Surface Properties of the Fluorine-Containing Graft Copolymer of Poly((perfluoroalkyl)ethyl methacrylate)-*g*-poly(methyl methacrylate)

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Introduction

Fluorine-containing copolymers have important applications as additives for modifying surface properties in the fields of coatings, adhesives, films, fibers, and moldings. Random copolymers containing fluorinated segments are more common than graft copolymers because of the difficulties in preparing well-defined two-phase graft copolymers. A two-phase graft copolymer is expected to have both the merits of good miscibility with each homopolymer and excellent surface properties. Therefore, graft copolymers have attracted particular attention in the field of surface modification of various polymers.[1,2]

There are lots of works on low-energy modifications of polymer surface by using additive fluorinated graft copolymers and block copolymers.[3−7] But most of the works are related to the graft copolymers that have main chains composed of more than two species of (meth)acrylates with fluorine and hydrocarbon because of the polymers' solubility problems in common solvents.[8] It is well-known that when fluorinated oligomers/polymers are added to various base polymers, they are very effective in low-energy surface modification due to surface accumulation.[9−13] But it is hard to find the surface modification effect of a two-phase fluorinated graft copolymer compared with other polymer systems. In this study, the surface properties of a fluorine-containing two-phase graft copolymer of poly((perfluoroalkyl)ethyl methacrylate)-*g*-poly(methyl methacrylate) (PFMA-*g*-PMMA) and its additive effect on the surface energy of PMMA were compared with the random copolymer of PFMA-*r*-PMMA and homopolymer blend of PFMA/PMMA. The PFMA-*g*-PMMA was prepared using the macromonomer technique and modified emulsion copolymerization method suggested by the authors in the previous paper.[8] (Perfluoroalkyl)ethyl methacrylate (FMA) was chosen as a fluoromonomer because its homopolymer (PFMA) exhibits extremely low surface energy and has a wide range of applications for surface modification agents.[14−16] Methyl methacrylate (MMA) was used because of its several good characteristics such as optical clarity, UV stability, high electrical resistivity, and hydrolytic stability.

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Table 1. Surface Free Energies of PMMA, PFMA, PFMA-*r*-PMMA, and PFMA-*g*-PMMA

	surface free energy (dyn/cm)		
type of polymer	polar	dispersion	total
PMMA	4.3	35.9	40.2
PFMA	0.9	9.0	9.9
PFMA-*r*-PMMA	2.0	10.6	12.6
PFMA-*g*-PMMA	1.1	9.1	10.2

Experimental Section

Preparation of Specimens and Surface Characterization. The graft copolymer of PFMA-*g*-PMMA (PFMA/PMMA = 36/64, w/w) was prepared by modified emulsion copolymerization with PMMA macromonomer(DP = 90) and FMA [$CF_3(CF_2)_5CH_2CH_2COOC(CH_3)$═$CH_2$] using toluene as a emulsification solvent. PFMA homopolymer and random copolymer of PFMA-*r*-PMMA (PFMA/PMMA = 52/48, w/w) were synthesized by radical polymerization.[8] The specimens for contact angle measurements were prepared by solvent diecasting. Each homopolymer of PMMA and PFMA were diecasted using the good solvent of chloroform and 1,1,2-trichlorotrifluoroethane (R-113). The mixed solvents of chloroform and R-113 ($CHCl_3$/R-113 = 1/2, w/w) were used for copolymers and preparation of surface modification test specimens composed of base PMMA and copolymer additives. The polymer contents in solution were 1.5 wt %. Solvent diecastings were done using a horizontal Teflon mold with clean slide glass which was enclosed. Polymer films were prepared by slow evaporation of solvents for 24 h by controlling the needle valve attached to the enclosure to prevent the sudden organization of a microdomain and to endow the free diffusion of additives to the polymer surface. After diecasting, vacuum evacuation was done at room temperature for 3 days. Typically, the thickness of the polymer films was about 10 μm, and surface roughness was within 0.1 μm like a mirror surface. To investigate the thermal effect of the diecasted-PMMA films modified by the copolymers, annealing were done at 140 °C and 24 h.

