

Surface Modification of LDPE with PE-PEO Graft Copolymer

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Received 12 March 1999; accepted 3 June 1999

ABSTRACT: Films of LDPE containing 1–10 wt % of various polymeric additives were prepared by different techniques. Three poly(ethylene-*graft*-ethylene oxide)s synthesized by grafting poly(ethylene-*co*-acrylic acid) with poly(ethylene oxide) monomethyl ether (MPEO), and two pure MPEOs having molecular weights 750 and 2000 were used as additives. The additives were mixed with LDPE both by blending in a common solvent and by melt mixing. The blends were then solvent cast from xylene onto glass Petri dishes or compression molded between glass plates. The film surfaces were studied by water contact angle measurements and by X-ray photoelectron spectroscopy (XPS), and melting points and heats of melting were recorded by differential scanning calorimetry (DSC). The blends had a two-phase morphology, with enrichment of the graft copolymers at the glass–polymer interface, as shown by contact angle values and XPS spectra. Large differences in the interface accumulation between the different film samples were observed. Films prepared by compression molding of solution-mixed blends exhibited much lower surface accumulation of graft copolymer at the glass–polymer interface than did the solvent cast or melt-mixed/compression-molded samples. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 316–326, 2000

Key words: surface modification; LDPE, poly(ethylene oxide); graft copolymer; polymer blend

INTRODUCTION

Adhesion of polyethylene to other materials is very low because of the low polarity and low surface energy of polyethylene. This is a drawback in applications such as gluing, painting, and printing. To improve the adhesion properties, it is necessary to modify the surface of polyethylene. One of the most common techniques is to introduce polar groups on the polymer surface by oxidation. This can be done by corona discharge or thermal treatment.^{1–3} Another way of obtaining a polar surface is to graft polymers with polar groups

onto the polyolefin.^{4,5} A different approach is to blend the polymer matrix with a suitable amphiphilic copolymer.^{6–8} The amphiphilic copolymer segregates preferentially to the surface, and a surface with different properties than the bulk may be obtained.

In a previous article we reported on the preparation and characterization of a graft copolymer having a polyethylene (PE) backbone grafted with polyethylene oxide (PEO).⁹ The poly(ethylene-*graft*-ethylene oxide) (PE-PEO) was prepared by coupling of poly(ethylene-*co*-acrylic acid) (PEAA) and poly(ethylene oxide) monomethyl ether (MPEO) by an esterification reaction (Fig. 1).

We also have reported on surface modification of, for example, polyurethanes by means of amphiphilic polymeric additives.^{10,11} It was shown

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Journal of Applied Polymer Science, Vol. 75, 316–326 (2000)

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CCC 0021-8995/00/020316-11

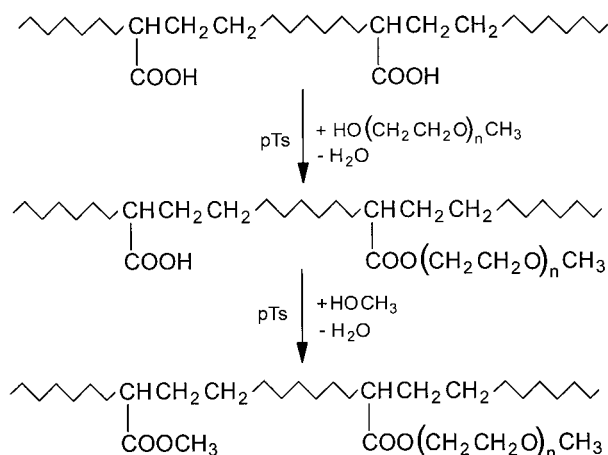


Figure 1 Grafting of PEAA with MPEO by esterification.

that because of their amphiphilic properties, the polymers enrich at the surface, thereby decreasing the surface energy of the matrix.

In the present article we report on the use of poly(ethylene-*graft*-ethylene oxide) as a surface modifier for polyethylene. Blends of LDPE and different polymeric additives were prepared. Three polyethylene-based graft copolymers, PE-PEO750, PE-PEO2000A, and PE-PEO2000B, were used and, as a comparison, two pure MPEOs with molecular weights 750 and 2000. Films were prepared by different techniques, and their surface properties were compared.

EXPERIMENTAL

Graft Copolymers

Three graft copolymers were used, one with MPEO750 side chains (PE-PEO750) and two with MPEO2000 (PE-PEO2000A and PE-PEO2000B). The graft copolymers were synthesized by coupling of poly(ethylene-*co*-acrylic acid) [(PEAA) 13.5% w/w acrylic acid, Exxon] and poly(ethylene oxide) monomethyl ethers [(MPEO) molecular weights 750 and 2000 from Janssen Chimica and Aldrich Chemical Company, Inc., respectively] via esterification reactions in *o*-xylene at 140°C with *p*-toluene sulfonic acid as catalyst. After the reaction between PEAA and MPEO was finished, methanol was added in excess in order to esterify residual carboxylic acid groups. A full report on the preparation and characterization of the PE-PEO graft copolymers was given in a previous

Table I Molecular and Thermal Data of Graft Copolymers and Homopolymers

	PEO Content (% w/w)	T_g (PEO) (°C)	T_m (PEO) (°C)	T_m (PE) (°C)
PE-PEO750	40	-65	3	92
PE-PEO2000A	45	—	40	95
PE-PEO2000B	53	—	41	92
LDPE	—	—	—	120
MPEO750	—	—	28	—
MPEO2000	—	—	58	—

article.⁹ Data on composition and thermal transitions for the copolymers are collected in Table I.

