

The Study of Surface Segregation and the Formation of Gradient Domain Structure at the Blend of Poly(Methyl Methacrylate)/Poly(Dimethyl Siloxane) Graft Copolymers and Acrylate Adhesive Copolymers

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ABSTRACT: The effect of siloxane chain length on surface segregation of poly(methyl methacrylate)-grafted poly(dimethyl siloxane) (PMMA-g-PDMS)/poly(2-ethylhexyl acrylate-co-acrylic acid-co-vinyl acetate) [P(2EHA-AA-VAc)] blends was investigated. The blends of PMMA-g-PDMS with P(2EHA-AA-VAc) showed surface segregations of PDMS components. The surface enrichments of PDMS in the

blends depended significantly on the PDMS chain length. Also, this blend showed the gradient domain structure. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 375–380, 2003

Key words: acrylate copolymer/siloxane graft copolymer blends; ATR-FTIR; surface segregation; gradient domain structure

INTRODUCTION

The surface segregation behavior of block or graft copolymers is very important in fields of adhesive, coating, lubricants, and surface modification.^{1–4} The surface segregations of copolymers or their blends are derived from components with low surface tension such as Si-containing or F-containing copolymers.

The surface properties of poly(dimethyl siloxane) (PDMS) containing polymer blends was investigated over the last 30 years. A key property of PDMS is its low surface energy, which results in surface segregation of PDMS in most polymer blend systems. Because polysiloxanes and their copolymers have very interesting properties such as elastomeric behavior; good thermal, UV, and oxidative stabilities; good weatherability; low surface energy; high gas permeability; biocompatibility; and electrical properties, they should be useful materials having surface segregations.^{5–8}

In our previous studies,^{9–13} surface segregation and gradient domain structure of poly(2-ethylhexyl acrylate-co-acrylic acid-co-vinyl acetate) [P(2EHA-AA-VAc)]/poly(vinylidene fluoro-co-hexafluoro-acetone) [P(VDF-HFA)] blends were investigated. It was found that the P(VDF-HFA) component was enriched on the surface, and P(2EHA-AA-VAc) component was pre-

cipitated on the bottom (contact with substrate: PDMS-coated paper) by using SEM, attenuated total reflection (ATR)-FTIR, X-ray, photoelectron spectroscopy (XPS), and so on.

Because surface tension of PDMS is comparable with that of fluoro polymers, such as P(VDF-HFA), blends of PDMS-containing copolymer with P(2EHA-AA-VAc) should provide surface enrichment (surface segregation).

For this study, we prepared several types of poly(methyl methacrylate)/poly(dimethyl siloxane) graft copolymers (PMMA-g-PDMS)^{14–17} and studied surface segregation of PMMA-g-PDMS/P(2EHA-AA-VAc) blends.

EXPERIMENTAL

Samples

Three types of PMMA-g-PDMS's and P(2EHA-AA-VAc)s used in this study were the same samples used in our previous study.¹⁸ Molecular characteristics and structures are listed in Table I.

Differential scanning calorimeter measurements

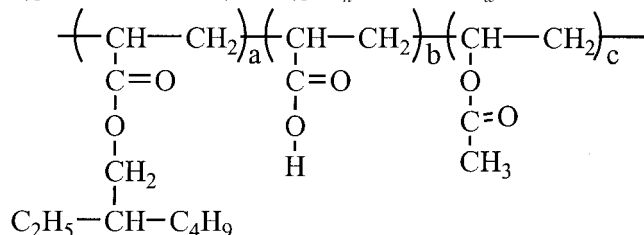
To evaluate the miscibility between components, the glass transition temperature (T_g) of P(2EHA-AA-VAc)/PMMA-g-PDMS blends were determined by using a 910 DSC DuPont 990 system at a heating rate of 10°C/min under nitrogen gas.

