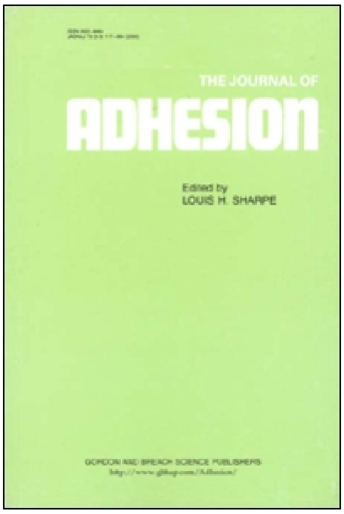

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Surface Properties for Blended Films of Poly(methylmethacrylate) and Terpolymers Composed of Methylmethacrylate, Methoxypoly(ethyleneglycol-methacrylate) and Poly(dimethylsiloxanemethacrylate)

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Surface Properties for Blended Films of Poly(methylmethacrylate) and Terpolymers Composed of Methylmethacrylate, Methoxypoly(ethyleneglycol-methacrylate) and Poly(dimethylsiloxanemethacrylate)

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Terpolymers composed of methylmethacrylate (MMA), poly(dimethylsiloxanemethacrylate) (PDMSMA) and methoxypoly(ethyleneglycolmethacrylate) (MPEGMA), which have blood compatibility, were blended with poly(methylmethacrylate) (PMMA) in order to improve their mechanical properties. It was expected that low surface free energy components such as the poly(dimethylsiloxane) (PDMS) and methoxy groups of terpolymer would predominate at the blend surface. The adsorptions of PDMS to the blended surfaces were confirmed *via* X-ray photoelectron spectroscopy (XPS). A large contact angle hysteresis was observed for the blended films *via* a dynamic contact angle. Advancing contact angles for blended films showed the same values as that of the silicone. The receding contact angles for those blends incorporating PDMSMA-rich terpolymer showed high values and decreased with hot water treatment, while MPEGMA-rich terpolymer blended films exhibited low values and maintained those values after hot water treatment. Adhesion tension relaxations for these blended films were also observed. These phenomena were interpreted to be caused by the reorganization of a hydrophobic segment to the polymer surface or hydrophilic segment to the water/polymer interface so as to decrease the surface or interfacial tension, respectively. Although the mechanical

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properties slightly decreased with blending of these terpolymers, the blended films could be applied for various practical uses.

Keywords: Terpolymer; dynamic contact angle; adhesion tension relaxation; X-ray photoelectron spectroscopy

1. INTRODUCTION

It is well known that a segment of a multi-component system such as a copolymer can selectively adsorb and orient to the surface of the system so as to minimize interfacial free energy in response to an environmental medium. Recently, the surface molecular mobility of a multi-component polymeric system has been investigated *via* dynamic contact angle (DCA) measurement and adhesion tension relaxation (ATR) [1, 2]. DCA is a useful tool to investigate these phenomena because a reorientation of surface segments can be directly reflected to contact angle hysteresis when a polymer is moved into a different medium. We [3–7] have already reported that copolymers having hydrophobic and/or hydrophilic side chains showed a high molecular mobility. In particular, terpolymers composed of methylmethacrylate (MMA), poly(dimethylsiloxanemethacrylate) (PDMSMA) having a hydrophobic side chain, and methoxypoly(ethyleneglycolmethacrylate) (MPEGMA) having a hydrophilic side chain show high molecular mobility [4]. In addition, a terpolymer having the same content of MPEGMA as PDMSMA exhibits significant blood compatibility.

In this study, we tried to blend MMA/PDMSMA/MPEGMA terpolymer into poly(methylmethacrylate) (PMMA) to obtain films having good mechanical properties, because the terpolymers are very weak. It was hypothesized that a poly(dimethylsiloxane) side chain and a terminal methoxy group of MPEGMA could be adsorbed and oriented to the polymer surface of a cast film, since they have a very low surface free energy. Therefore, it should be possible to obtain strong PMMA films having the same surface properties as the terpolymers.

The DCA and ATR of these blends were measured after dipping into and out of water. In addition, an XPS spectrum measurement was conducted.

2. EXPERIMENT

2.1. Preparation of Sample Polymers

Poly(methylmethacrylate) (PMMA) used was a commercially available grade (Aldrich Co., $M_w = 75{,}000$). Terpolymers composed of methylmethacrylate (MMA), poly(dimethylsiloxanemethacrylate) (PDMS-MA) and methoxypoly(ethyleneglycolmethacrylate) (MPEGMA), having different compositions were synthesized in methylethylketone (MEK) using *t*-butylperoxy(2-ethylhexanoate) as initiator at 70°C. The molecular structures of these monomers are shown in Scheme 1. PDMSMA and MPEGMA were supplied by Shin Etu Chemicals Co. and Sin Nakamura Chemicals Co., respectively.