Preparation of Blends

Solvent Blending

Blends of LDPE (Neste NCPE 4004) and the polymeric additives were prepared by solvent blending and precipitation. The additives, that is, the graft copolymers, PE-PEO750 and PE-PEO2000B, and pure MPEO750 and MPEO2000, respectively, were dissolved in boiling *o*-xylene under stirring for 1 h and then precipitated in stirred diethyl ether cooled in a bath of dry ice and methanol. The solvent was decanted and the blend was dried under vacuum at ambient conditions for 1 week. The amounts of additive in the blends were 0, 1, 3, and 10 wt % graft copolymer and 1.5 and 5 wt % MPEO, respectively. The compositions of the blends are given in Table II.

Table II Composition of Precipitated LDPE Blends for Compression Molding

Additive	Additive Conc. (%)	LDPE Conc. (%)
None	0	100
PE-PEO750	1	99
PE-PEO750	3	97
PE-PEO750	10	90
PE-PEO2000B	1	99
PE-PEO2000B	3	97
PE-PEO2000B	10	90
MPEO750	1.5	98.5
MPEO750	5	95
MPEO2000	1.5	98.5
MPEO2000	5	95

Melt Blending

Blends of LDPE containing 0%, 1%, 2%, and 4% PE-PEO2000B were prepared in a Brabender mixer using screw-type rollers. A dry-blended mixture of the polymers having a total weight of 40 g was fed to the mixer head. The mixing proceeded for 7 min at a temperature of 170°C and with a roller rate of 30 rpm. The blends were discharged from the mixer and cooled at ambient conditions.

Film Preparation

Solvent Casting

Films of LDPE containing 0, 1, 3, and 5 wt % graft copolymer PE-PEO750 or PE-PEO2000A, respectively, were solvent cast onto clean glass Petri dishes. Before casting, the dishes were cleaned by soaking in chromosulfuric acid for 24 h, followed by rinsing in distilled water and drying at room temperature overnight. The graft copolymers were blended with pure LDPE by dissolving both polymers in boiling *o*-xylene under constant stirring for 1 h. The hot solution was then poured onto a Petri glass dish maintained at 110°C in an oven. The dish was covered with aluminum foil and the solvent was allowed to evaporate slowly at 110°C for 24 h. The dish was then kept under vacuum for 3 days at ambient conditions. Contact angles and surface compositions were measured on both the glass- and air-facing sides of the solvent cast films.

Compression Molding

Blends prepared by solvent blending and melt blending were compression molded to films in a heated hydraulic press between a glass plate and a steel or Teflon plate. The blends were preheated for 3 min on the glass plate and then 3.5 min between the glass and the steel plate and then were compression molded for 5 min at 170°C. The plates were removed from the press and cooled at ambient conditions.

Analyses

Contact angles were determined for the glass- and air-facing sides of the cast films and for the glass-facing side of the compression molded films. By means of a motor-driven microsyringe, 5–10 μL of ultrapure water was pumped onto the film surface. The advancing contact angle was registered by a video camera. The droplet was then

withdrawn into the syringe until the edges of the drop moved, and the receding contact angle was then registered. The films were dried under vacuum at ambient conditions for 24 h before measurement.

The chemical composition of the film surfaces was analyzed by XPS, using a Kratos XSAM 800 instrument with a Mg K α X-ray source (1253.6 eV). Data were collected at 30° and 90° take-off angles between the sample and the analyzer. By tilting the samples, the analysis depth was decreased and a higher surface selectivity was obtained.¹²

The thermal properties of the blends were analyzed with a Mettler TA 3000 DSC system. The samples were first heated from –100°C to 160°C, kept at 160°C for 2 min, cooled down to –100°C, and then reheated to 160°C. Temperature scan rates were in all cases 10°C/min.

The melt mixed blend of LDPE/4% PE-PEO2000B and precipitated blend of LDPE/10% PE-PEO2000B were cryo-sectioned with a Leica Ultracut UCT microtome equipped with a diamond knife and a cryokit. The sections were stained with RuO₄ and examined with a JEOL 100U transmission electron microscope (TEM).

RESULTS AND DISCUSSION

We have previously reported on surface modification of polyurethanes by addition of small amounts of amphiphilic block and graft copolymers to the bulk polymer. In those cases the matrix material and the dispersed phase were both amorphous with relatively low glass transition temperatures, and the film samples were prepared by solvent casting. It was recognized that the driving force for surface accumulation was the decrease in the free surface energy of the air-facing surface caused by the hydrophobic segments of the amphiphile.^{10,11}

In the present system there is no difference in polarity between the LDPE matrix and the backbone of the amphiphile, while there is a large polarity difference between the matrix and the hydrophilic MPEO grafts. Consequently, there should be a strong tendency for the amphiphile to accumulate at a high-energy interface, such as the LDPE/glass interface, with the hydrophilic grafts facing the glass, rather than at the low-energy LDPE/air interface.

The matrix used in the present case, LDPE, is a semi-crystalline polymer. The amphiphilic graft

Table III XPS: Oxygen Content of Glass- and Air-Facing Sides of Solvent Cast PE/PE-PEO750 Films

Amount Copolymer (%)	Take-Off Angle (°) ^a	Glass-Facing Side				Air-Facing Side
		Total O Content (%)	Ether O (%)	Carboxylic O (%)	PEO Content (%)	Total O Content (%)
0	90	1.4	—	—	—	0.2
	30	1.8	—	—	—	0.5
1	90	13	8.3	4.7	25	1.4
	30	10	6.5	3.5	20	1.7
3	90	23	18	4.7	55	1.2
	30	14	10	3.5	30	1.7
5	90	21	16	4.7	48	1.3
	30	14	10	3.7	30	1.3

^a Angle between the sample and the analyzer.

copolymer is also crystalline with a micro-phase separated morphology with both the backbone and the grafts forming crystalline phases. Crystallization is a strong driving force for phase separation, but it is difficult to predict the mechanism for migration of the graft copolymer to the surface in a semi-crystalline matrix. However, in solution or in the molten state, diffusion and self-assembly of the amphiphile at a surface or interface should be possible.