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TABLE I
Composition and Structure of PMMA-g-PDMS and P(2EHA-AA-VAc)

2-ethylhexyl acrylate/acrylic acid/vinyl acetate[P(2EHA-AA-VAc)]

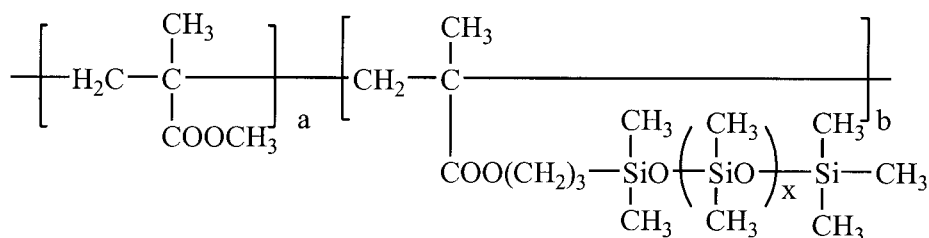
P(2EHA-AA-VAc)[a/b/c = 80/5/15(mol %)]; $M_n = 50,600$, $M_w = 274,000$



Poly(methyl methacrylate)/Poly(dimethyl siloxane) graft copolymers

PMMA-g-PDMS-01 ($x = 25$); $M_n = 7000$, $M_w = 13,000$, $M_w/M_n = 1.8$

PMMA-g-PDMS-02 ($x = 50$); $M_n = 26,7000$, $M_w = 37,500$, $M_w/M_n = 1.4$



ATR-FTIR

The ATR-FTIR measurements for the surface of film specimens were carried out by using a Nicolet 20SXB-FTIR with a prism of KRS-5 and two incidence angles of 45° and 90°.

SEM

The sectional layer of the P(2EHA-AA-VAc)/PMMA-g-PDMS blend was observed by using a Hitachi S-800 at room temperature. The films of the blends were embedded in epoxy resin. Then, the embedded blends were cut at -130°C with an ultramicrotome and stained with ruthenium tetroxide.

RESULTS AND DISCUSSION

Figure 1 shows the ATR-FTIR spectra of P(2EHA-AA-VAc)/PMMA-g-PDMS (50/50) blend surfaces in contact with air at the incidence angle of 45°. Figure 2 shows the ATR-FTIR spectra of P(2EHA-AA-VAc)/PMMA-g-PDMS (50/50) blend surfaces in contact with air at the incidence angle 90°. The surface of the P(2EHA-AA-VAc)/PMMA-g-PDMS-01 blend film did

not show the siloxane peak at incidence angle of 45° or 90°. On the other hand, the surface of the P(2EHA-AA-VAc)/PMMA-g-PDMS-02 blend film showed a very strong Si—O—Si peak between 1100 and 1200 cm^{-1} at incidence angles of 45° and 90°. This indicates that the surface was rich in siloxane polymer. At the same blend composition, the concentration of siloxane on the surface was significantly affected by siloxane chain length in graft copolymers. Siloxane concentration at the surface of these blends increased as siloxane chain length increased.

The ATR-FTIR spectra of P(2EHA-AA-VAc)/PMMA-g-PDMS-02 (50/50, 30/70, and 70/30) blends, coated onto the release liner (blend surface in contact with air), at an incidence angle 45°, are shown in Figure 3. The ATR-FTIR spectra of P(2EHA-AA-VAc)/PMMA-g-PDMS-02 (50/50, 30/70, and 70/30) blends, coated onto the release liner (blend surface in contact with air), at incidence angle of 90° is shown in Figure 4.

At all blend compositions, siloxane polymer is enriched on the surface of the blend film of P(2EHA-AA-VAc)/PMMA-g-PDMS-02 at incidence angles of 45° and 90°. On the other hand, the blends film of