$CH_2{=}C(CH3)COOCH_2CH_3$	MMA
$CH_2{=}C(CH_3)COO(CH_2CH_2O)_{23}CH_3$	MPEGMA (Mw=1,100)
$CH_2{=}C(CH_3)COO(Si(CH_3)_2O)_{20}Si(CH_3)_3$	PDMSMA (Mw=2,000)

SCHEME 1

The feeds in the polymerization of MMA/PDMSMA/MPEGMA terpolymers contained the same MMA content (50 wt%) but different PDMSMA and MPEGMA content. Here, the terpolymers are represented by R2-X. The number X denoted the feed content of PDMSMA.

2.1.1. Preparation of Blend Films

Blended films of PMMA with terpolymers were prepared as follows: Certain amounts of PMMA and terpolymer were dissolved in methylethylketone (MEK), the solution was cast on a Teflon^{TM} sheet and, after being dried in atmosphere for 24 hrs, the film was dried in a vacuum oven more than 24 hrs at 40°C. The blended films was cut into 20 × 50 mm and 5 × 5 mm pieces for dynamic contact angle (DCA) and X-ray photoelectron measurements (XPS), respectively. The blended films were represented by R2-X-Y. R2-X denoted a terpolymer as shown above and the number Y denoted the content of the terpolymer in the blended film. The reorientation of the hydrophilic segment was accelerated by heating at a higher temperature than the glass transition temperature (T_g). In order to reorient the poly(ethyleneglycol) (PEG) segment to the surface, the blended films were treated with hot water at 90°C for 3 hrs and then after cooling to room temperature, taken out of the water.

2.2. Measurements

2.2.1. Dynamic Mechanical Properties

We carried out dynamic mechanical properties measurements (torsional rigidity (G') and tan δ) using a DYNAMIC ANALYZER RDA II (Rheometrics Co.). As the purpose of the dynamic mechanical measurement in this paper was only to confirm that the mechanical properties of the terpolymers could be improved by blending with PMMA, the measurements were conducted from room temperature to a maximum of 150°C.

2.2.2. Dynamic Contact Angle Measurement

We carried out a dynamic contact angle measurement (DCA) to obtain fundamental data regarding the surface characteristics of the samples, using the Wilhelmy plate method. A sample plate hanging onto a load cell was dipped into and out of water. In principle, the adhesion tension ($F = \gamma_L \cos\theta = \gamma_S - \gamma_{SL}$) was measured and θ was calculated using F and the surface tension of water (γ_L) *via* this method. We measured DCA at a dipping velocity of 20 mm/min. The principle of the method has been described in detail elsewhere [1].

2.2.3. Adhesion Tension Relaxation Measurement

We also measured adhesion tension relaxation using the same sample plate and instrument as for the DCA. The principle of this method has been described elsewhere [4]. The measurement was performed as follows: first, the sample plate was mounted so that the bottom was just in contact with the liquid surface; then it was lowered 20 mm at a velocity of 100 mm/min and stopped. At this position, the force ($F_A(t)$)

applied to the sample plate in the advancing process was measured as a function of elapsed time (t) for 30 min. Then it was retracted 10 mm and $F_R(t)$ in the receding process was similarly measured for 30 min. Here, $F_A(t)$ and $F_R(t)$ can be described, respectively, as follows:

$$F_A(t) + F_b = P\gamma_L \cos\theta_A(t) = P(\gamma_S - \gamma_{\mathrm{SL},A}(t)) \tag{1}$$

$$F_R(t) + F_b = P\gamma_L \cos\theta_R(t) = P(\gamma_{\mathrm{S,R}}(t) - \gamma_{\mathrm{SL,aq.}}) \tag{2}$$

Where F_b is the buoyancy, and a constant value that does not depend on time. P is the perimeter of the sample plate. γ_S and γ_{SL} are the surface tension of the sample plate and interfacial tension between the sample plate and water, respectively. Suffix A and R indicate advancing and receding processes, respectively.

The variation of $F_R(t)$ was caused only by $\gamma_{\mathrm{S,R}}(t)$ which depended on the rate of reorientation of the hydrophobic segment in the part of the plate which was retracted from the water into the air. We were able to described the molecular mobility of the polymer *via* $F_A(t)$ and $F_R(t)$.

2.2.4. Light-scattering Measurement

In order to determine the phase separation of the blended films, the light-scattering measurement was carried out using a laser light-scattering measurement system (IST Planning Co., SALA-100G).

2.2.5. Gel Permeation Chromatography Measurement

The molecular weight of the synthesized terpolymers was determined using gel permeation chromatography (GPC) (SCL-6B, Shimadzu Manufacturing Ltd.) with the polystyrene (PSt) standard.

2.2.6. X-ray Photoelectron Spectroscopy Measurement

X-ray photoelectron spectroscopy (XPS) spectra were measured by a Shimadzu ESCA 850 X-ray photoelectron spectrometer using a Mg $K\alpha$ X-ray source. The X-ray gun was operated at 8 kV and 30 mA, and the analyzer chamber pressure was less than 1×10^{-6} Pa. Depth profiles were determined using the variable photoelectron take-off angle method. For this experiment, two types of sample holders, whose take-off angles (ϕ) were 15 and 90 degrees, were used. The sampling depth for each take-off angle $d(\phi)$ is described as follows:

$$d(\phi) = d \cdot \sin\phi \tag{3}$$

where d is the sampling depth for the take-off angle of 90 degrees.