Advancing contact angles were measured with an optical goniometer (Rame-hart, 100-series) at 20 ± 2 °C. Wetting liquids used for contact angle measurements were water and methylene iodide, which were suggested by Owens and Wendt.[17] Total surface free energies and their polar and dispersion components were calculated by Fowkes' equation as follows:[18]

$$\gamma_{LV}(1 + \cos\theta_c) = 2(\gamma_{SV}^{d}\gamma_{LV}^{d})^{0.5} + 2(\gamma_{SV}^{p}\gamma_{LV}^{p})^{0.5}$$

where p and d are the polar and dispersion components of each surface free energy, θ_c is the contact angle, and γ_{SV} and γ_{LV} are the interfacial tensions at solid−vapor and liquid−vapor interfaces, respectively. By measurement of the contact angles on a solid surface with two liquids which the polar and dispersion components of surface tensions are known, the total surface free energy of a solid and its components can be calculated.

Results and Discussion

Table 1 shows the comparison of surface free energies estimated from contact angle data for the surfaces of PFMA-*g*-PMMA, PFMA-*r*-PMMA, and homopolymers of PFMA and PMMA. The surface free energy of PFMA-*g*-PMMA is nearly the same as that of PFMA. The perfluoroalkyl group [$CF_3(CF_2)_5CH_2CH_2COO$−], the side chain of PFMA, is known to play a critical role for low-energy surface and arranged to the outermost layer at the air−polymer interface.[14−16] Hence the similar surface energy of PFMA-*g*-PMMA to PFMA indicates

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Table 2. Contact Angles Measured for the Surfaces of PMMA Containing PFMA-*g*-PMMA and PFMA-*r*-PMMA, Respectively, as a Function of FMA Content

	PFMA-*g*-PMMA				PFMA-*r*-PMMA			
	before annealing		after annealing		before annealing		after annealing	
content of FMA (FMA/PMMA, wt %)	water	methylene iodide	water	methylene iodide	water	methylene iodide	water	methylene iodide
0.0001	82.9	43.0	83.0	45.0	79.4	40.5	79.0	42.0
0.001	82.7	43.4	83.4	50.8	81.3	42.3	79.3	42.0
0.01	104.6	70.6	109.7	82.0	89.1	60.1	89.0	60.0
0.1	113.0	88.0	117.0	95.0	101.5	80.1	102.0	80.0
1	115.9	97.5	117.0	99.0	105.0	83.9	107.0	88.0

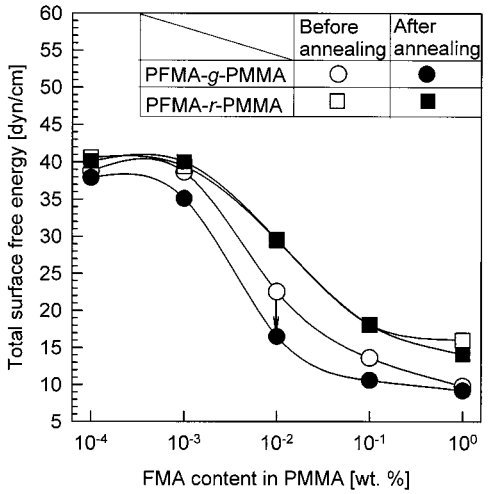

Figure 1. Variations of surface free energies for the surfaces of PMMA containing PFMA-*g*-PMMA and PFMA-*r*-PMMA, respectively, as a function of FMA content.

that the outermost layer of PFMA-*g*-PMMA surface is believed to be composed of perfluoroalkyl side chains of FMA segments. PFMA-*g*-PMMA exhibits a much lower surface free energy than PFMA-*r*-PMMA even though the graft copolymer contains less FMA content than the random copolymer. The reason seems that the distribution of MMA monomer units in the PFMA-*r*-PMMA dilutes the concentration of FMA units at the surface and thus moderates the impact of the FMA units on the surface properties. That is, the low surface energy effects by perfluoroalkyl groups of FMA segments at the outermost layer may be hindered by closely attached methyl ester groups of MMA segments at the molecular level which have a fairly higher surface energy than that of the perfluoroalkyl groups.