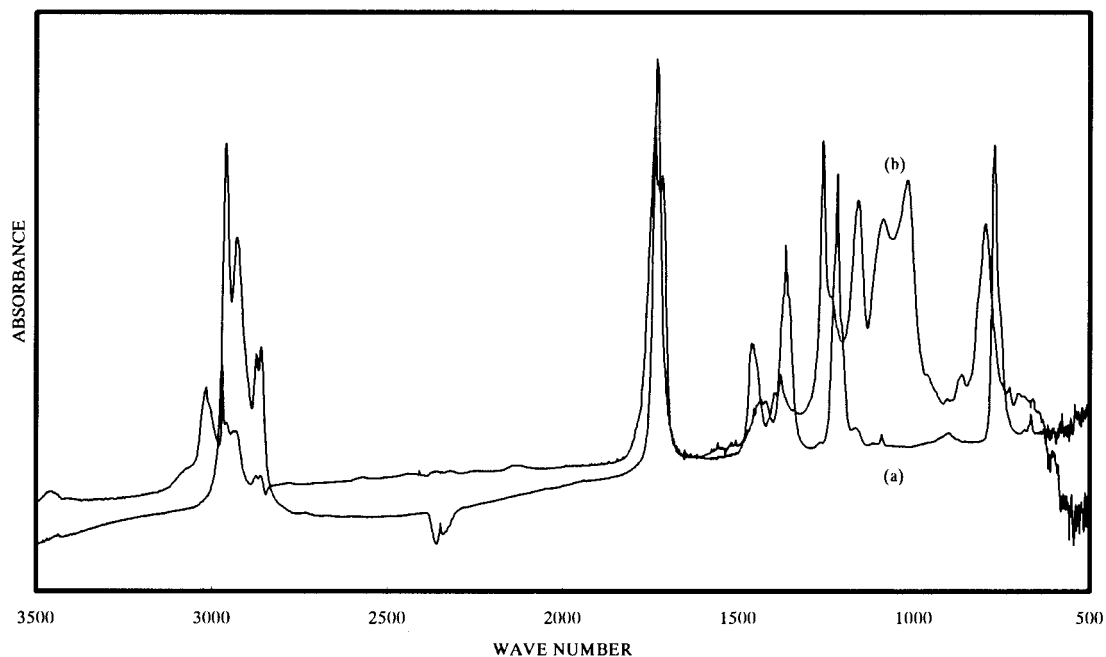


Figure 1 Infrared spectra for surface of the P(2EHA-AA-VAc)/PMMA-g-PDMS (50/50) blend by ATR-FTIR method (incidence angle: 45°). (a) (50/50) blend of P(2EHA-AA-VAc)/PMMA-g-PDMS-01; (b) (50/50) blend of P(2EHA-AA-VAc)/PMMA-g-PDMS-02.

P(2EHA-AA-VAc)/PMMA-g-PDMS-01 did not show siloxane-rich surfaces at all blend compositions. From the ATR-FTIR result, it is suggested that the concentration of siloxane at the surface was different depending on the siloxane chain length in the graft polymers.

From the ATR-FTIR results, it is confirmed that siloxane polymer migrated to the surface. To confirm miscibility of PMMA-g-PDMS and P(2EHA-AA-VAc), DSC experiments were conducted. DSC scanning results for these blends films are shown in Figure 5. The