3. RESULTS AND DISCUSSION

3.1. Characteristics of Synthesized Terpolymers

Table I shows the characteristics of the synthesized MMA/PDMSMA/MPEGMA terpolymers. The molecular weights of the terpolymers ranged from 20,000 to 50,000, and the distributions were around 2. The compositions of the terpolymers measured by NMR are also shown in comparison with the feeds in polymerization. The compositions of R2-45 and R2-05 were nearly equal to the feeds. Although the compositions of R2-35 and R2-25 were different from the feeds in the MMA contents, the ratios of PDMSMA content to MPEGMA were close to the feeds. The length of the PDMS and PEG side chains were 6.1 and 8.5 nm, respectively.

3.2. Bulk Properties of Blended Film

Since the blended films were semi-transparent, while the terpolymers were transparent, a light-scattering measurement of the blended films

TABLE I Characterization of MMA/PDMSMA/MPEGMA terpolymers

	Composition of terpolymers				*Molecular weight*		*Distribution*
Terpolymers	*MMA:PDMS-MA:MPEGMA Feed*		*(PDMSMA/MPEGMA) NMR*		*Mn*($\times 10^{-4}$)	*Mw*($\times 10^{-4}$)	*Mw/Mn*
R2-45	50:45:5	(9.0)	47:47:6	(7.8)	2.9	7.5	2.5
R2-35	50:35:15	(2.3)	33:42:25	(1.7)	5.3	9.4	1.8
R2-25	50:25:25	(1.0)	71:17:12	(1.4)	2.2	4.2	1.9
R2-05	50:5:45	(0.1)	54:4:42	(0.1)	2.6	4.6	1.8

were carried out. At a scattering angle of around 5 degrees, a small peak was observed for each blended film. It was clear that they underwent a micro-phase separation structure in the bulk of the blended film.

Dynamic mechanical properties (G' and tan δ) are shown in Figure 1. The dynamic modulus of the blended films were slightly lower than that of PMMA. $T_g s$ determined by the tan δ peak also decreased with the blending of a terpolymer from 125°C of PMMA to around 110°C of the blended films. Although the mechanical properties were slightly decreased with the blending of the terpolymer, the blended films exhibited enough positive properties which could make them applicable in practical usage.

3.3. Surface Properties of Blended Film

3.3.1. Surface Observation via Scanning Electron Spectroscopy

Figure 2 shows the photographs of scanning electron microscopy (SEM) for the solvent-cast surface and the hot-water-treated surface for R2-45-10 as a typical example. Although some small bumps were observed in photograph (a), the surfaces were relatively smooth. The texture showing phase separation could not be observed at the blended surface. A large change in the surface texture could not be observed even after hot-water treatment as shown in photograph (b). Because the outermost layers of the blended films were composed of the PDMS and PEG segments of the terpolymers, which could not phase separate, as shown in the following section, the surface texture showing phase separation could not be observed in spite of the phase-separated structure in bulk. From these observations, it was proven that a DCA measurement could be conducted without hindrance.

3.3.2. X-ray Photoelectron Spectroscopy Measurement

Atomic ratios of Si_{2p} and O_{1s} to C_{1s} *via* XPS for MMA blended with MMA/PDMSMA/MPEGMA terpolymers are shown in Table II. Atomic ratios (Si_{2p}/C_{1s}) calculated from the weight fraction of the blended films are also listed in the Table. More silicon atoms were

