

Improvement of the Polarity of Polyethylene with Oxidized Fischer–Tropsch Paraffin Wax and Its Influence on the Final Mechanical Properties

I. Novák,¹ I. Krupa,¹ A. S. Luyt²

¹Polymer Institute, Slovak Academy of Science, Dúbravská Cesta 9, 842 36 Bratislava, Slovakia

²Department of Chemistry, University of the Free State, Private Bag X13, Phuthaditjhaba, 9866, South Africa

Received 2 March 2004; accepted 30 April 2004

DOI 10.1002/app.21283

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The easy, low-cost modification of the polarity of low-density polyethylene (LDPE) and high-density polyethylene (HDPE) through blending with oxidized Fischer–Tropsch wax was investigated. A 10 wt % concentration of the wax increased the polar component of the total surface free energy 10 times for LDPE and 4.5 times for HDPE. Modified LDPE also had significantly higher adhesion to the polar substrate, which was represented by a

crosslinked epoxy-based resin. This behavior was not observed for HDPE. The conservation of the good mechanical properties of polyethylene was observed. The wax content had only a moderate influence on the mechanical properties. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 1164–1168, 2005

Key words: adhesion; mechanical properties; polyethylene (PE)

INTRODUCTION

Polyethylene (PE) has many useful applications because of its good mechanical properties and chemical resistance. It is widely used in packaging applications in the form of laminates with paper, aluminum, and so forth. Low-density polyethylene (LDPE) and high-density polyethylene (HDPE) have limitations in their adhesion because of their nonpolar nature, which leads to low surface free energy (SFE) and poor adhesive properties. Various methods have been used to improve PE adhesive properties, such as corona discharge,^{1,2} plasma surface modification,^{3,4} and chemical surface etching.^{5–8} Such types of surface modifications change the chemical composition and morphology of the PE surface. The presence of reactive polar groups in PE enhances its adhesive properties.

Another way of improving PE adhesive properties is its modification in the bulk by the addition of low amounts of polar polymers^{9,10} or low-molecular-weight additives.¹¹

The surface properties of PE are directly related to the properties of the bulk. The surface energy of the polymer is expected to be influenced by changes in the

bulk, including changes in the extent of phase separation and the degree of compatibility, which are reflected in the mechanical properties of blends.^{12–16}

Recently, we thoroughly investigated different crosslinked and uncrosslinked PE/wax blends.^{17–19} The extruded blends consisting of up to 20% wax were probably miscible in both the crystalline and amorphous phases. The oxidized wax slightly improved the polarity of linear LDPE. In this case, the blends were only mechanically mixed. The viscosity of the PE/wax blends (measured through the melt-flow index) behaved according to logarithmic additive rules. The crosslinking of PE/wax blends with dicumyl peroxide led to significant crosslinking of PE and grafting of wax chains onto PE chains.

The influence of oxidized wax on the polarity of LDPE and HDPE blends was investigated. The mechanical properties and the viscosity of the melt, given by the torque moment, were also determined.

EXPERIMENTAL

The following materials were used: LDPE Bralen RA 2–19 (melt-flow index = 1.7 g/10 min, density = 0.916 g cm⁻³, particle size < 50 μm) from Slovnaft (Bratislava, Slovakia), HDPE Stamydan HD 9089 V (melt-flow index = 8 g/10 min, density = 0.963 g cm⁻³ from DSM (Heerlen, The Netherlands), hard and brittle oxidized straight-hydrocarbon-chain paraffin wax (average molar mass = 785 g mol⁻¹, density = 0.940 g cm⁻³, C/O ratio = 18.8/1) from Schumann-Sasol (Sasolburg, South Africa), and a set of testing

Correspondence to: A. S. Luyt (luytas@qwa.uovs.ac.za).

Contract grant sponsor: Slovak Grant Agency; contract grant number: 2/1060/21.

Contract grant sponsor: South African National Research Foundation; contract grant number: 2050677.