Films of blends of LDPE and the amphiphilic copolymers were prepared by three different methods. The most simple one was to cast films from a solution of the two polymers onto a glass dish and evaporate the solvent. In the other methods, the blends were first prepared by precipitation from a common solution or by melt blending and then were compression molded into films. The surface properties of the films were shown to depend strongly on how the blends were prepared. When blending polymers by dissolution in a solvent and then casting, the polymers can segregate when the solvent evaporates. This can be avoided if the polymers are rapidly precipitated from solution into a nonsolvating medium. A problem that can occur in the latter case is that large aggregates of the graft copolymer may be formed in the PE matrix, due to different behaviors of the two polymers on precipitation. TEM analyses of the precipitated blends have shown large aggregates of the graft copolymers. By melt-blending in a Brabender mixer at high shear forces, the graft copolymer is evenly dispersed in the LDPE matrix. The shear forces breaks up the graft copolymer phase into small aggregates,

which was confirmed by TEM analysis of the melt-blended blends.

Surface Properties of Solvent Cast Films

Glass represents a high-energy surface, while the interface between LDPE and air represents a low-energy surface. On solvent-casting of a blend of LDPE and a PE-PEO graft copolymer, a preferential segregation of the high-energy MPEO grafts to the high-energy glass-polymer interface thus would be expected on solvent evaporation. The surface composition of films cast on glass plates were analyzed by XPS, and contact angles with water were determined.

XPS Analysis

In all blends, the oxygen content was, as expected, much higher on the glass-facing side than on the air-facing side of the cast films and increased with the copolymer content, as seen in Tables III and IV. In contrast, the XPS spectra for the air-facing sides indicated a constant oxygen content of approximately 1%, regardless of copolymer content.

In order to increase the surface selectivity of the XPS analysis, the samples were tilted to a take-off angle of 30° between the sample surface (glass-facing) and the analyzer. Quite contrary to what was expected, the oxygen content was found to be lower when the samples were tilted. This fact indicates a lower MPEO content in the outermost layer of the surface as compared to the layers just beneath the surface. This oxygen dis-

Table IV XPS: Oxygen Content of Glass- and Air-Facing Sides of Solvent Cast PE/PE-PEO2000A Films

Amount Copolymer (%)	Take-Off Angle (°) ^a	Glass-Facing Side				Air-Facing Side
		Total O Content (%)	Ether O (%)	Carboxylic O (%)	PEO Content (%)	Total O Content (%)
1	90	19	12	6.8	36	0.7
	30	12	7.4	4.2	24	0.9
3	90	16	10	6.4	30	1.3
	30	11	6.6	4.4	21	1.9
5	90	19	13	6.0	39	1.5
	30	11	7.3	4.1	21	0.9

^a Angle between the sample and the analyzer.

tribution may be an effect of the high vacuum environment in the analyzing chamber of the XPS spectrometer. Because of the high segmental mobility in the amorphous regions of the PE matrix, the polymer surface may reorient rapidly in various environments, to minimize the interfacial free energy.^{13–16} Vacuum represents a low-energy environment, and the MPEO chains at the surface may thus reorient, leaving the hydrophobic polyethylene backbone segments exposed to the vacuum.

The carbon C1s spectrum, as shown in Figure 2, is composed of one aliphatic carbon peak (285 eV) and two shoulders at higher bonding energies (286.7 and 289.2 eV), representing carbon bonded to an ether oxygen and carbon bonded to a carbonyl oxygen, respectively.¹⁷ The carbon C1s peaks were deconvoluted, and the amounts of ether and ester groups were estimated. The results from this analysis are shown in Table V. The ratio between the ether and ester group signals in the samples containing 3% and 5% PE-PEO750, respectively, changed significantly when the samples were tilted. The ether signal decreased and the ester increased, which is in accordance with the view that the MPEO chains reorient, leaving the backbone exposed to the vacuum environment. As evident from the molecular structure of the graft copolymers, the ester groups are situated close to the backbone and will stay close to the surface even if the MPEO chains have reoriented.

Pure MPEO should have an oxygen content of 33%. By using this value, the amounts of MPEO-grafts at the surface of the blends with PE-PEO750 and PE-PEO2000A, respectively, could

be calculated from the XPS analyses, taking into account also the contents of carbonyl oxygens. As seen from the values presented in Tables III and IV, the surface coverage is quite high. In the films containing 3% and 5% PE-PEO750, the average MPEO content of the glass-facing surface regions was about 50%.

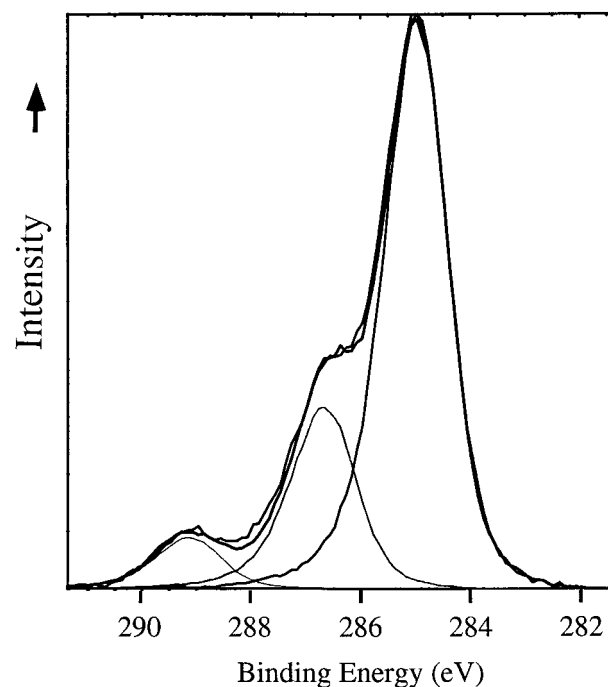


Figure 2 XPS analysis. Deconvoluted C1s spectrum on the glass-facing side of solvent-cast film. LDPE/5% PE-PEO750.