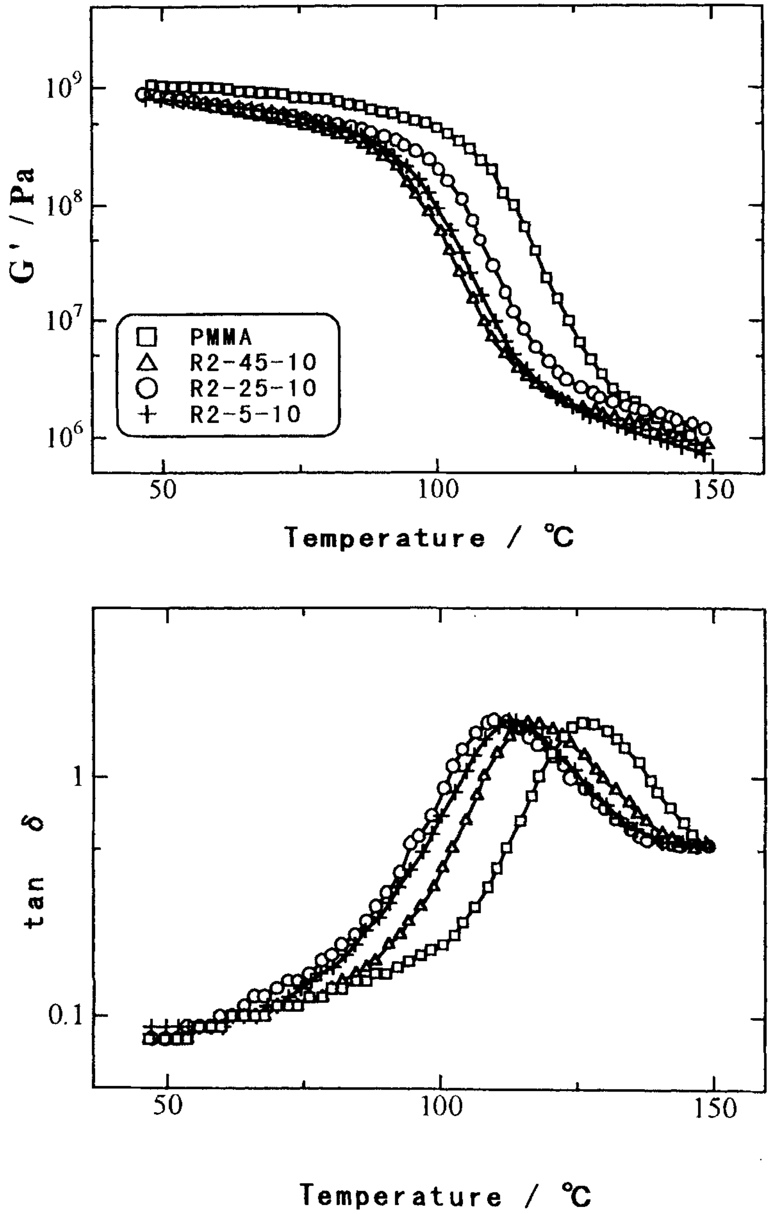

FIGURE 1 Dynamic mechanical properties (rigidity (G') and $\tan\delta$) for R2-X-10 series and PMMA films.

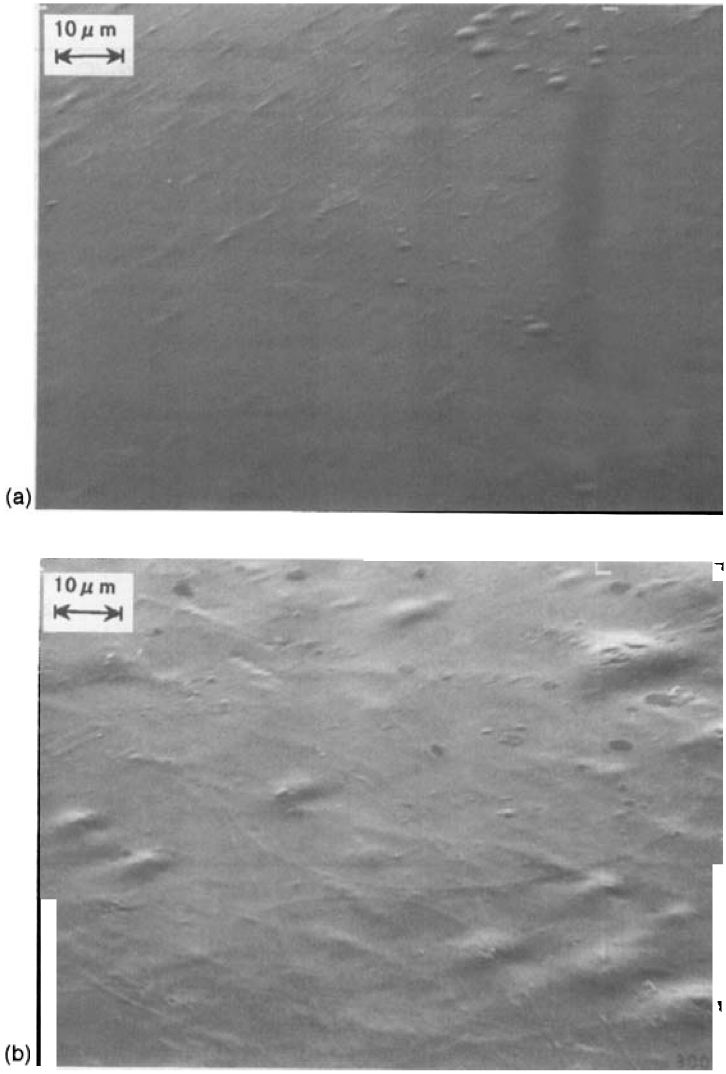

FIGURE 2 SEM photographs of surface of R2-45-10: (a) cast surface and (b) after hot-water treatment.

detected for the blended films than the calculated value. In addition, atomic ratios (Si_{2p}/C_{1s}) obtained by the 15-degree take-off angle sample holder (shallower analysis) showed larger values than for the 90-degree (deeper analysis). This fact illustrated that the low surface

TABLE II Atomic ratios of Si_{2p} and O_{1s} to C_{1s} (C = 100) for PMMA blended with terpolymers (*via* XPS)

