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ORIGINAL PAPER

Preparation and coating properties of an acrylic melamine resin containing silicone segments

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Abstract The aim of this study was the preparation of novel water repellent UV curable materials using acrylic modified melamine (AM) and poly-dimethylsiloxane (PDMS). UV curable acrylic melamines containing silicone segments (SiAMs) were synthesized by condensation of methylolmelamine, 2-hydroxyethyl acrylate, and carbinol-modified PDMS. The SiAM films with a 0.3 wt% PDMS segment that were cured by UV irradiation had higher transparency than that of a blended sample. Examination with a scanning electron microscope revealed that the blend sample has cohesion of the silicone segments, while such a phenomenon was not observed in the composite samples (SiAMs). From these results, it was confirmed that aggregation of the silicone segments was prevented by introducing the silicone segments into the acrylic melamine. By introducing 0.3 wt% of PDMS segments into AM, good water-shedding properties were confirmed, while several of the most attractive features of AM, such as hardness, adhesion, and refractive index, were maintained.

Keywords Hardness · Transparency · Radical polymerization · Water-shedding quality · Thin films · Silicone macromonomer

Introduction

Plastics such as polyethylene terephthalate (PET), polymethyl methacrylate (PMMA), styrene (St), polycarbonate (PC), and their alloys are used in widespread applications including consumer electronics, furniture, cars, and miscellaneous daily goods. These plastics, however, are easily scratched and stained because of their low surface hardness and water contact angles. In applications such as touch panels, cellular

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phones, displays, digital cameras, and lenses, not only hardness and antifouling but also certain color and transparency properties are required to protect the design or graphics of the base materials [1–6]. Acrylic resins are widely used for hard coatings on plastics. It is well known that acrylic resin polymers have high transparency, can improve the surface hardness of plastics [3, 4] and can be cured at a low temperature in a short time by UV irradiation [7]. Their antifouling properties, however, need to be improved, and therefore introduction of water-shedding capabilities to these paints has been widely investigated [8–13]. Antifouling properties can be imparted through incorporation of hydrophobic segments such as silicone or fluorine groups [14–20]. In the conventional composite paints described above, however, poor physical properties and instability of the water-shedding performance are often observed due to the nonuniformity of the polymer matrix and additive agents. To overcome these issues, non-composite silicone coatings such as those produced via sol–gel or addition reactions, and organic–inorganic hybrid systems have been widely investigated [21–26]. Such silicone coatings unfortunately possess lower refractive indices than general acrylic coatings. Such materials, when used in display, lens and optical waveguide applications, can result in deformation of the visual leg and a reduction in the contrast due to the differences in the refractive indices of the coatings and the substrates and may make it difficult to control optical interference [27–37].

Previously we reported a UV curable acrylic melamine that possesses the features of high transparency, high hardness, and high refractive index [38], and a transparent polymethylmethacrylate containing a silicone macromonomer that has water-shedding properties [39]. While the former polymer cured rapidly and had excellent transparency and hardness, and a high refractive index, it exhibited inferior water-shedding properties. The latter was excellent at water-shedding but inferior with respect to curing rate, hardness, and a low refractive index.

The aim of this study was to prepare novel acrylic melamine hybrid materials containing silicone segments to produce a polymer with similar or better performance than general acrylic resins in terms of transparency, hardness, refractive index, and rapid curing while also exhibiting water-shedding ability. To prevent the aggregation of silicone moieties to maintain the acrylic modified melamine (AM) properties of high hardness and high refractive index and the water-shedding property of silicone macromonomer, acrylic melamine hybrid materials containing silicone segment derivatives (SiAMs) were synthesized via condensation of melamine with formaldehyde, 2-hydroxyethylacrylate (HEA), and a given amount of poly-dimethylsiloxane (PDMS) bearing hydroxyl groups. The influence of the silicone moieties on the transparency, pencil hardness, water-shedding quality and other properties of the new polymers were investigated.

Experimental

Materials

Melamine was provided by Nissan Chemical. *Para*-formaldehyde (purity 92%) was provided by Mitsubishi Gas Chemical. HEA was provided by Kyoeisha Chemical.