TABLE I
Mechanical Properties of the LDPE/Wax Blends

LDPE/wax (w/w)	$\varepsilon_y \pm S\varepsilon_y$ (%)	$\sigma_y \pm S\sigma_y$ (MPa)	$\varepsilon_b \pm S\varepsilon_b$ (%)	$\sigma_b \pm S\sigma_b$ (MPa)	$E \pm S_E$ (MPa)
100/0	22.8 ± 0.5	8.6 ± 0.5	585 ± 15	10.4 ± 0.6	122 ± 9
98/2	21.2 ± 0.7	8.7 ± 0.4	548 ± 20	10.8 ± 0.6	130 ± 12
96/4	19.7 ± 0.8	8.5 ± 0.4	545 ± 12	10.8 ± 0.8	139 ± 15
94/6	19.3 ± 0.9	8.6 ± 0.3	520 ± 15	10.7 ± 1.2	124 ± 12
92/8	19.4 ± 0.7	8.9 ± 0.6	492 ± 20	11.0 ± 1.4	133 ± 18
90/10	19.9 ± 0.9	9.3 ± 0.5	490 ± 17	11.2 ± 1.2	128 ± 21

ε_y = elongation at yield; σ_y = yield stress; ε_b = elongation at break; σ_b = stress at break; E = Young's modulus of elasticity. $S\varepsilon_y$, $S\sigma_y$, $S\varepsilon_b$, $S\sigma_b$, and S_E are the respective standard deviations of these values.

liquids [twice distilled water, glycerine proanalysis (p.a.), formamide (p.a.), and 1-chloronaphthalene from Merck (Darmstadt, Germany), methylene iodide (p.a.) from Fluka (Heidelberg, Germany), and thiodiglycol, ethyl 2-aminobenzoate (p.a.), and ethylene glycol (p.a.) from Serva (Germany)].

The blends were prepared through the mixing of the components in a 50-mL mixing chamber of a Brabender PLE 331 plasticorder (Düsseldorf, Germany) at 150°C for 10 min at a mixing speed of 35 rpm. Slabs (1 mm thick) were prepared through the compression molding of the mixed composite with a Fontijne (The Netherlands) SR 100 laboratory hydraulic press at 180°C for 3 min. Dog-bone-shaped specimens with a working area of 35 mm × 3.6 mm × 1 mm were cut from the slabs. The mechanical properties were measured at room temperature with a Instron (England) 4301 5-kN universal testing machine at a deformation rate of 10 mm min⁻¹.

The SFE of the samples was determined from the contact angles (θ ; °) of a set of testing liquids with different polarities with a contact-angle meter (Zeiss, Germany). θ versus time t [$\theta = f(t)$] was extrapolated to $t = 0$, and the SFE and its polar component were evaluated with a computer program based on the least-squares method by minimization of the following relation:¹¹

$$\frac{(1 + \cos \theta)(\gamma_{LV}^d + \gamma_{LV}^p)}{2} = (\gamma_{LV}^d \gamma_s^d)^{1/2} + (\gamma_{LV}^p \gamma_s^p)^{1/2} \quad (1)$$

where γ_{LV} is the SFE of the testing liquid (mJ m⁻²); γ_{LV}^d and γ_{LV}^p are the dispersive and polar components of the SFE of the testing liquid, respectively; and γ_s^p and γ_s^d are the dispersive and polar components of the SFE of the polymer (mJ m⁻²), respectively:

$$\gamma_s^{\text{total}} = \gamma_s^p + \gamma_s^d \quad (2)$$

where γ_s^{total} is the total surface energy of the polymer (mJ m⁻²). It holds for the polar fraction (x_s^p) of the polymer that

$$X_s^p = \frac{\gamma_s^p}{\gamma_s^{\text{total}}} \quad (3)$$

The strength of the adhesive joint (SAJ) was measured via the peeling of the joint at an angle of 180° with an Instron 4301 universal testing machine. The rate of motion of the crosshead of the dynamometer used for the experiments was 2.5 mm min⁻¹. The adhesive joints were prepared via the spreading of a solution of poly(vinyl acetate) in ethyl acetate on technical cotton fabric (Molino, Liptovsky Mikulas, Skovakia) with a stainless steel coated ruler (Dioptra, Turnov, Czech Republic) with a slit of 0.12 mm. A foil of modified LDPE and technical cotton fabric was impregnated with the solution of poly(vinyl acetate). Applying pressure with a rubber cylinder created the adhesive joints. Then, the material was dried to a constant weight and cut into strips (25 mm × 150 mm). The peeling was performed along the length of the adhesive joint. The values of the strength of adhesive joint (P) was calculated as follows:

$$P = F_m/b \quad (4)$$

where F_m is the mean force of peeling (N) and b is the width of the adhesive joint (m).

