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Notes

Surface Modification of Poly(methyl methacrylate) Film by Siloxane Graft Copolymers

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The surfaces of polymers have been known to be of importance in many applications of polymers.[1] Azrak[2] and Pennings[3] showed that the polar groups of random copolymers could be oriented at surfaces by the influence of environment. Gaines[4] has reported the surface concentration of siloxane block copolymers. We[5-7] have reported on the surface modification of polymer films by addition of tailor-made graft copolymers synthesized by the macromer method. This technique is quite attractive in surface modification since a desired functional group can be incorporated into a graft copolymer by copolymerizing a functional macromer with a surface-active comonomer (or vice versa), which makes it possible for the graft copolymer to accumulate on the surface.

In this note, we report on the effective surface modification of poly(methyl methacrylate) (PMMA) films by adding small amounts of siloxane graft copolymers, evaluated by contact angle toward water droplet and FT-ATRIR, SEM, and ESCA measurements.

Results and Discussion

Contact Angle. The details of the results of the contact angle measurements have been reported.[5] Siloxane graft or random copolymers of 0.5-1.0 wt % were enough to make the PMMA film completely hydrophobic on the air-side surface. On the glass-surface, the contact angle change, though observed, was not significant. Even with 10 wt % graft copolymer, the decrease in contact angle was small. The extent of surface modification on the air side seems to be dependent only on the percent siloxane content in the blends.

FT-ATRIR, ESCA, and SEM. FT-ATRIR spectra obtained with a Ge prism at an incident angle of 45° give the average concentration to about a 5000-Å depth at 1000 cm^{-1}. The absorptions at 740 cm^{-1} (coupling of CH_2 and skeletal vibration) and 795 cm^{-1} ($SiCH_3$ rocking) were taken as the characteristic absorptions of PMMA and the siloxane graft copolymer, respectively. The changes in the relative absorbance at 795 cm^{-1} and 740 cm^{-1} are given in Table I.

Contrary to results of the contact angle measurement, by which a higher concentration of the graft copolymer on the air-side surface was clearly suggested even at a concentration of 0.1% graft copolymer,[5] concrete differences between the surfaces of the two sides could not be observed until 10% graft copolymer was added to PMMA. Measurement of the blend film using a KRS-5 prism showed that the average concentration to 15000 Å is much lower than that to 5000 Å even at the air-side surface of the modified PMMA film with 10% graft copolymer. This fact suggests that at a concentration of 10% graft copolymer to bulk PMMA, the graft copolymers are distributed in the region between the surface and about a 10000-Å depth, and the relative concentration of the graft copolymer is in the order air-side surface > glass-side surface ≫ inner part of the film.

Table I
FT-ATRIR Relative Absorbance of Various Siloxane Polymer-PMMA Blend Films

GM-411/PMMA, wt %	A_{795}/A_{740}[a] air-side surface	A_{795}/A_{740}[a] glass-side surface
0	0.23[b]	0.23[b]
0.1	0.30	0.22
0.5	0.27	0.28
1.0	0.44	0.43
10	2.45	2.10

[a] A_{795} and A_{740} are characteristic absorptions of polysiloxane and PMMA, respectively. [b] There may be some contamination of silicone grease in PMMA.

Information about regions closer to the surfaces can be obtained by ESCA measurments. The results with an Al $K\alpha_{1,2}$ source, which gives the average concentration to about 20-Å depth, are consistent with the contact angle data in regard to the concentration of the graft copolymer at the air-side surface being higher than that at the glass-side surface even for the blend film containing small amounts (0.1-1.0%) of graft copolymer. Also, the change in the concentration at the glass-side surface is smaller compared to the air-side surface. Furthermore, the concentration of the graft copolymer at both surfaces is higher than the average concentration of the graft copolymer in the bulk calculated from the weight percent of the added graft copolymer.

Surface morphological data were obtained by SEM. The photographs of the air- and glass-side surfaces of the blend film containing 10% GM-411 are shown in Figure 1. The siloxane component seems to form a larger domain on the glass-side surface than on the air-side surface, which indicates a finer distribution of the graft copolymer on the air-side surface. But a closer look at the photographs may indicate concave polysiloxane phase separation on the glass-side surface and convex polysiloxane domains on the air-side surface. This difference in morphology may have a close relation to the difference in contact angles of the air- and glass-side surfaces.