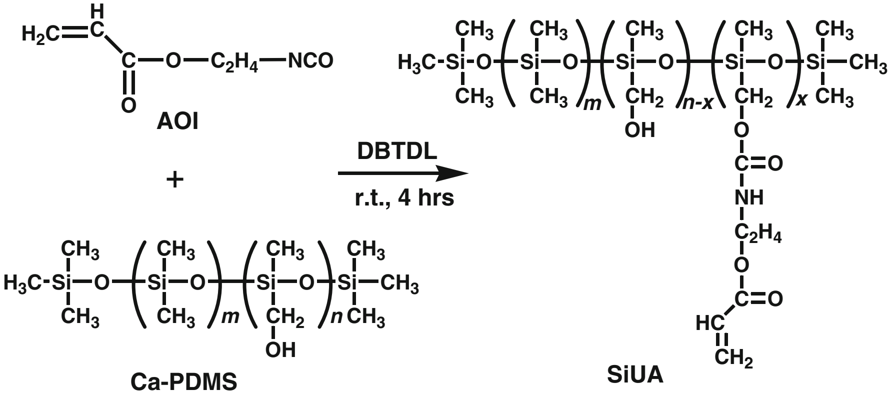
Para-toluenesulfonic acid (PTS), used as the catalyst for the condensation reaction, was provided by Meiyu Sangyo, and 4-methoxyphenol (MEHQ; Kishida Chemicals) was used as the polymerization inhibitor. Carbinol-modified PDMS (Ca-PDMS, product name: X-22-4039, Mn = 3399, mgKOH/g = 58) was provided by Shin-Etsu Chemical Co., Ltd. Acryloyloxy ethyl isocyanate (AOI) was supplied by Showa Denko K.K. and was used as received. Dibutyltin dilaurate (DBTDL) was used as the catalyst for the urethane reaction and was provided by Tokyo Kasei Kogyo. 1-Hydroxy-1-cyclohexylphenyl ketone (Irgacure 184; BASF, Japan) was used as a photoinitiator. All other solvents and reagents were purchased from Nacalai Tesuque Inc., and used without further purification.

Synthesis of PDMS macromonomers with acrylic side chains attached through hydroxyl groups of the PDMS (SiUAs)