Sample	Si_{2p}/C_{1s}			O_{1s}/C_{1s}	
	Calc[a]	90 *deg*[b]	15 *deg*[b]	90 *deg*[b]	15 *deg*[b]
R2-45-1	0.10	8.1	19.9	41.0	41.4
R2-45-2	0.20	14.7	27.5	40.9	40.7
R2-45-5	0.50	10.8	28.1	39.1	42.0
R2-45-10	1.00	12.5	28.0	42.8	41.9
R2-45-20	2.00	16.7	35.7	36.1	44.2
R2-45		17.2	33.9	38.5	44.8
R2-35-1	0.08	7.3	27.3	37.4	43.2
R2-35-2	0.16	12.0	20.9	42.2	45.2
R2-35-5	0.40	11.0	26.4	40.5	42.6
R2-35-10	0.80	14.1	26.7	41.3	40.8
R2-35-20	1.60	16.8	26.3	34.0	42.5
R2-35		30.8	42.8	36.0	44.0
R2-25-1	0.06	10.7	23.7	41.7	41.0
R2-25-2	0.12	14.2	23.9	42.1	40.0
R2-25-5	0.30	12.5	23.6	42.1	40.9
R2-25-10	0.60	16.2	26.2	41.8	42.4
R2-25-20	1.20	16.3	27.9	40.8	42.7
R2-25		19.2	32.5	44.2	42.7
R2-15-5	0.20	14.4	26.6	43.3	42.5
R2-15-10	0.40	12.2	27.0	43.2	40.9
R2-15-20	0.80	10.5	21.7	36.7	41.1
R2-15		14.6	30.8	43.7	42.5
R2-05-1	0.02	2.2	13.2	37.4	35.2
R2-05-2	0.04	3.7	11.8	36.4	41.6
R2-05-5	0.10	7.7	15.2	41.9	36.1
R2-05-10	0.20	6.8	22.6	39.4	41.9
R2-05-20	0.40	8.7	23.3	36.8	41.4
R2-05		12.2	31.4	45.6	43.4

[a] Calculated with molecular composition of Si_{2p}/C_{1s}; [b] Take-off angle.

free energy PDMS segment adsorbed and oriented to the surface of the blended films. On the other hand, atomic ratios (O_{1s}/C_{1s}) did not depend on the composition of the blended terpolymer and weight fraction of the blend films. Atomic ratios (O_{1s}/C_{1s}) for PMMA, PEG and PDMS, of which the blended surfaces were composed, were 0.4, 0.5 and 0.5, respectively. Because there was not a significantly-large difference in these values, atomic ratios (O_{1s}/C_{1s}) did not vary with the composition of the blended films.

It is well-known that a hydrophobic segment adsorbs and orients to the surface of a multi-component polymeric system in the air, and a hydrophilic segment reorients to the interface of a polymer and water, so as to minimize interfacial free energy, when the polymer having great molecular mobility is immersed in water. Therefore, we tried to treat with hot water at 90°C that was nearer to the glass transition temperature (T_g) of PMMA, which was a matrix resin of the blended films and the backbone molecule of the terpolymers. Since the blended films exhibited relatively high mobility in hot water, the hydrophilic PEG segment and the ester group were easily able to reorient to the polymer/water interface. We already reported [8, 9] that a perfluoroalkyl segment could reorient to the surface of poly(perflororoctylmethacrylate) by heat treatment at a higher temperature than T_g. The treated blended films were taken out from the water into the air after cooling to room temperature which was lower than the T_g of PMMA. Therefore, the reoriented hydrophilic segment could be fixed near the blended surface.

Table III shows the atomic ratios of Si_{2p} and O_{1s} to C_{1s} *via* XPS for MMA blended with MMA/PDMSMA/MPEGMA terpolymers before and after treatment with hot water (90°C). Both atomic ratios, Si_{2p}/C_{1s} and O_{1s}/C_{1s}, decreased with hot water treatment. The decrease in atomic ratios of Si_{2p}/C_{1s} showed that the hydrophobic PDMS segment was swapped in the water for a hydrophilic PEG segment and ester group. The decrease of the atomic ratios of O_{1s}/C_{1s} was due to the MMA segment being adsorbed with the ester group.

TABLE III Atomic ratios of Si_{2p} and O_{1s} to C_{1s} (C = 100) for PMMA blended with MMA/MPEGMA/PDMSMA terpolymer before and after hot-water treatment (*via* XPS; take-off angle 15 deg)

		Terpolymer content/wt%					
		5		10		20	
		Si_{2p}/C_{1s}	O_{1s}/C_{1s}	Si_{2p}/C_{1s}	O_{1s}/C_{1s}	Si_{2p}/C_{1s}	O_{1s}/C_{1s}
R2-45	before[a]	28.1	42.0	28.0	41.9	35.7	44.2
	after[b]	23.9	38.4	28.9	39.4	30.7	40.7
R2-35	before	26.4	42.6	26.7	40.8	26.3	42.5
	after	24.3	39.3	22.5	37.7	24.7	39.3
R2-25	before	23.6	40.9	26.2	42.4	27.9	42.7
	after	29.1	39.0	21.8	37.5	23.1	40.6
R2-15	before	26.6	42.5	27.0	40.9	21.7	41.1
	after	21.2	34.0	18.5	35.9	23.9	37.4
R2-05	before	15.2	36.1	22.6	41.9	23.3	41.4
	after	16.6	33.2	14.4	27.9	22.0	37.5

[a] Untreated; [b] After hot-water treatment.