Table V XPS: The Carbon C1s Peak on the Glass-Facing Side of Solvent Cast PE/PE-PEO750 and PE/PE-PEO2000A Films, Deconvoluted into Aliphatic-, Ether-, and Carboxylic Carbon Peaks

Sample	Take-Off Angle (°) ^a	C—C (%)	C—O (%)	C=O (%)	C—O/C=O
Pure LDPE	90	100	0	0	—
	30	100	0	0	—
1% PE-PEO750	90	86	7.5	4.1	1.8
	30	89	6	3.2	1.9
3% PE-PEO750	90	67	24.5	6.7	3.7
	30	83	13	4.4	3.0
5% PE-PEO750	90	70	22	6.4	3.4
	30	82	12.5	4.6	2.7
1% PE-PEO2000A	90	77	15	8	1.7
	30	89	7	4	1.9
3% PE-PEO2000A	90	84	9	6	1.5
	30	90	6	4	1.6
5% PE-PEO2000A	90	75	18	8	2.4
	30	87	9	5	1.9

^a Angle between the sample and the analyzer.

Contact Angle Measurements

Measurement of water contact angles gives a good estimate of the polarity and the mobility of the polymer chains present in the outermost atomic layers of the surfaces. In Figure 3, results from measurement of water contact angles for solvent cast films are shown. A considerable decrease in the contact angles was observed for the glass-facing sides of films containing graft copolymer, as compared with pure LDPE film, the receding angle for films containing graft copolymer being approximately 90° lower than that for LDPE. The presence of the hydrophilic MPEO grafts at the surface decreases the interfacial energy, as demonstrated by the low values of the contact angles. The hysteresis in the contact angles was also significant. This fact indicates that hydration of the surface by contact with water occurs, that is, the MPEO segments close to the surface become hydrated and reorient toward the aqueous phase, thus effectively minimizing the interfacial free energy.¹³ On the air-facing side, only a small decrease of the contact angles, approximately 15°, was observed with increasing graft copolymer content. This result is in accordance with the results from XPS analysis in which low oxygen contents indicated a low content of MPEO grafts on the air-facing side. It can thus be concluded from the contact angle measurements that solvent cast films show a substantial enrichment of

graft copolymer at the high-energy glass interface.

Surface Properties of Compression Molded Films

The strong enrichment of PE-PEO graft polymer at the high-energy glass interface in solvent-cast films from LDPE/PE-PEO blends is presumably driven by the decrease in the interfacial energy caused by the graft copolymer. When solvent is present during film formation, the viscosity of the medium is low enough to allow large-scale diffusion of the graft copolymer. However, in a melt, a similar diffusion and accumulation can be anticipated, but the viscosity of the medium should be considerably larger as well as the relaxation times for reptation for the graft copolymer. The time for reaching an equilibrium surface excess should consequently be much longer.

The polymer blends prepared by solvent blending and precipitation of the polymers in cold diethyl ether, and those prepared by direct melt mixing, were compression molded between a glass plate and a steel or Teflon plate. The glass-facing sides of the films were analyzed by XPS and water contact angle measurements.

XPS

Blends prepared by precipitation from solution showed a surface behavior, with respect to the