Resistance of the Surface Modification to Hexane Washing. It is very important to sustain such surface modification for a long time in order to maintain meaningful surface modification. Contact angle measurement after treatment with *n*-hexane clearly indicated that the PDMS was completely washed away due to its solubility in *n*-hexane, and consequently the blend film was deprived of any surface modification. Similarly, contact angle measurements[5] indicated that PMTS and MTS-45 were completely removed from the surface. On the other hand, the siloxane graft copolymers and the random copolymer MTS-25 were resistant to *n*-hexane extraction from the blend film surface. It is interesting that graft copolymers GM-211 and GM-411, both having siloxane contents similar to that of MTS-45, were not extracted. The resistance of graft copolymers to solvent extraction may indicate that the graft copolymers are accumulated on the surface with

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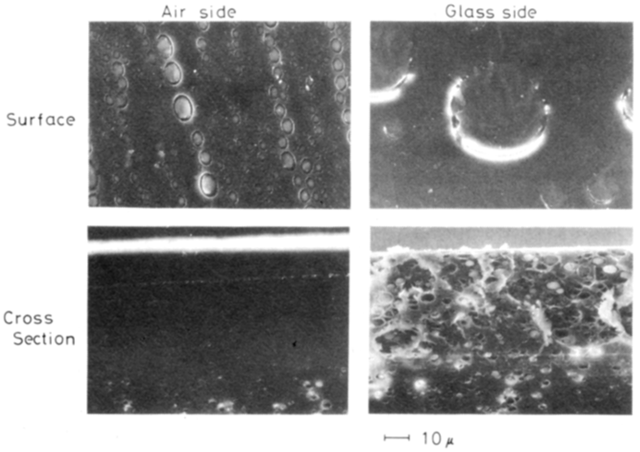

Figure 1. Observation of blend film containing 10% GM-411 by SEM.

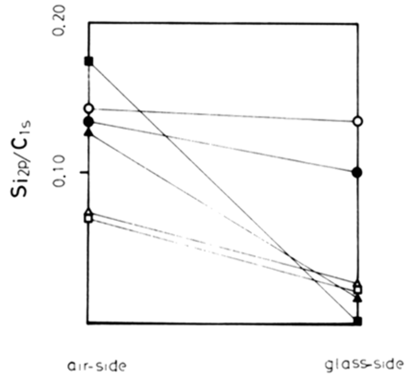

Figure 2. Relative ESCA intensity of the blend films containing 1% siloxane polymers. Before *n*-hexane treatment: (●) GM-411; (■) MTS-45; (▲) MTS-25. After *n*-hexane treatment: (○) GM-411; (□) MTS-45; (△) MTS-25.

the backbone PMMA chain embedded in the bulk PMMA as an anchor segment. The comparison in Figure 2 of ESCA data of the blend films of MTS-25, MTS-45, and GM-411 before and after extraction clearly indicates that siloxane random copolymer MTS-45 was washed away from the surfaces. In the blend system of MTS-25, only part of the siloxane polymers was washed away. However, the major part of the siloxane polymers remained even after *n*-hexane treatment. There was almost no change of the distribution of GM-411 in PMMA blend film during *n*-hexane treatment.

Observation by SEM indicates the formation of about 0.1-0.5 pits by *n*-hexane treatment of the blend film containing 1% siloxane polymers. The formation of pits is remarkable in the case of the polymer blend of MTS-45, which lost hydrophobicity of its surfaces during *n*-hexane treatment. This may indicate that the random copolymers, accumulated on the surfaces, were washed away. This pit formation was not noted in the polymer blend containing graft copolymer GM-411.

From the data mentioned above, a simplified picture of the graft copolymers in the blend film might be drawn as shown in Figure 3. (1) Siloxane graft copolymers phase separate on both the air- and the glass-side surfaces. The concentration of graft copolymers seems to be higher at or near the surfaces. (2) Under low surface energy conditions, the siloxane graft copolymers will accumulate at the air-side surface, resulting in a sharp change in the contact angle and ESCA. Although the average concentration of the graft copolymer at the glass-side surface seems to be similar to that at the air-side surface, the concentration at the glass-surface interface seems to be different from that of the average surface. The polar groups (presumably the carbonyl groups of the PMMA segment) might be oriented at the glass-surface interface by the high-energy glass-surface environment. This situation seems to be reflected in the slight change in contact angle at the glass-side surface. FT-ATRIR cannot distinguish differences in concentration in such a shallow layer.

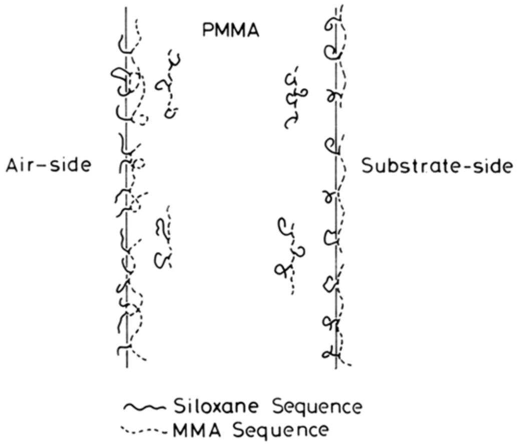

Figure 3. Simplified conceptual picture of the distribution of the graft copolymer in bulk PMMA.