To compare surface modification abilities, PFMA-*g*-PMMA and PFMA-*r*-PMMA were added to PMMA in various FMA contents from 0.0001 to 1.0 wt %, and estimation of surface energy was done (Figure 1) with measured contact angle data (Table 2). The contact angles for PMMA surfaces containing less than 0.001 wt % of FMA show no evident change with the FMA content regardless of the copolymer type. That is, they are comparable to the intrinsic contact angles for the PMMA surface of 79.8 and 41.2° with water and methylene iodide, respectively.[18] However as FMA content increases more than 0.001 wt %, the contact angles increases with both copolymers. The contact angles of the graft copolymer increase more than the random copolymer with the same content of FMA, and 0.1 wt % is required to reach the copolymer's surface energy itself comparing to almost 1% of random copolymer. Therefore, the low-energy surface modification effect of the graft copolymer is better than that of the random copolymer during solvent diecasting and annealing.

In the literature, although the contents of fluorinated graft/block copolymers vary according to based polymers, additive copolymer types, and their ingredients of main or side chains, contents of fluorinated segments of about 0.5 wt % to reach the lowest surface energy of the films are typical.[3−7,9] Also as described in our previous paper, it is difficult to synthesize the two-phase graft copolymer of PFMA-*g*-PMMA with a fluorinated long side chain used in this study by solvent copolymerization because of solubility problems of the graft copolymer during the reaction.[8] Of course, it seems possible to synthesize a graft copolymer with a shorter side chain, because the solubility may increase. That is, in the case of using a mixture of fluorinated monomer with different side chain lengths, the shorter side-chain length fluoro monomer may react faster and the resultant graft copolymer may have better solubility in common solvents than the longer side-chain length monomer used in this study.[5] Even though the synthesis method is different and there are some differences in solubility of the fluorinated graft copolymer, the contact angles of water for PMMA surface modified by the graft copolymer of poly((perfluoroalkyl)ethyl acrylate)-*g*-PMMA (PFA-*g*-PMMA) are less than present study at about 72, 105, and 109° at 0.01, 0.1, and 1 wt % FA in order.[5] The reasons for the higher water contact angles found in this study seem to come from the following: (1) There is a larger repeat unit of FMA between PMMA branches because our study used a higher molecular weight PMMA macromonomer (DP = 90), and there is the resultant good surface accumulation tendency. (2) As mentioned above for the solubility of the graft copolymer, it may be possible that the graft copolymer used in this study has a longer fluorinated side chain than that used in previous work.

Assuming that the density differences are negligible and FMA segments are completely arranged at the outermost layer because of their high surface active characteristics, the depth of FMA segment layer formed at the surface is estimated about 1.0 Å with 0.001 wt % FMA. According to the literature, the length of the perfluoroalkyl side chain of PFMA is about 15 Å.[19,20] This fact indicates that, with less than 0.001 wt % FMA, the amount of FMA segments is not sufficient to form a monolayer of perfluoroalkyl side chain at the surface. To obtain a good monolayer of perfluoroalkyl side chain at the air−polymer interface, the content of FMA should be more than 0.001 wt %. The FMA content needed may explain the rapid increase in contact angles more than 0.01 wt % FMA. From Figure 1, whereas the total surface energy for the random copolymer is nearly unchanged by annealing, the graft copolymer is significantly lowered from 0.001 to 0.1 wt % FMA. Figure 2