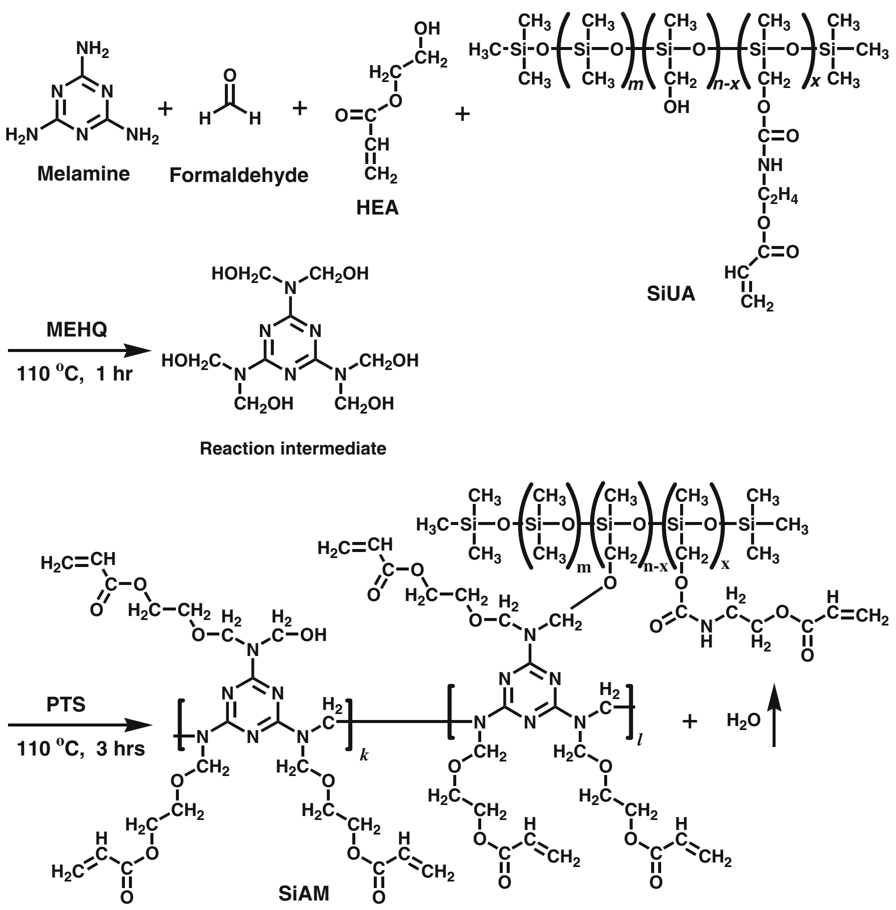
PDMS macromonomers with acrylic side chains, SiUAs, were synthesized via a reaction between the hydroxyl group of Ca-PDMS (mgKOH/g = 58) and the isocyanate group of AOI. A typical synthesis (of SiUA1) is shown in Scheme 1. A given amount of AOI and DBTDL (ca. 250–500 ppm) as catalyst were added to the Ca-PDMS, and the reaction was carried out with stirring at rt for 4 h. The molar ratio of reactive groups in Ca-PDMS and AOI was varied from 1:1 (5 g:0.2135 g) to 1:2 (5 g:0.4275 g). The product of the former reaction was noted as SiUA1 and of the latter as SiUA2. The reaction was followed using Fourier transform infrared (FTIR) analysis, and completion was confirmed by the disappearance of the peak attributed to the –NCO moiety (at 2270 cm^{-1}).

Synthesis of acrylic melamines containing silicone segments (SiAMs)

A typical synthesis is shown in Scheme 2. First, melamine was reacted with *para*-formaldehyde in a 1:6 molar ratio and different amounts of HEA and SiUAs in the presence of an appropriate quantity of MEHQ with stirring at 110 °C for 1 h. Then a



Scheme 1 Synthetic route to SiUAs



Scheme 2 Synthetic route to SiAMs

given amount of PTS was added, and the reaction was maintained at 110 °C. The product was obtained following dehydration for about 3 h. The reaction molar ratio of melamine, *para*-formaldehyde, and the hydroxyl groups of HEA and the SiUAs was fixed at 1:6:6. SiUA1, SiUA2, and Ca-PDMS were used as the SiUAs containing hydroxyl groups, and the corresponding products were named SiAM1, SiAM2, and SiAM0, respectively. Moreover, the amount of PDMS was varied from 10 to 20 wt%. For instance, the name of each product is written as SiAM1-0, SiAM1-10, and SiAM1-20, etc. The compositions of the SiAMs are summarized in Table 1. The condensation reaction was confirmed by the appearance of an IR peak attributed to the ether bond (at 1,100 cm^{-1}) in the products. A typical FTIR spectra (for SiAM1-10) is shown in Fig. 1. Because it was expected that monomers such as HEA and SiUAs remained in the products, the SiAMs were purified by washing and drying after reprecipitation from methanol. For a comparison material, the polymer (AM) prepared from melamine, *para*-formaldehyde and HEA (1:6:6) with no SiUAs was synthesized using the same procedure.

Table 1 Feed composition and synthetic results for the SiAM series of polymers

SiUAs

Sample code	Ca-PDMS Feed composition Molar equiv.	AOI Feed composition Molar equiv.
Ca-PDMS	1	0
SiUA1	1	1
SiUA2	1	2

SiAMs

Sample code	SiUA feed composition		Melamine content analyzed value (wt%)	Silicone content analyzed value (wt%)	M_n
	Compound	wt%			
SiAM0-10	Ca-PDMS	10	23.0	1.0	5,600
SiAM0-20	Ca-PDMS	20	23.9	0.5	3,600
SiAM1-10	SiUA1	10	26.6	0.5	3,200
SiAM1-20	SiUA1	20	26.6	0.4	3,900
SiAM2-10	SiUA2	10	27.2	0.5	5,300
SiAM2-20	SiUA2	20	26.7	0.3	16,000
AM	–	–	19.1	0.0	2,400