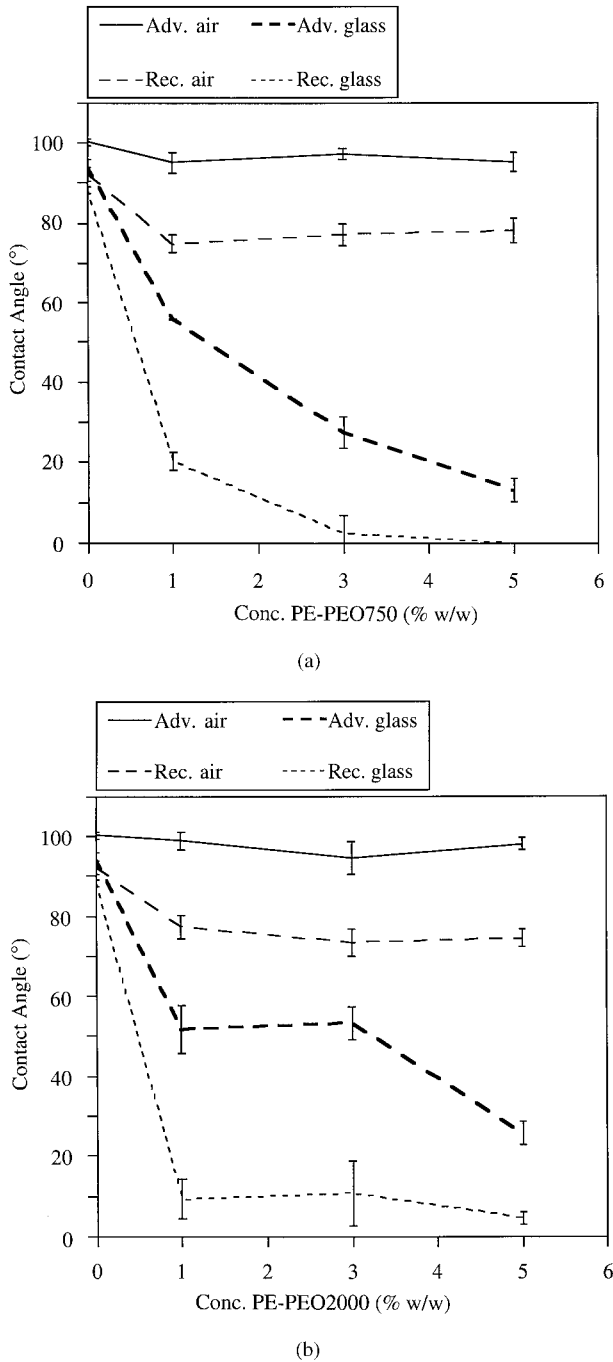


Figure 3 Water contact angles of solvent cast films with increasing copolymer content. (a) PE-PEO750; (b) PE-PEO2000A.

MPEO chain lengths, very different from the solvent-cast and melt-mixed blends and exhibited much lower contents of graft copolymer at the surface. As seen in Figure 4, the glass-facing surfaces of LDPE blends with 3% and 10% PE-

PEO750, respectively, had very low oxygen contents, less than 1%. The films containing 3% and 10% PE-PEO2000B, had substantially higher oxygen contents, that is, 7–8%, which corresponds to a concentration of MPEO grafts at the surface of 21–24%. The graft copolymer PE-PEO2000B proved to be more surface-selective, presumably because of the longer side chains and the lower grafting density, as compared to PE-PEO750.

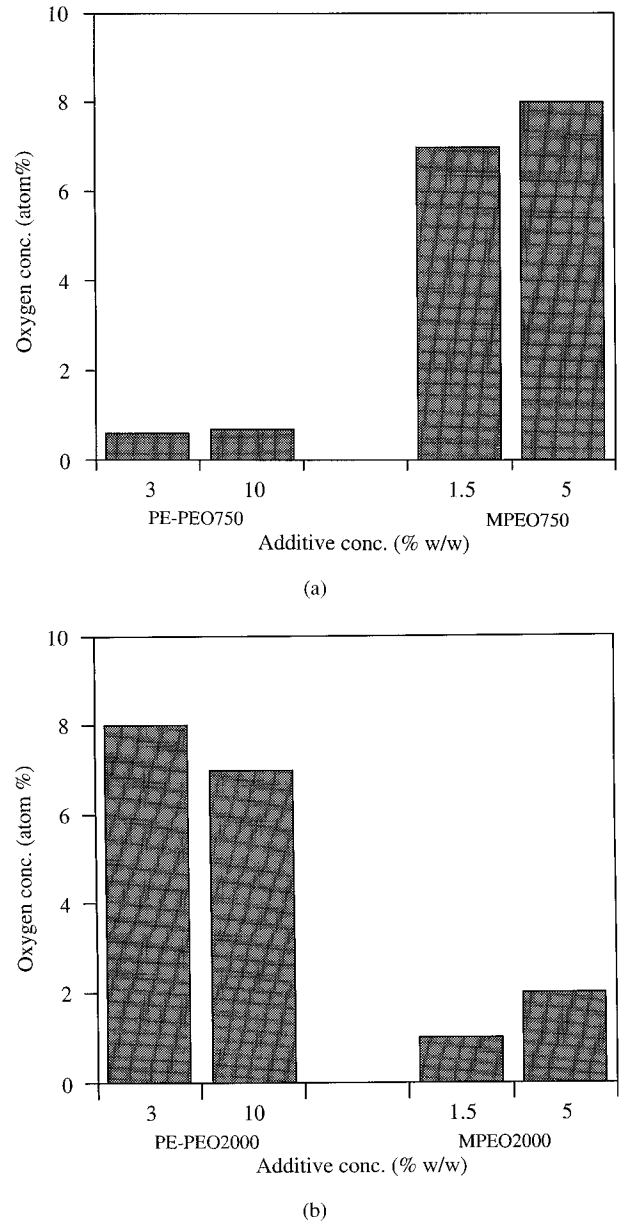


Figure 4 XPS analysis. Oxygen content on the surface of compression-molded films from precipitated blends. (a) PE-PEO750 and MPEO750; (b) PE-PEO2000B and MPEO2000.

The precipitated blends had low contents of graft copolymers at the surface. The preparation procedure, which involves dissolution and precipitation of the polymers, enables large aggregates of graft copolymer to be formed. On compression molding of this mixture, the large aggregates do not dissolve easily in the matrix, and migration of the molecules to the surfaces is hindered. Indeed, TEM analysis of the LDPE/10% PE-PEO2000B blend confirmed that the graft copolymer was present as large, lamellae-shaped aggregates.

Pure MPEO is not compatible with LDPE and should, if possible, segregate to the high-energy interface. To investigate the behavior of pure MPEO in relation to that of the graft copolymers, blends were prepared from LDPE and pure MPEO750 and MPEO2000, respectively. Compression-molded films were analyzed with XPS. The films containing MPEO750 showed an oxygen content of 7–8% at the glass–polymer interface, while the films containing MPEO2000 had 1–2%. The migration of MPEO can continue as long as the matrix LDPE is in the molten state. When the matrix has crystallized upon cooling, the structure will be more or less locked. Any migration of MPEO can only occur in the amorphous regions of LDPE. When the temperature is further decreased, MPEO2000 will crystallize, while MPEO750 may continue to migrate even at room temperature because of its low crystallinity and small size, thus increasing the surface accumulation.