3.3.3. Dynamic Contact Angle

We already reported [4] on the dynamic contact angle (DCA) of terpolymers used in this study. For the discussion, the composition dependence of DCA for these terpolymers is shown in Figure 3. In the Figure, DCAs for PMMA blended with terpolymers of 10 wt% (R2-X-10 series) are also plotted. The advancing contact angle (θ_A) for the terpolymer slightly increased with an increase in PDMSMA content. These values were approximately the same as those of PDMS. Therefore, it was clear that a PDMS side chain was predominant on the terpolymer surface in the air. The receding contact angle (θ_R) for the terpolymer increased with an increase in PDMSMA content and showed much lower values than θ_A. Johnson and Dettre have shown

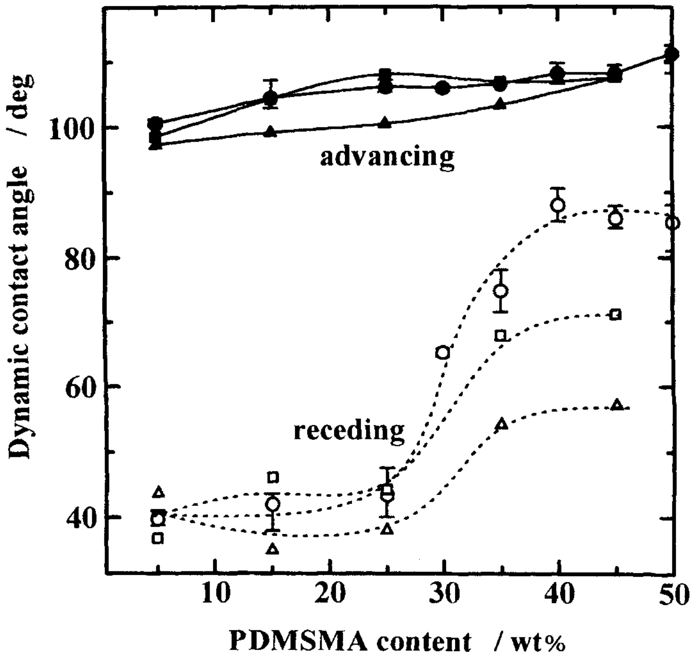

FIGURE 3 Dynamic contact angle for MMA/PDMSMA/MPEGMA terpolymers and PMMA blended with terpolymer of 10 wt% (R2-X-10 series) plotted against the PDMSMA content of terpolymer. ●, ○ : terpolymer; ■, □ : untreated R2-X10 series; ▲, △ : hot water treated R2-X-10 series. *solid*: advancing contact angle, *open*: receding contact angle.

[10] that, at a heterogeneous surface, a hydrophobic component predominately contributed to θ_A and a hydrophilic one to θ_R. The large values of θ_A for the terpolymer were due to low surface tension segments such as PDMS and methoxy terminal groups of MPEGMA. Since the hydrophilic PEG segment could be reoriented to the polymer/water interface so as to minimize interfacial tension when the polymers were immersed in water, θ_R exhibited low values. In a low PDMSMA content region, *i.e.*, a high MPEGMA content region, θ_R for the terpolymers exhibited low values, while, in a high content region, they exhibited almost the same values as PDMS. In the water, a hydrophilic MPEG side chain could be reoriented to the water/polymer interface to decrease interfacial free energy and could be predominant at the polymer surface. Since the PDMSMA-rich surfaces of these terpolymers were composed of a relatively thick PDMS layer, allowing interruption of the motion of the MPEG segment, the MPEG side chain could not migrate to the surface even in water.

Figure 4 shows the DCA for PMMA blended with terpolymers as a function of their content. θ_As did not depend on the content and exhibited the same value as that of PDMS even in the low terpolymer content region. It was clear that the small amount of blending of the low surface tension PDMS segment resulted in a high θ_A. In the region of low terpolymer content, θ_Rs for films blended with terpolymer which had low PDMSMA content (high MPEGMA content) showed lower values than that of the terpolymer itself. There were two factors in making a surface structure of a multi-component polymeric system when it was cast from solvent. One was the surface tension of the segment or chemical group. The lowest surface tension component predominated the polymer surface. The other was the solubility of the polymer with a solvent. The component which had high solubility with the solvent could be adsorbed to the surface with an evaporating solvent. In this case, the low surface tension components were PDMS and the terminal methoxy group of the MPEGMA side chain. We reported [11] the surface tension of the methoxy group as 11 – 13 mN/m. The most soluble component with the solvent used (MEK) in these blended films was the PMMA segment. The solubility parameter of PMMA was equal to MEK. Therefore, the segment of PMMA could coexist with other components in the low terpolymer content region.