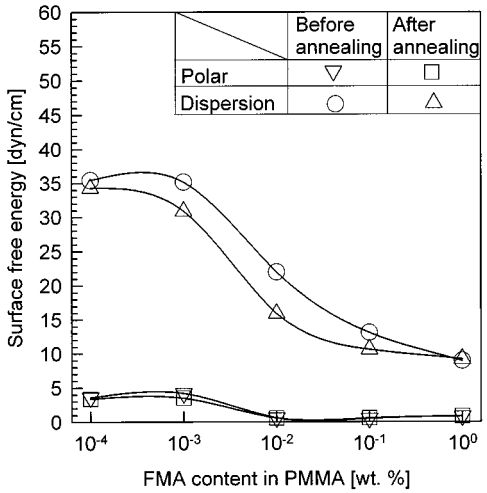

Figure 2. Variations of polar and dispersion components of surface free energies for the surfaces of PMMA containing PFMA-*g*-PMMA as a function of FMA content.

represent changes of polar and dispersion components of surface energy for the graft copolymer before and after annealing. In the case of the random copolymer, annealing did not change both components. However for the graft copolymer, annealing can lower the dispersion components even though the polar components do not vary significantly. Because the decreasing effect of the dispersion component mainly comes from the exposure of the perfluoroalkyl side chain to the surface, annealing may enhance the conformation of the FMA segments at surface and the low surface energy modification effect of the graft copolymer.

A number of explanations can be possible for the difference of surface energy lowering effects between the random and graft copolymers during diecasting and annealing. One explanation is related to the strengthening of the microdomain formation after the diecasting process. That is, because the graft copolymer has more concentrated FMA segments than the random copolymer, additional microdomain formation of FMA segments from the surface-segregated graft copolymer occurs with resultant greater lowering of the surface energy. On the other hand, in the random copolymer it is hard to form microdomains by annealing due to its even distribution for each segment of MMA and FMA. Another explanation may come from hydrophobicity differences between the two polymers and anchoring effect of PMMA branches in the graft copolymer. Even if both polymers are highly hydrophobic with long fluorinated side chains, if there is small difference in surface energy, the more hydrophobic polymer moves to the surface by annealing.[12] Although both polymers show very low surface energy (Table 1), there is a difference of surface energy between two polymers of 2.4 dyn/cm. This may be the reason for the additional surface energy decrease of the graft copolymer. Also, the graft copolymer has fairly long branches of PMMA which have a affinity with based PMMA, PMMA branches may have a anchoring effect during solvent diecasting, and additional surface segregation occurs during the annealing of the graft copolymer.

The total surface energy of the PFMA/PMMA blend containing 1.0 wt % of PFMA in PMMA was 10.0 dyn/cm which was measured without annealing. This is nearly the same as that of PFMA-*g*-PMMA containing 1.0 wt % of FMA after annealing. Therefore the surface modification effect of PFMA in the PFMA/PMMA blend might be stronger than FMA segments of PFMA-*g*-PMMA. The MMA segments in the backbone of the random copolymer and branched segments of the graft copolymer are expected to provide an anchoring effect to the PMMA base and reduce the effect of the segregation of the copolymers to the surface compared to PFMA in the PFMA/PMMA blend. Among the three type of polymer systems, the homopolymer blend is best for lowering the surface energy, but the high hydrophobicity of PFMA hinders miscibility with other polymers, for example, PMMA.[8] The graft copolymer has nearly the same effect as PFMA, far superior to the random copolymer for surface energy modification. Due to the PMMA branches, the graft copolymer is expected to have better miscibility with PMMA than with PFMA. The graft copolymer is a better surface modification agent than the random copolymer or PFMA homopolymer, because the comonomer variability allows both excellent surface energy modification and good miscibility with base polymers.