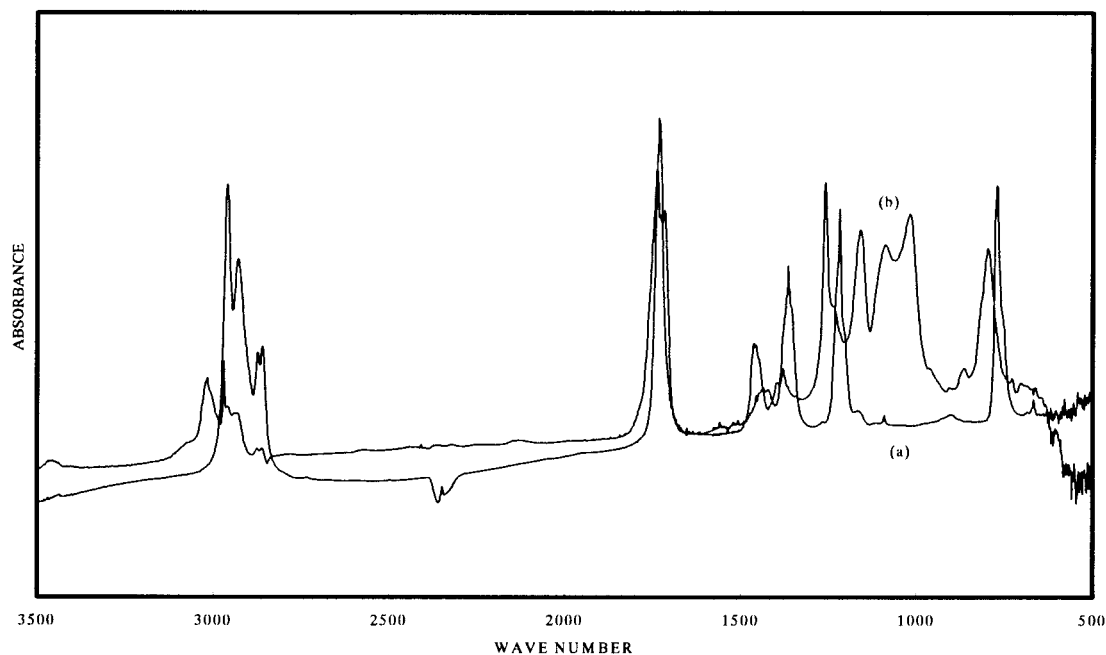


Figure 2 Infrared spectra for surface of the P(2EHA-AA-VAc)/PMMA-g-PDMS (50/50) blend by ATR-FTIR method (incidence angle: 90°). (a) (50/50) blend of P(2EHA-AA-VAc)/PMMA-g-PDMS-01; (b) (50/50) blend of P(2EHA-AA-VAc)/PMMA-g-PDMS-02.

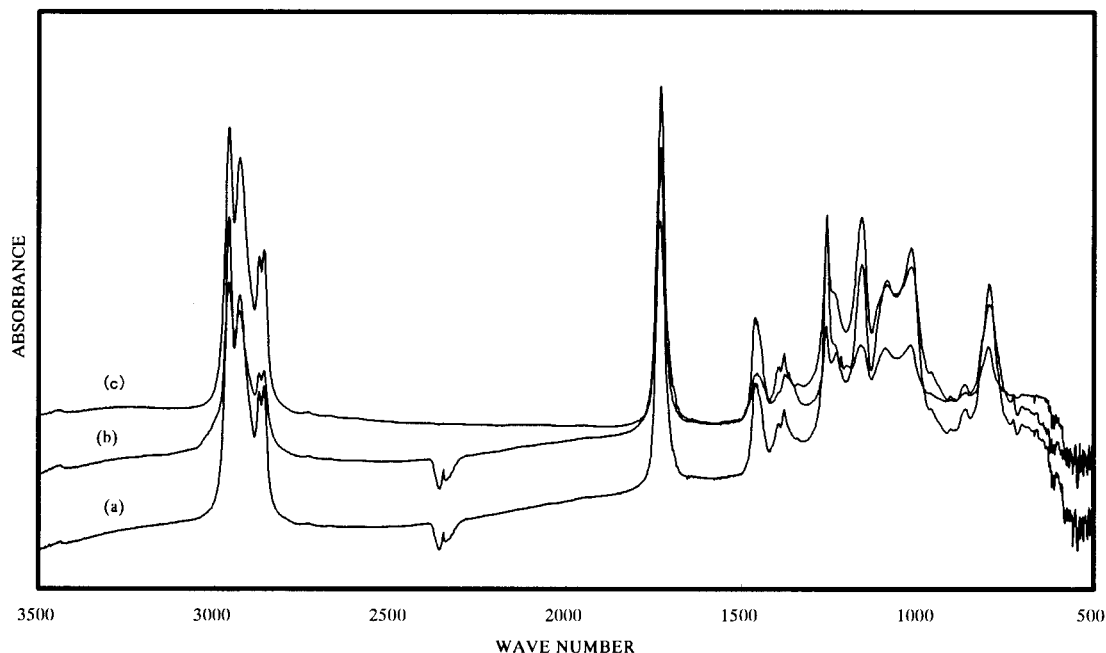


Figure 3 ATR-FTIR spectra for P(2EHA-AA-VAc)/PMMA-g-PDMS-02 blends according to compositional change at the 45° incidence angle. (a) P(2EHA-AA-VAc)/PMMA-g-PDMS-02 = 50/50; (b) P(2EHA-AA-VAc)/PMMA-g-PDMS-02 = 30/70; (c) P(2EHA-AA-VAc)/PMMA-g-PDMS-02 = 70/30.

blend films showed two T_g 's, which are -70 and 120°C , respectively. There is no T_g shift of the two components after blending, indicating that the two components, P(2EHA-AA-VAc) and PMMA-g-PDMS, are not compatible.

