method in order to improve the mechanical performance without the lowering the transparency. Figure 6 shows SEM photographs of a fracture cross section of PMMA and PMMA-PSUMA hybrid copolymer with 80 wt% of PSUMA. As can be seen from Figure 6, phase separation by introduction of silica components was not observed in PMMA-PSUMA hybrid copolymer, and the morphology was similar to that of PMMA. This high uniformity in PMMA-PSUMA hybrid copolymer seems to not only originate from the dispersion of silica at molecular order but also the high affinity of PSUMA components with PMMA by copolymerization.

As described above, in this study, an original organic-inorganic hybrid material can be prepared by using poly silicic acid urethane methacrylate. The organic-inorganic hybrid copolymer, PMMA-PSUMA, is superior in terms of transparency, elastic modulus and surface hardness, heat-resistance and size stability. The PMMA-PSUMA hybrid copolymers are expected to be an excellent substitute for PMMA. More detailed characterization and further modification of PMMA-PSUMA hybrid copolymer are currently being conducted.

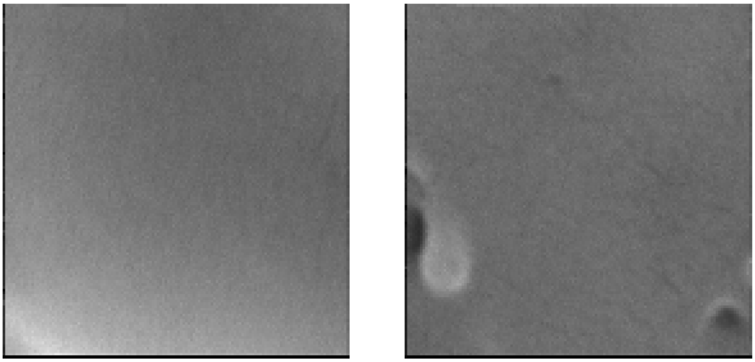


Figure 6. SEM photographs of fracture cross section, (a) PMMA and (b) PMMA-PSUMA hybrid copolymer containing 80wt% of PSUMA.

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