RESULTS AND DISCUSSION

Mechanical properties

The mechanical properties of the investigated blends are summarized in Tables I and II. Young's modulus of the LDPE/wax blends slightly increased with an increase in the wax content, whereas that of the HDPE/wax blends slightly decreased. This was consistent with the observation that the degree of crystallinity (X_c ; determined from the specific enthalpy of melting) of wax was higher than that of LDPE. As discussed in our previous articles,^{19,20} the specific enthalpy of melting of PE/wax blends behaves according to the additive rule. The following specific enthal-

TABLE II
Mechanical Properties of the HDPE/Wax Blends

HDPE/wax (w/w)	$\varepsilon_y \pm S\varepsilon_y$ (%)	$\sigma_y \pm S\sigma_y$ (MPa)	$\varepsilon_b \pm S\varepsilon_b$ (%)	$\sigma_b \pm S\sigma_b$ (MPa)	$E \pm S_E$ (MPa)
100/0	10.0 ± 0.5	20.4 ± 0.2	1149 ± 82	19.5 ± 0.5	561 ± 21
98/2	10.5 ± 0.7	20.9 ± 0.7	1033 ± 38	20.0 ± 0.8	544 ± 18
96/4	10.2 ± 1.2	20.1 ± 1.2	1018 ± 22	19.7 ± 1.5	583 ± 22
94/6	10.9 ± 1.5	20.9 ± 1.4	978 ± 18	17.9 ± 1.2	562 ± 24
92/8	10.2 ± 1.0	20.2 ± 1.6	952 ± 32	16.9 ± 11.4	540 ± 30
90/10	10.6 ± 1.4	21.0 ± 1.1	925 ± 28	16.1 ± 0.9	507 ± 22

ε_y = elongation at yield; σ_y = yield stress; ε_b = elongation at break; σ_b = stress at break; E = Young's modulus of elasticity. $S\varepsilon_y$, $S\sigma_y$, $S\varepsilon_b$, $S\sigma_b$, and S_E are the respective standard deviations of these values.

pies of melting were found for the unblended samples with differential scanning calorimetry: 109 J g⁻¹ for LDPE, 216 J g⁻¹ for HDPE, and 174 J g⁻¹ for wax. X_c was estimated as the ratio of the specific enthalpy of melting of the components (ΔH_m) to the specific enthalpy of melting for 100% crystalline PE (ΔH_m^+):

$$X_c = \frac{\Delta H_m}{\Delta H_m^+} \quad (5)$$

When we used the value $\Delta H_m^+ = 293 \text{ J g}^{-1}$,²¹ the following values of X_c were found: 37 wt % for LDPE, 74 wt % for HDPE, and 59 wt % for wax.

The wax content had no significant influence on the yield point (elongation at yield and yield stress) for the HDPE/wax blends. The values for pure HDPE and for all the blends were very similar. A slight decrease in the elongation at yield and an increase in the stress at yield were observed for the LDPE/wax blends. This was probably caused by the slight increase in X_c .

The ultimate properties, such as the elongation and stress at break, were more dependent on the wax concentration. Generally, the tensile strength at break depends on the polymer or material structure in a complicated way. The tensile strength is strongly affected by the drawability of the polymer before failure. Materials that undergo strain (orientation) hardening during stretching have higher

strength at break than materials that do not undergo strain hardening. In our case, only one sample underwent significant strain hardening before stretching. On the other hand, all the samples showed cold drawing and had good deformability. The decrease in the elongation at break with an increase in the wax content was not very pronounced in either investigated system. The wax content influenced the stress at break of the LDPE/wax and HDPE/wax blends in different ways. In the LDPE/wax blends, the stress at break increased very slightly with an increase in the wax content. On the other hand, for the HDPE/wax blends, a decrease in the stress at break was observed.

Total surface free energy (SFE)

The improvement in the polarity of generally nonpolar PE has significant practical importance. SFE must be taken into account when interactions with solid and liquid materials are investigated (e.g., the coating, inking, and bonding of final products). Generally, the SFE of unmodified PE is 31–34 mJ m⁻². It depends on X_c of the polymer, antistatic additives during the polymerization process, and so forth.

The SFE of the nonmodified LDPE and HDPE was low, as shown in Tables III and IV. It had values of 31.1 mJ m⁻² for LDPE and 30.9 mJ m⁻² for HDPE, and the polar component of the SFE was 0.7 and 1 mJ m⁻² for LDPE and HDPE, respectively.

