

## **Study on the surface properties and morphology of blends of HDPE/PE-g-PDMS**

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### **SUMMARY**

Film surface properties and morphology of blends of HDPE with PE-g-PDMS were studied by contact angle, ESCA and SEM measurements. All the results showed clearly the surface enrichment of PDMS segments on the film surface although the difference in the surface tension of the two components is smaller than that between PDMS and hydrophilic polymers. According to the SEM results, the PDMS segments were enriched on the surface in separate domains.

### **INTRODUCTION**

Researchers generally agree that a surface enrichment of polydimethylsiloxane (PDMS) segments occurs when a PDMS-containing block or graft copolymer is blended with a corresponding homopolymer with a surface tension lower than that of PDMS(1-3). Work by LeGrand *et al*(1) on blends of poly(bisphenol A carbonate) (PAC) with its segmented copolymer containing PDMS, PAC/(PAC-PDMS)<sub>n</sub>, indicated that the surface of the blends was covered by PDMS. The same result was also claimed by Kawakami *et al*(2) on the blends of poly(methyl methacrylate) (PMMA) with PMMA-g-PDMS. On the other hand, Dwight *et al*(3) concluded that about 70% of the surface of PAC/(PAC-PDMS)<sub>n</sub> blends was covered by PDMS when the content of (PAC-PDMS)<sub>n</sub> was in the range of 0.01%--10%. Further work by Schmitt *et al*(4), using ESCA in conjunction with ion scattering spectroscopy (ISS), showed that PAC did even exist on the surface of (PAC-PDMS)<sub>n</sub> copolymers. These authors set up two models for the morphology of the surface of (PAC-PDMS)<sub>n</sub> copolymers, depicting perpendicular orientation of domains of each segment to the surface.

Work done in this laboratory on the synthesis of the graft copolymer PE-g-PDMS, a backbone polyethylene with PDMS pendant side chains of uniform length, by copolymerization of ethylene and the macromer CH<sub>2</sub>=CH-CH<sub>2</sub>-PDMS as well as its use in modifying the wear property of HDPE has been reported(5). This paper presents the results of our recent studies on the surface properties and morphology of blends of semi-crystalline high-density polyethylene (HDPE) with PE-g-PDMS.

### **EXPERIMENTAL**

#### **Sample Preparation**

The synthesis of the graft copolymer PE-g-PDMS by slurry copolymerization of ethylene with allyl-terminated PDMS catalyzed by a vanadium catalyst has been reported previously(5). The graft copolymer samples (G-11 and G-14) used to blend with HDPE were synthesized by copolymerization of ethylene with different quantity of the same PDMS macromer ( $\bar{M}_n=8.9 \times 10^5$ ) in the feed. The PDMS content in these samples was characterized by  $^1\text{H-NMR}$  to be 3% (G-11) and 16% (G-14), respectively. Films of blends of HDPE and PE-g-PDMS in various proportions were obtained by casting a 2% decalin solution on glass at  $130^\circ\text{C}$ . After complete evaporation of the solvent, films of blends were dried in vacuo at ambient temperature for at least 24 hours.

#### Instruments

Contact angle of water on the surface of the films was measured by a contact angle goniometer (G-2, Japan). The surface composition was analyzed by ESCA (VG, ESCALAB, MK) with MgBe radiation. Morphological study was done by SEM (JXA-840).

#### RESULTS AND DISCUSSION

The advanced contact angle of water ( $\theta_a$ ) on the blend film surface increased with increase in the content of graft copolymer PE-g-PDMS in the HDPE/PE-g-PDMS blends (Fig. 1). With the progress in PE-g-PDMS content in the blends, from 0% to 2.5% for sample G-14 (16% PDMS in PE-g-PDMS) or to 13% for G-11