In contrast to the precipitated blends, melt mixed blends showed a high enrichment of graft copolymer at the glass-facing surface on compression molding. A graph showing the oxygen content of the surface as a function of the graft copolymer content in the blends is given in Figure 5. In the blend containing 4% PE-PEO2000B, the oxygen content in the surface was 21 mol %. This figure is comparable with the oxygen contents measured for glass-facing sides of solvent cast films, that is, about 20%. The Brabender mixer seems to be very efficient in dispersing the graft copolymer in the LDPE matrix at the temperature used (170°C), and this may be a reason for the high surface accumulation on compression molding.

Contact Angle Measurements

In Figure 6(a,b), the results of water contact angle measurements on the compression-molded films

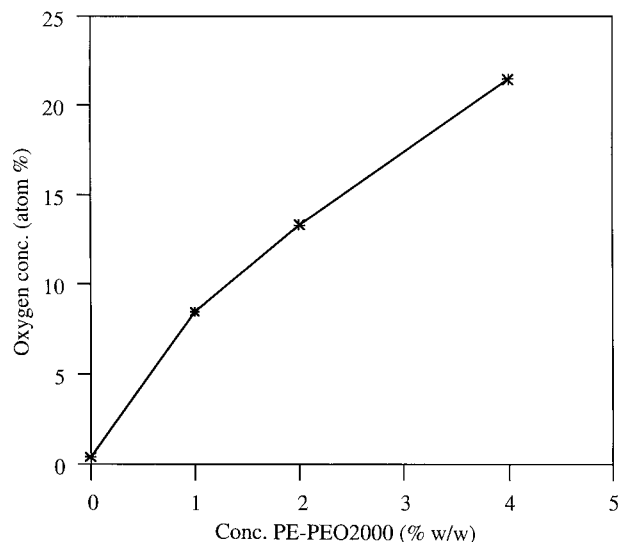
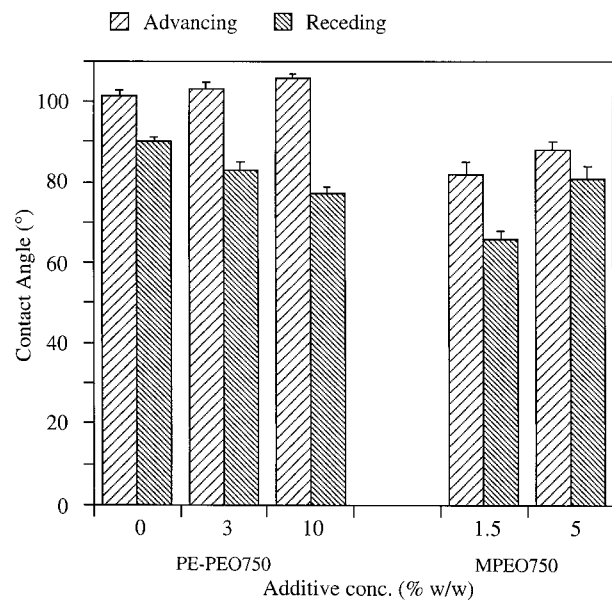


Figure 5 XPS analysis. Oxygen content on the surface of compression-molded films from melt mixed blends of LDPE and PE-PEO2000B.

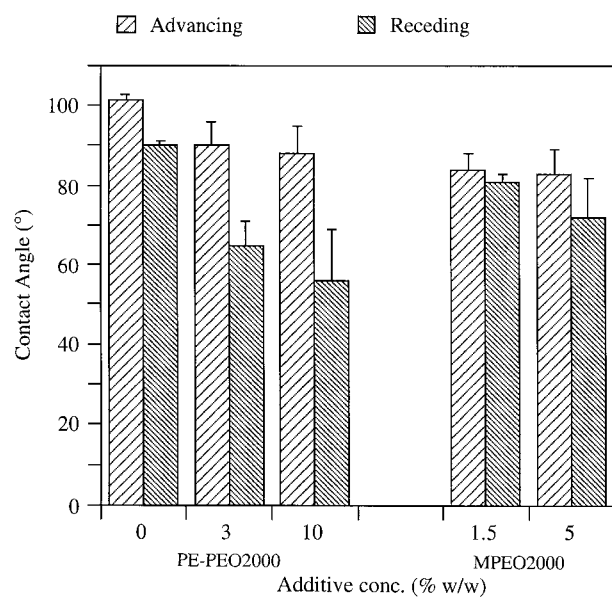
from precipitated blends of PE and PE-PEO750 and PE-PEO2000B, respectively, are shown. As compared to pure LDPE, a small decrease in the receding angle, 13°, for the blend containing 10% PE-PEO750 was observed. The advancing angles did not change appreciably (4° increase). The contact angle hysteresis increased with increasing content of copolymer. The oxygen content of the glass–polymer interface was measured by XPS and found to be less than 1%. However, the surface hydrates on contact with water, which leads to a decrease in the receding contact angle. This should be an effect of the graft copolymer present at the blend surfaces. The blends containing MPEO750 had lower advancing angles and smaller hysteresis than the corresponding blends with the graft copolymer.

For the precipitated blends containing PE-PEO2000B, a greater effect was observed. The advancing angle decreased by about 10° and the receding angle by about 30° to approximately 60°. In these blends the XPS analysis showed higher oxygen contents, 7–8%. As a comparison, blending of PE with MPEO2000 had different effects: both advancing and receding angles decreased about 15°, and the hysteresis was very small.

For the LDPE/PE-PEO2000B blends prepared in Brabender mixer, the contact angles were much lower compared to those of pure LDPE (Fig. 7); the decrease in the advancing angle was 50° and the receding angle 60°. The advancing angles



(a)



(b)

Figure 6 Water contact angles of compression-molded films from precipitated blends. (a) PE-PEO750 and MPEO750; (b) PE-PEO2000B and MPEO2000.

were approximately the same as those measured for solvent cast blends (cf. Fig. 2), which also had about the same oxygen contents in the surface, as measured by XPS. The decrease in the receding angles was smaller, and accordingly, the hysteresis was not as pronounced as for the solvent-cast blends.