TABLE III
 γ_{sr} , γ_{sr}^p , γ_{sr}^d , and x_s^p of the LDPE/Wax Blends

LDPE/wax (w/w)	γ_s /(mJ/m ²)	γ_s^p (mJ/m ²)	γ_s^d (mJ/m ²)	x_s^p
100/0	31.1	0.7	30.4	0.02
98/2	31.5	1.9	29.6	0.06
96/4	32.6	3.5	29.1	0.11
94/6	33.9	4.3	29.6	0.13
92/8	35.7	5.7	30.0	0.16
90/10	36.8	7.0	29.8	0.19
0/100	37.6	8.0	29.6	0.21

TABLE IV
 γ_{sr} , γ_{sr}^p , γ_{sr}^d , and x_s^p of the HDPE/Wax Blends

HDPE/wax (w/w)	γ_s (mJ/m ²)	γ_s^p (mJ/m ²)	γ_s^d (mJ/m ²)	x_s^p
100/0	30.9	1.0	29.9	0.03
98/2	30.9	1.5	29.4	0.05
96/4	32.2	2.4	29.8	0.07
94/6	33.4	3.1	30.3	0.09
92/8	34.9	4.0	30.9	0.11
90/10	36.6	4.4	32.2	0.12
0/100	37.6	8.0	29.6	0.21

The modification of PE with various methods influences the SFE because of increasing polarity (e.g., oxidation and grafting with maleic anhydride, itaconic acid, and acrylamide).¹⁰ The modification of polyolefins in the melt with a low amount of a polar copolymer (e.g., ethylene/vinyl acetate, ethylene/acrylic acid, or ethylene/methacrylic acid copolymer) is also often used to increase the surface energy and particularly its polar component.^{10,11} The surface and adhesive properties of these materials are reported in our previous article.¹² Polyolefins may be modified with some low-molecular-weight compounds with polar functional groups; this is similar to the case of organic acids and their metallic salts.¹³

γ_s , γ_s^p and γ_s^d , and x_s^p of the LDPE/wax and HDPE/wax blends are summarized in Tables III and IV. The oxidized wax improved the polarity of the blends; for all the blends, both the SFE values and their polar components were higher than the values for neat PE. The increase in the polar component was exceptionally pronounced: 10 wt % oxidized wax increased the polar fraction of LDPE 10 times and that of HDPE 4 times. This was a remarkable finding. The oxygenic groups in the Fischer-Tropsch wax improved the surface and adhesive properties of the polyolefin with which it was blended. The improvement of the PE surface properties by mixing with oxidized wax in the melt¹⁷ was determined by the miscibility with wax containing carbohydrate macromolecules with polar oxygenic functional groups. More details about the mutual miscibility and compatibility of PE/wax blends can be found in our previous articles.¹⁷⁻¹⁹ In low amounts (≤ 10 wt %), the compatibility of oxidized wax and PE was very good, and the changes in the mechanical properties were very low. An increase in the polarity of the blends was found to be higher for LDPE than for HDPE. This could be caused by different X_c values. More likely, the wax chains, containing oxidized groups, were localized primarily in the amorphous part of PE. Because LDPE had more amorphous phase, oxidized groups were distributed over a

TABLE V
Strength of the Adhesive Joints (Peel Tests) of the HDPE/Wax and LDPE/Wax Blends to Crosslinked Epoxy Resin

PE/wax (w/w)	$P_{LDPE} \pm S_{P,LDPE}$ (N/m ⁻¹)	$P_{HDPE} \pm S_{P,HDPE}$ (N/m ⁻¹)
100/0	56 ± 4	124 ± 12
98/2	41 ± 3	37 ± 3
96/4	86 ± 6	46 ± 4
94/6	105 ± 8	57 ± 5
92/8	166 ± 10	69 ± 6
90/10	149 ± 11	96 ± 8

P_{LDPE} and P_{HDPE} = strengths of adhesive joints; $S_{P,LDPE}$ and $S_{P,HDPE}$ = standard deviations.

TABLE VI
Total Torque Moment (TM) of the LDPE/Wax and HDPE/Wax Blends

LDPE/wax (w/w)	TM (Nm)	HDPE/wax (w/w)	TM (Nm)
100/0	6.5	100/0	8.0
98/2	6.0	98/2	7.5
96/4	5.5	96/4	6.5
94/6	5.5	94/6	6.5
92/8	5.0	92/8	6.0
90/10	4.5	90/10	6.0

Brabender PLE 331, temperature = 150°C, 35 rpm, 10 min.

larger area and modified the final polarity more effectively.