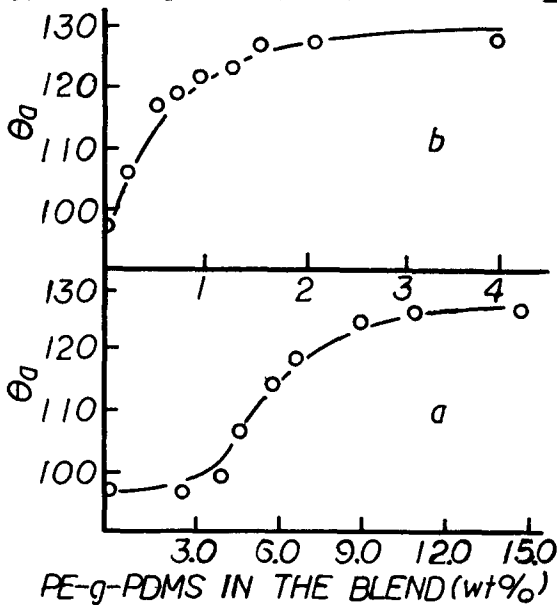


Figure 1 Relationship between  $\theta_a$  and content of PE-g-PDMS in blends

- a G-11 (3 wt%, PDMS)
- b G-14 (16 wt%, PDMS)

(3% PDMS in PE-g-PDMS), the  $\theta_a$  value changed from that of pure HDPE to that of pure PDMS. This indicates the progressive enrichment of PDMS segments on the film surface of HDPE/PE-g-PDMS blends, as a result of the low surface tension of 14 dynes/cm for PDMS as compared to 28 dynes/cm for HDPE at  $130^\circ\text{C}$  of film forming temperature. It is interesting to note that, as long as the PDMS content in the blends remained the same, and enough to show typical PDMS surface property, it did not matter what was the content of PDMS in the graft copolymers with the same side-chain length. the increase in PDMS con-

tent in PE-g-PDMS means an increase in the number of PDMS branch chains. The above results indicate that the mode of distribution of PDMS grafts along the PE chain dose not affect the enrichment behavior of PDMS.

Fig. 2 shows the intensity of signals in ESCA, arising from the core levels of  $C_{1s}$ ,  $Si_{2p}$  and  $O_{1s}$ . The intensity ratios of  $I_{C_{1s}}/I_{Si_{2p}}$ ,  $I_{C_{1s}}/I_{O_{1s}}$  and  $I_{O_{1s}}/I_{Si_{2p}}$  are listed in Table 1. We are more interested in the intensity ratio of  $I_{C_{1s}}/I_{Si_{2p}}$ , because it is indicative of the surface composition of HDPE/PE-g-PDMS blends. For pure PDMS, the ratios  $I_{C_{1s}}/I_{Si_{2p}}$  and  $I_{O_{1s}}/I_{Si_{2p}}$  are 1.66 and 1.36, respectively, because of the difference in electron escape depths(6). In Table 1, values of the ratio  $I_{O_{1s}}/I_{Si_{2p}}$  are about the same as that of pure PDMS, but those of  $I_{C_{1s}}/I_{Si_{2p}}$  are much higher than the value (1.66) for PDMS itself. Assuming that the intensity ratio of  $I_{C_{1s}}/I_{Si_{2p}}$  for PDMS segments in the polymer blends is the same as that for pure PDMS and ignoring the difference in electron mean free paths between  $C_{1s}$  and  $Si_{2p}$ , we

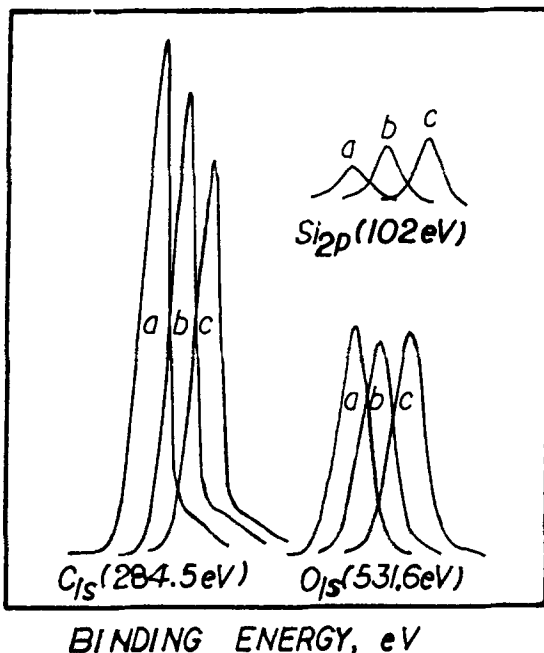


Figure 2 ESCA spectra of the surface of HDPE/PE-g-PDMS blends

wt% of PE-g-PDMS G-14  
a 0.19 b 0.91 c 1.5

Table 1 Experimental Intensity Ratios of Surfaces of HDPE/PE-g-PDMS Blends

Sample number	Bulk composition (wt%, PDMS)	Polymer/air interface		
		$I_{C_{1s}}/I_{Si_{2p}}$	$I_{C_{1s}}/I_{O_{1s}}$	$I_{O_{1s}}/I_{Si_{2p}}$
26	0.030	17	12	1.38
27	0.080	6.5	3.8	1.72
28	0.15	3.5	2.6	1.34
29	0.24	3.0	2.5	1.22