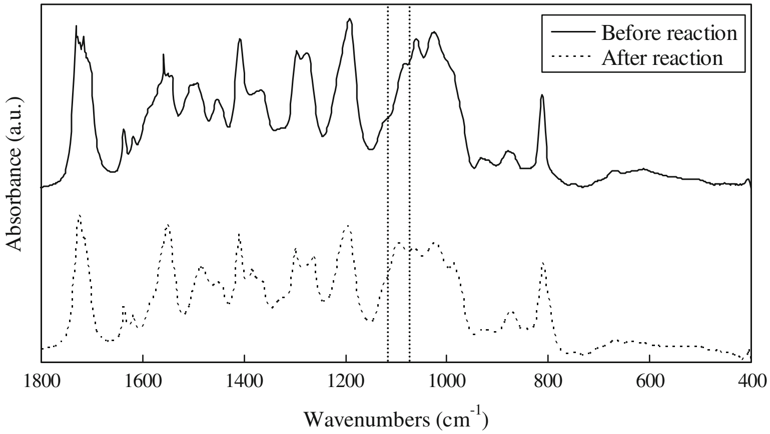


Fig. 1 IR spectra of SiAM1-10

Preparation of coated PET specimens by photopolymerization

The photoinitiator (Irgacure 184, 5 wt%) was added with stirring to the purified SiAMs in 2-butanone to prepare the coatings. The coatings were then each spread on 100 μm of PET film to a thickness of 4 μm. Ultraviolet light (UV; Yamahachi Dental MFG, Hyper LII, 2 min) was used to irradiate the system to induce polymerization after vaporization of the solvents. Purified acrylic melamine, Ca-PDMS, SiUA1, SiUA2, and a mixture of 10 wt% SiUA1 in purified AM were cured by the same procedure and used as references.

Measurements

The synthesized SiUA and SiAM resins were characterized by ^{1}H-NMR (Bruker AVANCE 200 MHz NMR spectrometer) and FTIR (Nicolet AVATAR320S spectrometer). Chemical shifts in the ^{1}H-NMR spectra are reported as δ values (ppm). Acetone-d_6 was used as the solvent. The silicone content of the SiAMs was determined from NMR spectra using DMF as the standard in chloroform-d solvent. FTIR spectra were measured in the region of 4000–400 cm^{-1} using the liquid film method with a Zn–Se crystal cell. The molecular weight of synthesized SiAMs was determined using gel permeation chromatography (GPC; TOSOH, HLC-8220).in tetrahydrofuran solvent with monodisperse polystyrene as the analytical curve. Gas chromatography (GC; Hitachi High-Tech, G-3500) was used to estimate the amount of remaining HEA in SiAMs by calculating the peak area ratio to the internal standard (1:1 mixture of HEA and ethylene glycol monobutyl ether). To calculate the melamine content, the elemental nitrogen content was measured using the method of Kjeldahl with rapid determination of nitrogen-automatic equipment (Nakayama rika, KJEL-AUTO, Model No. DTP-4). The haze of the coated PET film was evaluated using a HAZE-GARD II (Toyoseiki) following method JIS K7316-1. Transmittance in the region of visible light (380–780 nm) was measured using a UV–Vis spectrophotometer (Hitachi High-Tech, U-3310). Refractive indices were measured using a multiwavelength Abbe refractometer (Atago DR-M2) at 589(D) nm. A pencil hardness (Cotec, WOLF WILBORN TEST-DUAL) test (JIS K5600-5-4) was used to evaluate the surface hardness of the coating films at room temperature. Contact angles of the coating films with water and oleic acid were measured using a contact angle tester (Kyowa Interface Science, CA-X). Scanning electron microscope (SEM) analysis of the coating films was performed at 15 kV using a JEOL electron probe microanalyzer (JXA-800). Adhesion between the coating layer and the substrate was measured using method JIS K5600-5-6. Dynamic mechanical analysis (DMA) measurements on the polymer were carried out using a SII nanotechnology model DMS6100 viscoelastometer at 1 Hz from −130 to 200 °C at a heating rate of 2 °C/min. The test pieces were cut into 50 × 50 × 0.1 mm sizes after adding the Irgacure 184 (5 wt%) to the resins and curing by ultraviolet light.