Table II
Characteristics of Siloxane Polymers

polymer	siloxane content,[a] wt %	$\bar{M}_n \times 10^{-4}$ [b]	$\bar{M}_w/\bar{M}_n$ [b]	no. of grafts
GM-211[c]	42	4.23	1.84	4.0
GM-411[d]	43	5.77	1.46	2.7
PMTS[e]	70	12.5	2.20	
MTS-25[f]	24	10.2	1.36	
MTS-45[f]	44	12.3	1.41	
PDMS[g]	100	4.0		

[a] Determined by ^1H NMR ($CDCl_3$). [b] Determined by GPC and correlated to standard polystyrene. [c] Graft copolymer of ω-methacrylylsiloxane macromer ($\bar{M}_n$ = 5020) with MMA. [d] Graft copolymer of ω-methacrylylsiloxane macromer ($\bar{M}_n$ = 9200) with MMA. [e] Poly[(3-(methacryloyloxy)propyl)tris(trimethylsiloxy)silane]. [f] Random copolymers of MTS with MMA. [g] Poly(dimethylsiloxane).

Experimental Section

The syntheses of the polymer samples used in this study were reported elsewhere.[6] Characteristics of the polymer samples are listed in Table II.

Binary blends of PMMA ($\bar{M}_n = 6.7 \times 10^4$, $\bar{M}_w = 14.8 \times 10^4$) with one of the siloxane polymers varying in content from 0 to 10 wt % were prepared in THF. Films were prepared by casting 6–8% (w/v) solutions of THF on micro glass slides and allowing the solvent to evaporate during a 24–36-h period. The films were detached from the slide glass by dipping into water and dried under vacuum for 48–72 h. Contact angles for both air- and glass-side surfaces were measured at 20 °C on water droplets on a Kyowakagaku Model CA-A goniometer. FT-ATRIR spectra were recorded on a Digilab FTS-20 B/D, and ESCA spectra were recorded on a Kokusaidenshi Model ES-200 at an output level of 10 kV (20 mA) under a vacuum of 10^{-8} torr at 20 °C. The absorptions of C_{1s} and Si_{2p} and relative intensities were determined.

Registry No. PMMA (homopolymer), 9011-14-7.

Supplementary Material Available: Contact angle changes for water droplets for various siloxane polymer–PMMA blends at 20 °C (Suppl. Figure 1), FT-ATRIR spectra on the air-side surface of PMMA blend films containing various amounts of GM-411 (Suppl. Figure 2), FT-ATRIR spectra of PMMA blend film containing 10% GM-411 at different depths (Suppl. Figure

3), relative ESCA intensity of PMMA blend films containing various amounts of GM-411 (Suppl. Figure 4), contact angle changes for water droplets at 20 °C on the air-side surface of various siloxane polymer-PMMA blends treated with *n*-hexane (Suppl. Figure 5), observation by SEM of air-side surfaces of blend films containing 1% siloxane polymers GM-411 and MTS-45 before and after *n*-hexane treatement (Suppl. Figure 6), and ESCA of the air-side surface of PMMA blend film containing 1% GM-411 (Suppl. Figure 7) (8 pages). Ordering information is given on any current masthead page.

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Thermodynamic Interaction Parameter χ Determined by Small-Angle X-ray Scattering

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The thermodynamic interaction parameter χ is an important measure for solubility of polymers in solvents[1] and compatibility between different polymers. While osmometry has successfully been employed to determine this parameter in solution, experimental difficulties are encountered in its application to polymer–polymer systems. For such systems a few attempts have been made to apply scattering methods such as light scattering,[2] small-angle X-ray scattering (SAXS),[3] and neutron scattering.[4] In this study we measure χ for polymer–solvent systems by SAXS and compare it with results obtained by other methods, in order to examine the reliability of this technique as a means for determining χ.

According to the Flory–Huggins theory[1] the excess chemical potential $\Delta\mu_1$ per mole of solvent is given by the equation

$$\Delta\mu_1 = RT\{\ln(1 - \phi_2) + (1 - V_1/V_2)\phi_2 + \chi\phi_2^2\} \quad (1)$$

where ϕ_2 is the volume fraction of the polymer and V_1 and V_2 are the molar volumes of the solvent and the polymer, respectively. Although originally eq 1 was not meant to apply to dilute solutions, we can reinterpret it as a definition of χ applicable to all concentrations.