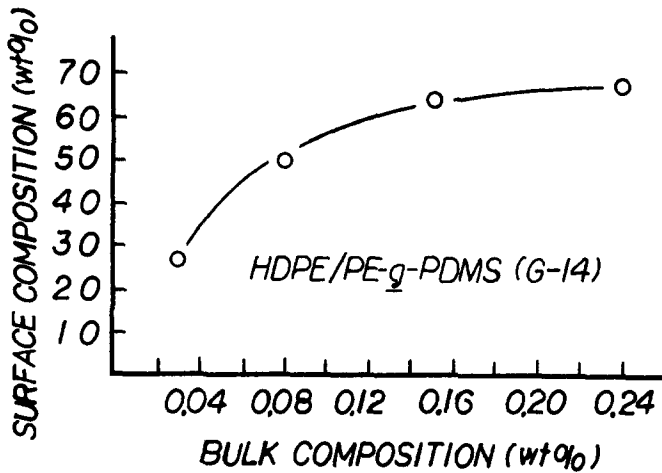


Figure 3 Relationship between bulk and surface compositions

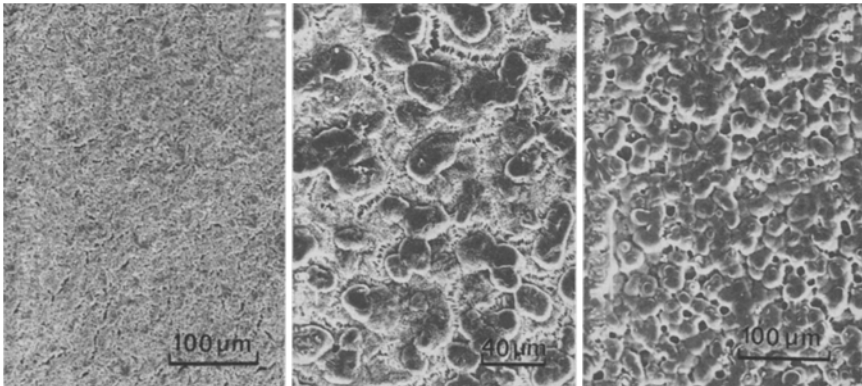


Figure 4 Surface morphology of HDPE/PE-g-PDMS blends  
wt% of PE-g-PDMS G-11  
a 4.2 b 8.1 c 15

can calculate semi-quantitatively the surface composition of HDPE/PE-g-PDMS blends; the results thus obtained are shown in Fig. 3. One could see that the content of PDMS segments on the film surface (about 40Å depths) was hundreds times of that in the bulk. This result is in agreement with that obtained by contact angle measurements.

Morphology of the surface of HDPE/PE-g-PDMS blends was studied using SEM. Since HDPE was semi-crystalline, the PDMS phase on the film surface could be easily identified (dark regions, Fig. 4). According to Young's equation,  $\gamma_{\min} = \gamma_{PE} - (\gamma_{PDMS} + \gamma_{PE/PDMS}) = 9.7 \text{ dynes/cm} > 0$ , PDMS segments should spread

on HDPE surface. But as shown clearly in Fig. 4, the PDMS segments were enriched on the film surface of polymer blends appeared as separate domains, suggesting that Young's equation is correct for small molecules but not suitable for polymer systems because of the inhibition of configuration and also of the geometry in block and graft copolymers(7).

It should be noted that, although the  $\theta_a$  value shows typical PDMS property when the PDMS content in the blends was about 0.2%, the film surface of HDPE/PE-g-PDMS blends was not covered completely by PDMS segments (Fig. 3 and Fig. 4). The differences between  $\theta_a$  and ESCA and  $\theta_a$  and SEM might be due to the high sensitivity of  $\theta_a$  to lower tension component on a compositional heterogeneous surface(8).

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