Results and discussion

Characterization of acrylic melamine containing silicone segments (SiAMs)

The SiAMs were obtained as clear and colorless liquids and were soluble in solvents such as chloroform and THF. The synthetic results are shown in Table 1. The melamine and silicone content were calculated based on measurements collected using GC, the Kjeldahl method, and NMR techniques. Even though the amount and kind of the SiUAs were changed in the initial feed composition, the silicone concentration of the products was nearly the same value for all of the polymers. This result is due to the bulky silicone components, which limit the number of SiUAs that can be introduced through the condensation reaction in comparison with the compact hydroxyl group of HEA. Molecular weights of the SiAMs were larger value than AM because of the condensation reaction between SiUA and methylolmelamine.

Optical properties of acrylic melamines containing silicone segments (SiAMs)

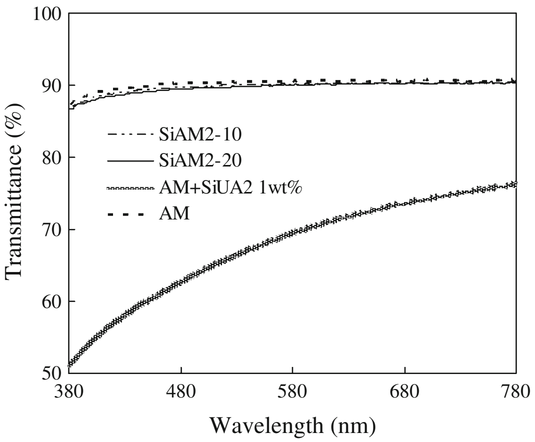
The optical properties of the SiAM series of coated films are summarized in Table 2. The visible light transmittance of the SiAM2 series of coated PET films is shown in Fig. 2. As can be seen from these results, the synthesized SiAM series exhibited higher transmittance and lower haze (Hz) than that of a mixed AM + SiUA2 coated film (Mixture). The SiAMs were found to have high transmittance (~90% T) and low haze (~0.6%) values. On the other hand, the mixed coated film was opaque, with a haze value over 1%. To investigate this opaque phenomena of the mixed coated film, an SEM photograph was taken (Fig. 3). As can be seen in the image, cohesion of the silicone portion occurred at the whitening point in the mixed coated film. It was considered that the difference in the solubility parameters of the AM and silicone groups led to aggregation of the silicone. In the case of the SiAM coated films, their clear and colorless appearance was observed because the AM and silicone groups were covalently bound at the molecular level. The refractive indices of the SiAMs were much the same values as that for AM because the introduced silicone content was low. Therefore, the SiAMs maintained the high refractive index and features of AM.

Table 2 Optical characteristics of the SiAM series of polymers

	T^{a} @400 nm (%)	T^{a} @600 nm (%)	Haze (%)	Refractive index n_D
SiAM0-10	88.3	90.5	0.60	1.564
SiAM0-20	87.9	90.2	0.57	1.569
SiAM1-10	88.1	90.1	0.62	1.574
SiAM1-20	89.1	90.9	0.59	1.568
SiAM2-10	88.2	90.2	0.57	1.568
SiAM2-20	87.9	90.1	0.64	1.565
AM	88.8	90.6	0.60	1.564
SiUA1	64.0	89.5	0.67	1.433
SiUA2	75.9	88.5	0.70	1.448
AM + SiUA2 1 wt%	54.3	70.4	2.15	1.562
AM + SiUA2 10 wt%	47.6	63.3	25.60	–