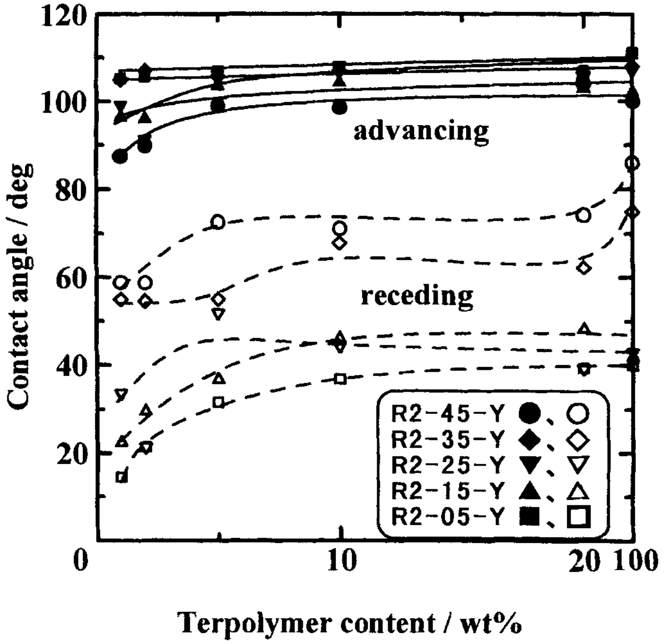

FIGURE 4 Dynamic contact angle for PMMA blended with MMA/PDMSMA/MPEGMA terpolymers plotted against the terpolymer content. *solid:* advancing contact angle, *open:* receding contact angle.

Because the highly hydrophilic ester group arranged subsurface could be reoriented to polymer/water interface, θ_R exhibited low values.

Figure 5 shows the dynamic contact angles (DCA) as a function of the terpolymer content for PMMA blended with MMA/PDMSMA/MPEGMA after hot-water treatment. θ_A did not depend on the content and exhibited the same values as the untreated surface shown in Figure 1. This fact illustrated that the PDMS segment predominantly contributed to θ_A even after hot water treatment. θ_{RS} for the hot-water-treated blended films also exhibited low values. θ_{RS} for the films blended with terpolymers having high PDMSMA content decreased with hot-water treatment, while those blended with terpolymers having low PDMSMA content exhibited almost the same value as for the untreated series shown in Figure 4.

DCA for PMMA blended with 10 wt% of terpolymers (R2-X-10 series), before and after hot-water treatment, are also plotted in

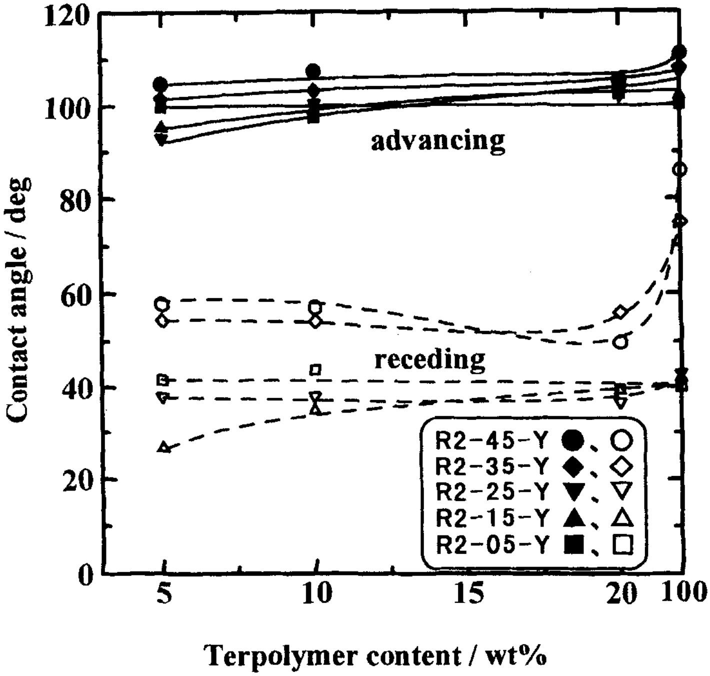

FIGURE 5 Dynamic contact angle for PMMA blended with MMA/PDMSMA/MPEGMA terpolymers after hot-water treatment plotted against the terpolymer content. *solid:* advancing contact angle, *open:* receding contact angle.

Figure 3, as a function of the PDMSMA content of the blended terpolymer. θ_{RS} did not depend on the content. However, θ_{RS} for both before and after hot-water treatment exhibited almost the same value as that for the terpolymer in the region of a PDMSMA content < 25 wt% (MPEGMA-rich region). In this region, hydrophilic PEG segments predominated in the water. In the PDMSMA-rich region, large differences in θ_R could be observed. θ_{RS} for untreated blended films were lower than for terpolymers. Atomic ratios (Si_{2p}/C_{1s}) of blended films were less than for the terpolymer, as shown by XPS measurement. θ_{RS} for blended films decreased with hot water treatment. It was clear that the PEG segment reoriented to the surface in hot water, and the reorganized surface structures could be fixed by cooling from 90°C to room temperature.