Conclusions

The surface properties of the two-phase graft copolymer of PFMA-*g*-PMMA were investigated and compared to those of PFMA-*r*-PMMA and PFMA homopolymer. The ability of FMA-containing polymers for lowering surface energy seems mainly determined by the hydrophobicity and the structure of the polymers. The surface modification effect of PFMA in a PFMA/PMMA blend might be higher than that of PFMA-*g*-PMMA. Annealing enhances the graft copolymer's ability to lower the surface free energy to nearly the same level as that of the PFMA homopolymer. This means that FMA segments of the graft copolymer have good surface modification ability compared to the random copolymer. The reason for the poorer surface modification activity of the random copolymer seems to come from less hydrophobicity than that of PFMA or PFMA-*g*-PMMA and hindrance of perfluoroalkyl groups by methyl ester groups of MMA segments. Due to PMMA branches, the graft copolymer is expected to have better miscibility with the PMMA homopolymer. PFMA-*g*-PMMA used in this research is a better surface modification agent than both the random copolymer and PFMA homopolymer because of its good miscibility with other polymers and its extraordinary ability of lowering the surface energy.

References and Notes

(1) Noshay, A.; McGrath, J. E. *Block Copolymers: Overview and Critical Survey*; Academic Press: New York, 1977; pp 13−16.
(2) Andrade, J. D. *Surface and Interfacial Aspects of Biomedical Polymers*; Plenum Press: New York, 1985; Vol. 1, pp 373−394.
(3) Chujo, Y.; Hiraiwa, A.; Kobayashi, H.; Yamashita, Y. *J. Polym. Sci.* **1988**, *26*, 2991.
(4) Yamashita, Y.; Tsukahara, Y.; Ito, H. *Polym. Bull.* **1982**, *7*, 289.
(5) Yamashita, Y.; Tsukahara, Y.; Ito, H.; Okada, K.; Tajima, Y. *Polym. Bull.* **1981**, *5*, 335.
(6) Tsukahara, Y.; Kohno, K.; Inoue, H.; Yamashita, Y. *Nippon Kagaku Kaishi* **1984**, *6*, 1070.
(7) Oshiebe, Y.; Ishigaki, H.; Ohmura, H.; Yamamoto, T. *Kobunshi Ronbunshu* **1989**, *46*, 89.
(8) Park, I. J.; Lee, S.-B.; Choi, C. K. *Polymer* **1997**, *38*, 2523.
(9) Park, I. J.; Lee, S.-B.; Choi, C. K. *J. Appl. Polym. Sci.* **1994**, *54*, 1449.

(10) Park, I. J.; Lee, S.-B.; Koh, J. *Hwahak Konghak* **1992**, *30*, 303.
(11) Bernett, M. K. *Polym. Eng. Sci.* **1977**, *17*, 450.
(12) Phillips, R.; Dettre, R. *J. Colloid Interface Sci.* **1976**, *56*, 251.
(13) Landsam, M.; Manrell, G *J. Appl. Polym. Sci.* **1975**, *19*, 2235.
(14) Johnson, R. E.; Dettre, R. H. *Polym. Prepr.* **1987**, *28*, 48.
(15) Ramharack, R.; Nguyen, T. H. *J. Polym. Sci. C* **1987**, *25*, 93.
(16) Park, I. J.; Lee, S.-B.; Choi, C. K.; Kim, K.-J. *J. Colloid Interface Sci.* **1996**, *181*, 284.
(17) Owens, D. K.; Wendt, R. C. *J. Appl. Polym. Sci.* **1969**, *13*, 1741.
(18) Wu, S. *Polymer Interface and Adhesion*; Marcel Dekker: New York, Basel, 1982; pp 169−213.
(19) Volkov, V. V.; Plate, N. A.; Takahara, A.; Kajiyama, T.; Amaya, N.; Murata, Y. *Polymer* **1992**, *33*, 1316.
(20) Collette, C.; Bourgeois, C.; Taupin, C.; Quet, C.; Tran, M. D. *Analusis* **1989**, *17*, 464.

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