[a] Transmittance

Fig. 2 Visible light transmittance of SiAM2 series coated film



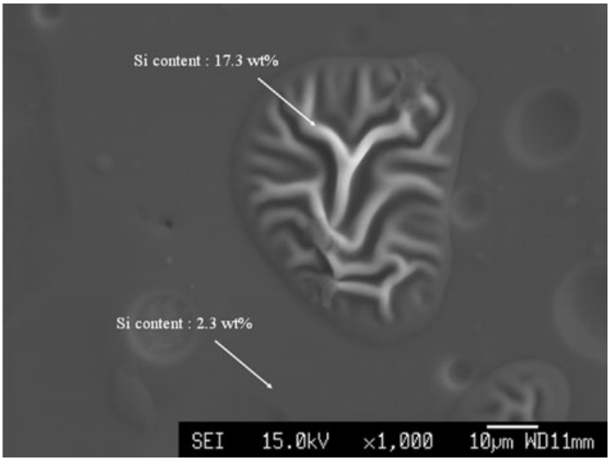


Fig. 3 SEM photograph of the mixed coated film (mixture)

Physical properties of acrylic melamines containing silicone segments (SiAMs)

The surface properties of the SiAM coated films that were irradiated with UV light are shown in Table 3. Although it was predicted that the surface hardness would decrease as the amount of acryloyl groups decreased, the SiAM1 and SiAM2 series polymers had the same pencil hardness (2H) compared with AM. This result is because the silicone content of the SiAM products was low. Not surprisingly, the SiAM0 polymers exhibited low pencil hardness (1H). In this case, the silicone moieties of SiUA0 (Ca-PDMS) cannot react when exposed to UV irradiation. The low silicone content of, the synthesized SiAM series of polymers also enabled them to adhere to the PET film at the same level as AM.

Notably, the water contact angle of the SiAM series coated films increased from 84° to over 90° upon addition of only 0.3 wt% silicone. However, the water contact

Table 3 Physical characteristics of SiAM coating films

	Pencil hardness	Contact angle (°)		Adhesion to PET
		Water	Oleic acid	
SiAM0-10	1H	96.1	45.4	OK
SiAM0-20	1H	96.3	42.3	OK
SiAM1-10	2H	93.7	41.2	OK
SiAM1-20	2H	96.9	43.7	OK
SiAM2-10	2H	93.7	42.6	OK
SiAM2-20	2H	98.5	46.4	OK
AM	2H	84.2	30.5	OK
SiUA1	–	78.4	27.4	NG
SiUA2	–	90.9	33.1	NG
AM + SiUA2 1 wt%	–	95.4	28.9	OK
AM + SiUA2 10 wt%	–	71.7	19.7	OK

angle did not increase any further when the density of silicone increased over 0.3 wt%. Similar tendencies were observed in the contact angles for oleic acid. These results revealed that 0.3 wt% silicone in the AM resin is a sufficient quantity for improving the water repellent properties of AM. The limit on the water contact angle seems to be caused by saturation of the silicone units on the material surface.

To gain more insight into the relationship between the Si element content and the contact angle, the Si content of a cross-section of the surface of the coating layer was investigated using EPMA measurements. The Si content of the surface side was larger (1.8 wt%) than that of the bottom side (1.1 wt%) for SiAM2-10. Therefore, it

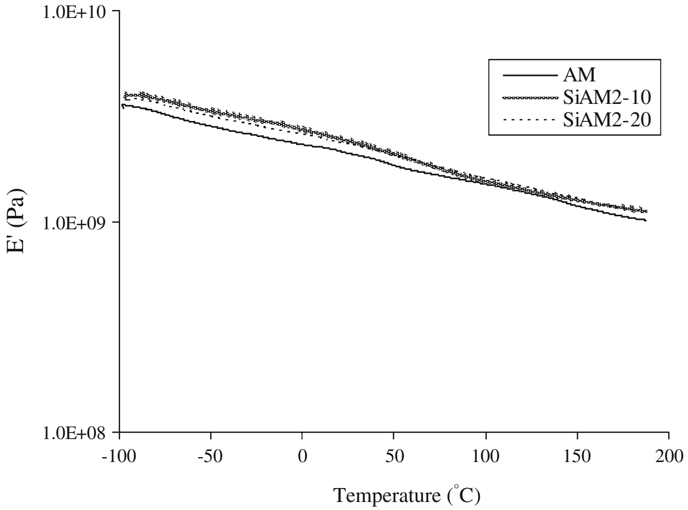


Fig. 4 Temperature dependence of the storage modulus (E') for the SiAM2 series of polymers