A general thermodynamic theorem[5] relates $\Delta\mu_1$ with the scattering law $S_m(0)$ per monomeric unit of the polymer observed at zero scattering angle by the equation

$$S_m^{-1}(0) = -(M_u/RTV_1)\partial\Delta\mu_1/\partial c \quad (2)$$

where M_u is the molar mass of the monomeric unit and c is the mass concentration of the polymer. Therefore integration of $S_m^{-1}(0)$ with respect to c yields $\Delta\mu_1$, which in turn determines χ through eq 1.

Monodisperse polystyrenes of four different molar masses were obtained from Pressure Chemical Co. Spectral grade toluene (E. Merk Co.) was dried over calcium hydride and fractionally distilled. SAXS measurements were made at 25.0 °C with a Kratky camera using Cu Kα radiation. The scattering law $S_m(h)$ per monomeric unit ($h = 4\pi(\sin\theta)/\lambda$) was determined by the excess scattered intensity $I(h)$ of the polymer through the relation

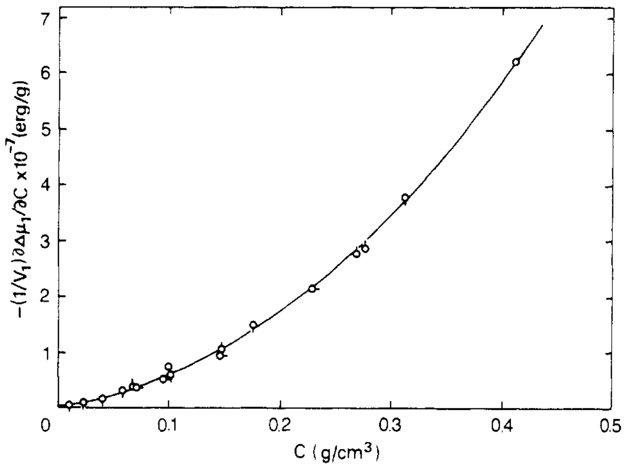

Figure 1. Value of $-(1/V_1)\partial\Delta\mu_1/\partial c$ plotted as a function of concentration c of polystyrene in toluene for molar masses M = 1.75 × 10⁴ (○), 3.7 × 10⁴ (ȯ), 5.0 × 10⁴ (○-), and 1.1 × 10⁵ (ϙ). The solid curve is used for the calculation of $\Delta\mu_1$.

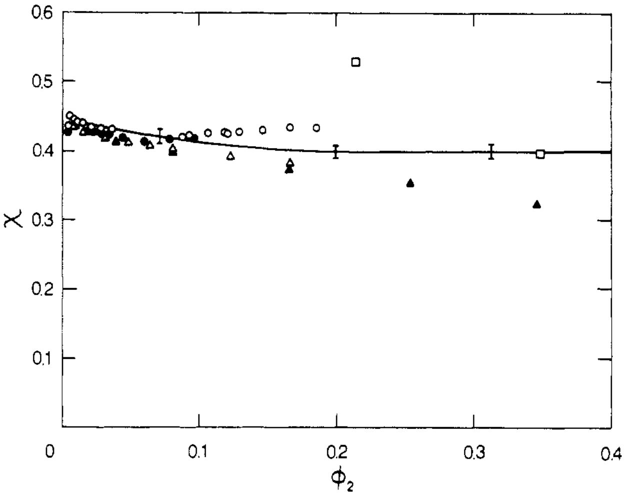

Figure 2. Thermodynamic interaction parameter χ plotted vs. volume fraction ϕ_2 of polystyrene in toluene. The solid curve represents the result by SAXS obtained in this work. The vertical bars indicate the errors in graphical integration. Other symbols show the results observed by other methods: (●) calculated from osmotic pressure measured by Schick et al.[7] for M = 5.4 × 10⁵ at 27 °C; (○) data from osmotic pressure measured by Kuwahara et al.[6] for M = 1.33 × 10⁵ at 30 °C; (△) obtained from light scattering by Scholte[2] for M = 1.63 × 10⁵ at 25 °C; (□) obtained from vapor pressure measured by Bawn et al.[8] for M = 2.9 × 10⁵ at 25 °C; (▲) calculated from sedimentation equilibrium measured by Scholte[9] for M = 1.54 × 10⁵ at 25 °C.

$$S_m(h) = (1/KcM_u)(a^2/Pd)I(h)$$

where a is the sample-to-detector distance, d is the sample thickness, and P is the intensity of the primary beam, which was determined by using a secondary standard sample, a Lupolen platelet. The contrast factor K is given by

$$K = i_e(z - \bar{v}_2\rho_e)^2N_A$$

where i_e is the Thomson constant, z is the number of moles of electrons per unit weight of the polymer, $\bar{v}_2$ is the partial

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