Strength of adhesive joint (SAJ)

The efficiency of PE modification with oxidized wax was tested by the determination of the SAJ between PE and the crosslinked epoxy-based substrate. The SAJ values of the HDPE/wax and LDPE/wax blends to a crosslinked epoxy-based substrate, determined by 180° peeling tests, are summarized in Table V. There were some common and some different features for the two PE matrices. On the one hand, the dependence of SAJ on the wax content was not consistent in both cases. The SAJ for the HDPE/wax blends at first significantly decreased with 2 wt % wax in the blends. After that, the SAJ increased with an increase in the wax content, but the SAJ values of all the HDPE blends were lower than that for neat HDPE. On the other hand, different results were observed for the adhesive joints of the LDPE/wax crosslinked epoxy resin. The SAJ in this system was, with the exception of 2 wt % wax in the blend, higher than that for the nonmodified polymer. A 10 wt % concentration of wax in LDPE more than doubled the SAJ. This was probably the result of the higher crystallinity of HDPE in comparison with LDPE, as already discussed for the SFE measurements. Another potential explanation for this behavior is that a boundary layer of wax, with very low cohesive strength, was formed on the polymeric surface because of the lower solubility of wax in HDPE in comparison with LDPE. This layer considerably weakened the adhesive joint.

Total torque moment

The total torque moment of all the investigated blends is summarized in Table VI. This parameter characterizes the viscosity of the melt. The torque moment of the blends decreased with an increase in the wax content because the melt viscosity of the wax was much lower than that of PE.

CONCLUSIONS

Oxidized wax improved the polarity of the blends. The increase in the polar component of the total SFE was exceptionally pronounced, especially for the LDPE matrix, for which the polar component increased 10 times with respect to that of unmodified PE.

The modification of LDPE with oxidized wax significantly improved the SAJ between LDPE and an epoxy-based substrate. When 10 wt % wax was used, the SAJ increased two times. This behavior was not observed for HDPE.

Young's modulus of the LDPE/wax blends slightly increased with an increase in the wax content, whereas that of the HDPE/wax blends slightly decreased. This fact was probably associated with a change in X_c of the PE/wax blends. The wax content had no significant influence on the yield point (elongation at yield and yield stress) for the HDPE/wax blends. A slight decrease in the elongation at yield and an increase in the yield stress were observed for the LDPE/wax blends. In the LDPE/wax blends, the stress at break increased very slightly with an increase in the wax content. For the HDPE/wax blends, a decrease in the stress at break was observed.

The wax modified the viscosity of the blends. The torque moment of the blends decreased with an increase in the wax content over the entire concentration range.

References

- Hansen, M. H.; Finlayson, M. F.; Castille, M. J.; Goins, J. D. *Tappi J* 1993, 76, 171.
- Bhat, N. V.; Upadhyay, D. J. *J Appl Polym Sci* 2002, 86, 49.
- Oiseth, S. K.; Krozer, A.; Kasemo, B.; Lausmaa, J. *Appl Surf Sci* 2002, 202, 92.
- Wickson, B. M.; Brash, J. L. *Colloid Surf A* 1999, 156, 201.
- Wu, S.; Ji, G.; Shen, J. *Mater Lett* 2002, 4216, 1.
- Bag, D. S.; Ghosh, S. N.; Maiti, S. *Eur Polym J* 1998, 34, 855.
- Cho, J. S.; Beag, Y. W.; Han, S.; Kim, K. H.; Cho, J.; Koh, S. K. *Surf Coat Technol* 2000, 128, 66.
- Balamurugan, S.; Mandale, A. B.; Badrinarayanan, S.; Vernekar, S. P. *Polymer* 2001, 42, 2501.
- Akovali, G.; Borun, T. T.; Bazramli, E.; Erinc, N. K. *Polymer* 1998, 39, 1363.
- Novák, I.; Pollák, V. *Angew Makromol Chem* 1994, 220, 189.
- Chodák, I.; Novák, I. In *Polypropylene: An A-Z Reference*; Karger-Kocsis, J., Ed.; Kluwer: Dordrecht, 1999; p 790.
- Novák, I.; Florián, Š. *Polym Int* 2001, 50, 49.
- Novák, I. *Angew Makromol Chem* 1996, 236, 35.
- Santos, J. M.; Ribeiro, M. R.; Portela, M. F.; Bordado, J. M. *Chem Eng Sci* 2001, 56, 4191.
- Kang, E. T.; Neoh, K. G.; Li, Z. F.; Tan, K. L.; Liaw, D. J. *Polymer* 1998, 39, 2429.
- Pesetskii, S. S.; Jurkowski, B.; Kuzawkov, A. I. *Int J Adhes Adhes* 1998, 18, 351.
- Krupa, I.; Luyt, A. S. *Polymer* 2001, 42, 7825.
- Krupa, I.; Luyt, A. S. *J Appl Polym Sci* 2001, 81, 973.
- Krupa, I.; Luyt, A. S. *Polym Degrad Stab* 2000, 70, 111.
- Krupa, I.; Luyt, A. S. *Polym Degrad Stab* 2001, 73, 157.
- Wunderlich, B. ATHAS (Wunderlich Databank), Knoxville, TN.