The SEM photograph of a sectional layer for P(2EHA-AA-VAc)/PMMA-g-PDMS = 30/70 is shown in Figure 6. Ellipsoidal domains corresponding to the P(2EHA-AA-VAc) particle are observed with increasing sizes from surface to bottom. P(2EHA-AA-VAc), having high

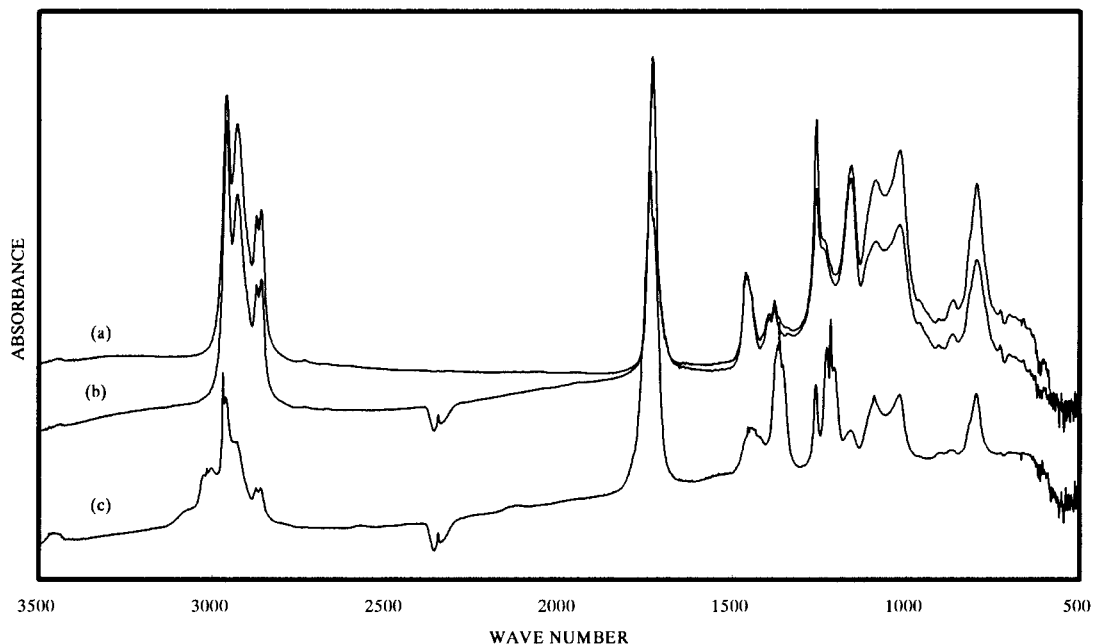


Figure 4 ATR-FTIR spectra for P(2EHA-AA-VAc)/PMMA-g-PDMS-02 blends according to compositional change at the incidence angle 90°. (a) P(2EHA-AA-VAc)/PMMA-g-PDMS-02 = 70/30; (b) P(2EHA-AA-VAc)/PMMA-g-PDMS-02 = 50/50; (c) P(2EHA-AA-VAc)/PMMA-g-PDMS-02 = 30/70.

surface tension, formed the domains. On the other hand, PMMA-g-PDMS, having low surface tension, formed a continuous matrix.

As can be seen in the photo, P(2EHA-AA-VAc)/PMMA-g-PDMS shows surface segregation of PMMA-g-PDMS and gradient domain morphology in which the diameter of dispersed domains is gradually increasing with increasing distance from the surface. According to our previous studies,^{19,20} the surface segregation and gradient domain structure in immiscible polymer blends are caused by the difference of the specific gravity and the surface tension between components. Because specific gravity of P(2EHA-AA-VAc) is lower than that of PMMA-g-PDMS, the surface segregation and gradient domain in this system is caused by a great difference of surface tension between P(2EHA-AA-VAc) and PMMA-g-PDMS.