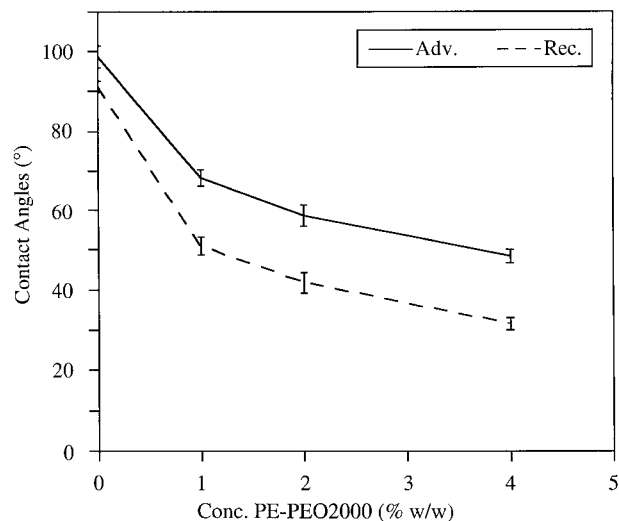


Figure 7 Water contact angles of compression-molded films from melt-mixed blends of LDPE and PE-PEO2000B.

Transmission Electron Microscopy

TEM analysis was performed on melt-blended LDPE/4% PE-PEO2000B and precipitated LDPE/10% PE-PEO2000B blends stained with RuO_4 to improve contrast. The RuO_4 reacts with the oxygen in the MPEO side chains of the graft copolymer, while the LDPE matrix remains unaffected. As seen in the micrographs of melt-blended LDPE/4% PE-PEO2000B in Figures 8 and 9, the graft copolymer was evenly distributed in the LDPE matrix as domains with dimensions from 2

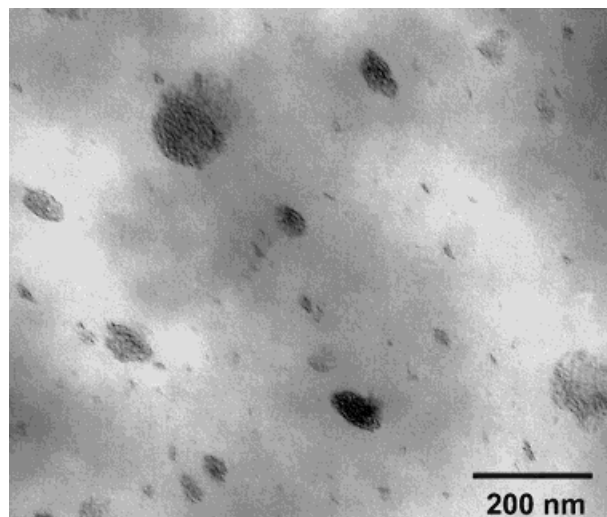


Figure 8 TEM micrograph. Melt-mixed blend, PE/4% PE-PEO2000B. Bar, 200 nm.

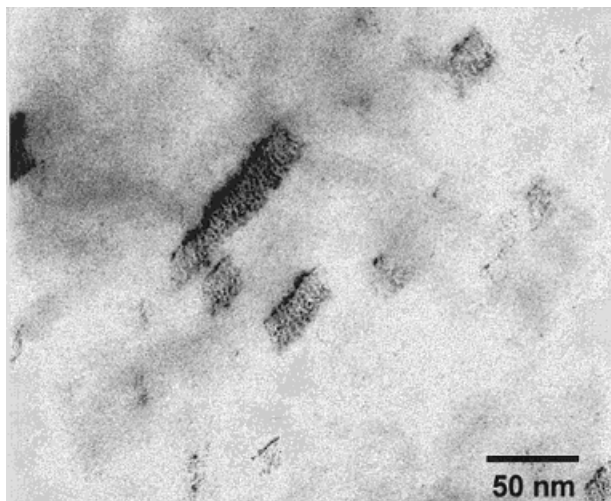


Figure 9 TEM micrograph. Melt-mixed blend, PE/4% PE-PEO2000B. Bar, 50 nm.

nm to 200 nm. The graft copolymer in the domains seems to have a phase-separated morphology, as indicated by the small black and white dots in the domains seen in Figure 9. The black areas in the micrographs correspond to MPEO stained with RuO_4 , and the white areas to unstained polyethylene backbones. Both the MPEO side chains and the PE backbone crystallize, which also was proven by DSC measurements. A melting peak at 38°C was seen in the thermogram, corresponding to melting of the MPEO side chains. The crystallization behavior of the pure graft copolymer has been studied previously, where a strongly phase-separated structure was seen.⁹ In the precipitated blends with 10% PE-PEO2000B, the graft copolymer forms thin (5–30 nm) and very long (0.5–1.5 μm) aggregates dispersed in the LDPE matrix.