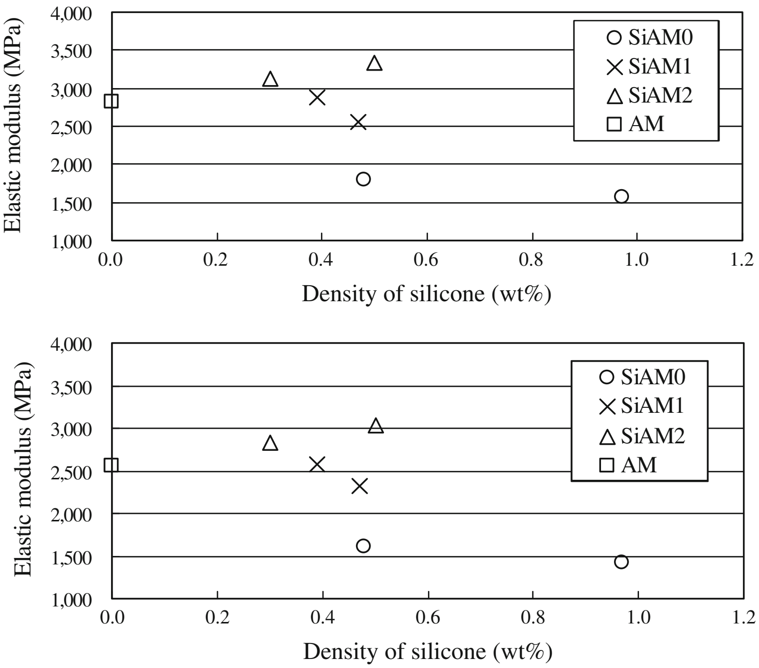


Fig. 5 Relationship between the density of silicone in the polymer and the polymer's elastic modulus at −50 °C (upper) and 25 °C (lower)

can be concluded that the silicone side chain has a tendency of segregating on the surface side.

Results of the DMA analysis of the SiAM2 series of polymers are shown in Fig. 4. SiAM2 was found to have a high elastic modulus value from −100 °C to 200 °C that was equivalent to or greater than the value for AM. It is notable that the SiAMs also possess heat-stability and high hardness properties similar to those of AM. The relationship between silicone density and elastic modulus is shown in Fig. 5. The elastic modulus of the SiAMs decreased with increasing silicone content. Interestingly, the SiAM2 series of polymers had higher elastic moduli than AM. This increased value originates from the larger molecular weight of SiAM2 compared to that of AM, and also the high density of acryloyl moieties compared to those in SiAM0 and SiAM1. Moreover, the SiAM0 series of polymers had low elastic moduli because of their low cross-link density. These results also further explain the low pencil hardness of the SiAM0 series of polymers.

Conclusion

In this study, novel hybrid materials comprised of melamine, acrylic, and silicone segments (SiAMs) were prepared. The synthetic hybrid materials have high transparency compared with a mixture of acrylic melamine and silicone resins.

Moreover, the SiAMs feature high refractive indices, high hardness, high water contact angles, and good adhesion to PET films. Notably, the SiAMs possess the characteristics that represent the good points of each of the three components. The high refractive index originates from the melamine moiety. The high hardness is derived from the melamine and acryloyl groups. The SiAMs could be cured rapidly at low temperature by UV irradiation because they contain acryloyl groups. Understandably, the high water contact angles are a feature of the silicone moiety. In addition, the synthesized SiAMs posses the above many features while also maintaining high transparency. Therefore, these materials can be applied as a surface treatment and adjustable optical interference layer for plastic substrates.

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