Inoue et al.² reported that the polysiloxane segments of PDMS-PMMA block copolymer and their PMMA blends were accumulated on the air side surfaces of solution-cast film and surface segregation was significantly affected by siloxane chain length in block copolymers. Gorelova et al.⁷ reported that the surface segregation of siloxane, in blends of PMMA/MDMS graft copolymers in poly(vinyl chloride), was influenced by the siloxane chain length. Similar surface segregation of siloxane segments for some types of siloxane-containing block copolymers was reported by McGrath et al.^{21,22} It was noticed that the siloxane surface segregation substantially depended on the block length of siloxane.

These results support the observation that surface segregation of PMMA-g-PDMS took place in the P(2EHA-AA-VAc)/PMMA-g-PDMS blends and was significantly influenced by the siloxane chain length in

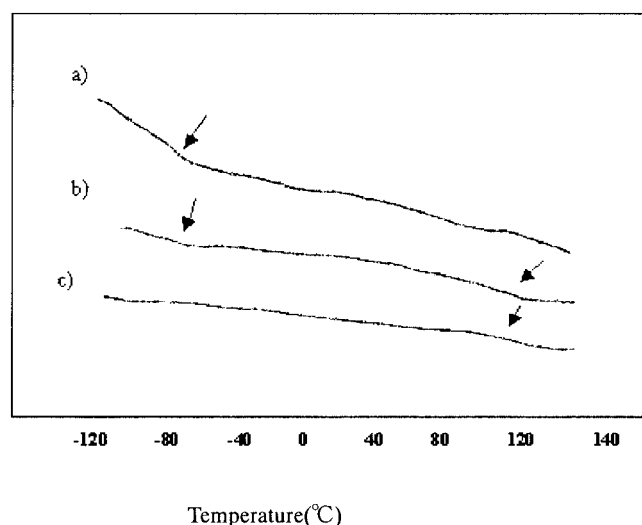


Figure 5 DSC Thermogram of (a) P(2EHA-AA-VAc); (b) P(EHA-AA-VAc)/PMMA-g-PDMS-02 = 50/50; (c) PMMA-g-PDMS-02.

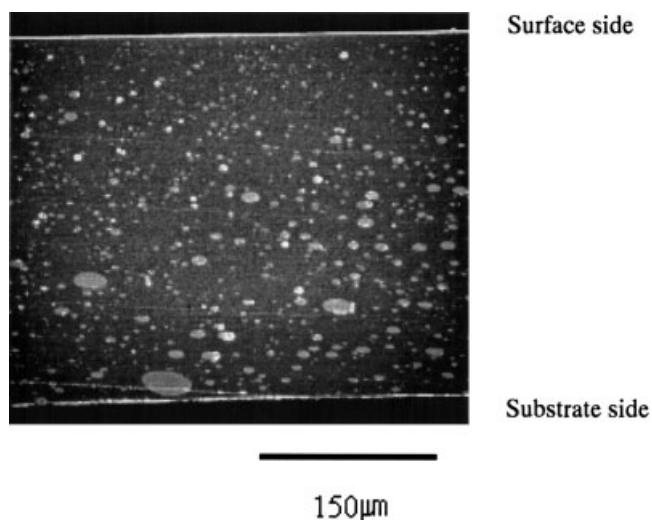


Figure 6 SEM photographs of sectional layer for P(2EHA-AA-VAc)/PMMA-g-PDMS-02 = 70/30 blends. The dispersed domains are from P(2EHA-AA-VAc).

PMMA-g-PDMS. Also, a gradient domain structure was confirmed through SEM measurement of PMMA-g-PDMS/P(2EHA-AA-VAc) blend films.

CONCLUSION

The effect of siloxane chain length on surface segregation of PMMA-g-PDMS/P(2EHA-AA-VAc) blends was investigated. The blends of PMMA-g-PDMS with P(2EHA-AA-VAc) showed surface segregation of the PDMS component. The surface enrichment of PDMS in the blends depended on the PDMS chain length, specifically, a PDMS chain length in PMMA-g-PDMS increased, and the concentration of PDMS at the blend surface increased.

SEM photography indicated a gradient domain structure. It is considered that P(2EHA-AA-VAc), having high surface tension, formed the domains, and PMMA-g-PDMS, having low surface tension, moved to the surface. Also, it is considered that PMMA-g-PDMS, having higher specific gravity than that of P(2EHA-AA-VAc), migrated to substrate, and domains of P(2EHA-AA-VAc) are moved to the surface side.

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