DSC Measurements on Blends

Melting points and melting enthalpies for the precipitated blends were determined by DSC, and the results from these measurements are presented in Table VI. In all blends the melting point of the LDPE phase was found at a temperature around 113°C . Melting peaks from the MPEO grafts in the graft copolymer can be seen for both concentrations in the blends with PE-PEO2000B, but only for the 10% blend with copolymer PE-PEO750. DSC traces for blends containing 10% PE-PEO2000B and 5% MPEO2000 are given in Figure 10. The melting temperatures of the MPEO phase in the graft copolymer were found to

be $15\text{--}25^\circ$ lower than the melting temperatures of MPEO in blends with LDPE and pure MPEO, as seen in Table V. This is in accordance with the results from DSC measurements on the pure graft copolymers reported in a previous paper.⁹ The melting enthalpy of PEO side chains in the blends with graft copolymer PE-PEO2000B were about 30% lower than for MPEO in the blends with LDPE and pure MPEO2000. The PEO chains in the graft copolymer are bonded to the backbone and consequently are hindered in their crystallization. These irregularities result in a lower melting temperature and melting enthalpy compared to those measured for pure MPEO dispersed in an LDPE matrix. In the latter system, the driving force for phase separation is very strong because of the different polarities of PE and MPEO and because of crystallization of both phases.

CONCLUSIONS

Surface properties of a film prepared from a polymer blend are strongly dependent on the method of preparation for the blend and the film, respectively. For the system LDPE/PE-PEO graft copolymer, dissolution of the polymers in a common solvent and casting on a glass plate is a very simple method of film preparation, and a large part of the amphiphilic copolymer will end up at the glass–polymer interface. Dissolution of the polymers in a common solvent and precipitation in a nonsolvent can lead to problems with inclusions of large aggregates of graft copolymer in the matrix, and much less graft copolymer will accumulate at the surface when the blend is compression-molded. Melt mixing is an efficient method

Table VI DSC: Melting Enthalpy (ΔH_m) and Temperature (T_m) of LDPE and PEO Phases in Precipitated Blends

	ΔH_m (PE) (J/g)	T_m (PE) ($^\circ\text{C}$)	ΔH_m (PEO) (J/g)	T_m (PEO) ($^\circ\text{C}$)
10% PE-PEO2000B	-119	114	-80	40
5% MPEO2000	-117	113	-124	54
3% PE-PEO2000B	-119	113	-69	39
1.5% MPEO2000	-117	112	-98	53
10% PE-PEO750	-122	113	-15	1.6
5% MPEO750	-144	113	-40	27

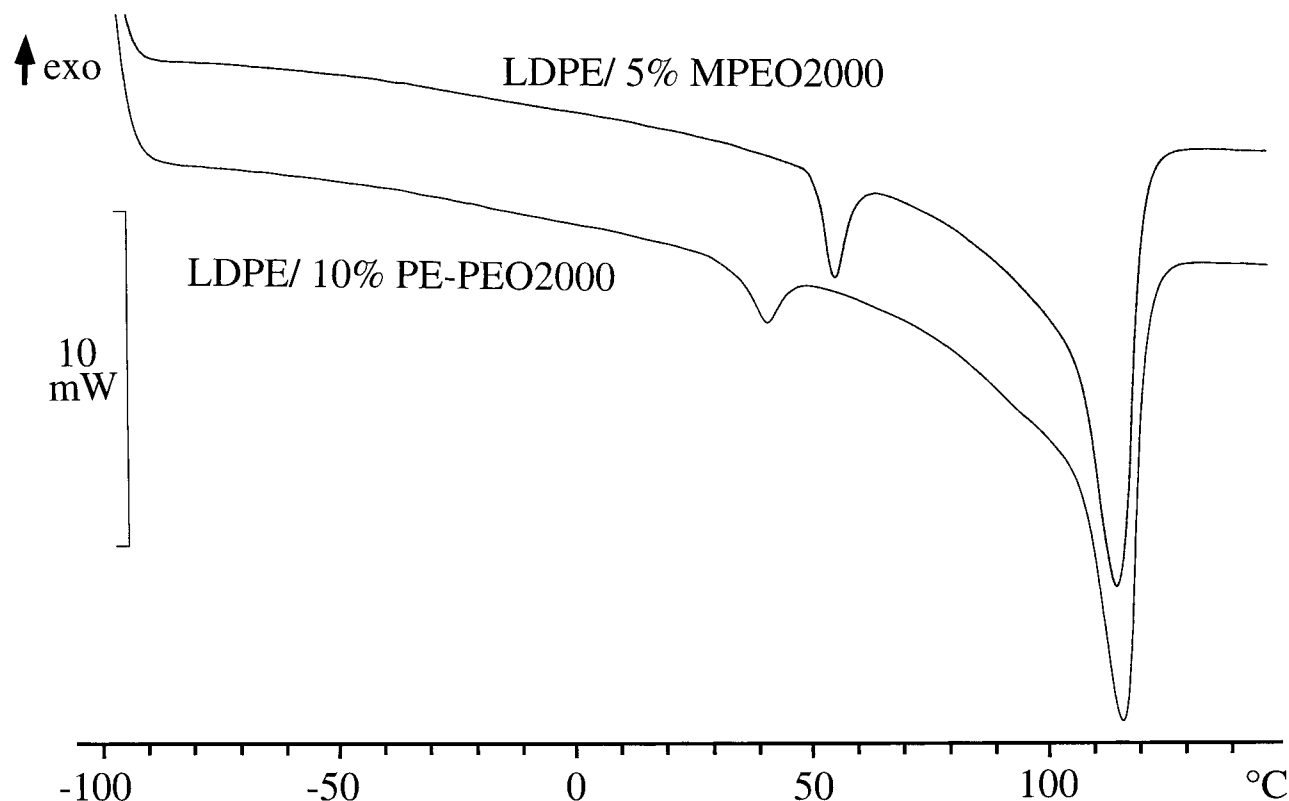


Figure 10 DSC traces of precipitated blends. Top trace: LDPE/5% MPEO2000; bottom trace: LDPE/10% PE-PEO2000B.

for dispersing the graft copolymer into the matrix, and the high shear forces break down the large aggregates of the graft copolymer. At compression molding, the graft copolymer accumulates at the surface and changes the surface properties.

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