3.3.4. Adhesion Tension Relaxation

Figure 6 shows the adhesion tension relaxation ($F(t)$) for MMA blended with terpolymers of 10 wt% (R2-X-10 series). $F_A(t)$ increased with elapsed time. This was due to the reorientation of the PEG segment to the copolymer/water interface, resulting in a reduction of $\gamma_{SL,A}(t)$ in Eq. (1). The surface of R2-05-10 was composed of many PEG segments which were retracted to the surface with the adsorption of the methoxy group. Since the outermost surface of this sample was composed of an extremely thin layer of methoxy groups, the reorganization of the PEG segment of this sample occurred very quickly. Therefore, $F_A(t)$ did not show such a large relaxation. The surface of R2-45-10 was composed of many PDMS segments and exhibited their thick layer. Therefore, $F_A(t)$ of this sample also did not

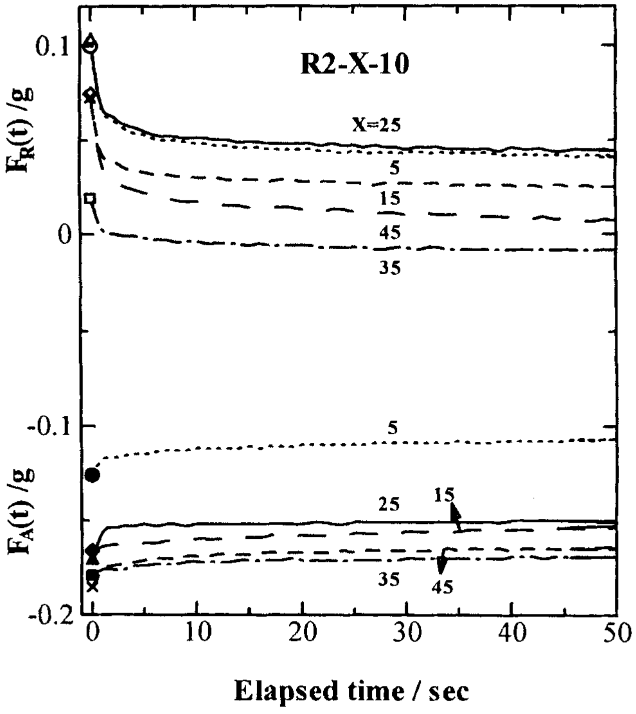

FIGURE 6 Adhesion tension for PMMA blended with MMA/PDMSMA/MPEGMA terpolymer as a function of elapsed time.

show such a large relaxation. On the other hand, the largest relaxation of $F_A(t)$ was observed for R2-25-10 which had the same content of MPEGMA as that of PDMSMA in the blended terpolymer. The surface of this sample was covered with PDMS segments in the air, and a significant amount of PEG segments, which coexisted on the surface, could be reorganized in water. Takahara *et al.* [12] also reported that adhesion tension increased with elapsed time for some segmented poly(etherurethaneureas).

On the other hand, $F_R(t)$ decreased with elapsed time. This was due to the reorientation of the PDMS segment and methoxy terminal group of MPEGMA to the surface that was retracted from water to air, resulting in a reduction of $\gamma_{\mathrm{S,R}}(t)$ in Eq. (2). A large relaxation of $F_R(t)$ was observed for all samples.

After the initial large relaxation, both $F_A(t)$ and $F_R(t)$ relaxed gradually for several minutes. It took more than 5 minutes to equilibrate. From these results, it could be shown that reorganization could take place in a matter of minutes.

4. CONCLUSION

Terpolymers composed of methylmethacrylate (MMA), poly(dimethylsiloxanemethacrylate) (PDMSMA) and methoxypoly(ethyleneglycolmethacrylate) (MPEGMA), were synthesized and blended in poly(methylmethacrylate) (PMMA). The blended films were semitransparent and phase separations were observed in their bulk, while their surfaces were smooth and homogeneous. The dynamic moduli of the blended films were slightly lower than PMMA. T_gs determined from the $\tan\delta$ peak shifted to lower temperature. More silicon atoms were detected for blended films *via* XPS measurement than the calculated value. θ_As for blended films did not depend on the terpolymer content and exhibited the same value as that of PDMS. From these results, it was clear that the low surface free energy PDMS segment adsorbed and oriented to the surface of the blended films. θ_Rs for blended films showed much lower values than θ_As and decreased with hot-water treatment. It could be shown that a hydrophilic PEG segment could be reoriented in water to decrease the interfacial tension of the polymer/water interface. Adhesion tensions for blended films also varied with elapsed time, and large relaxations could be observed. Based on these results, it could be shown that reorganization could take place in a matter of minutes.

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