

Modification of the Polarity and Adhesive Properties of Polyolefins Through Blending with Maleic Anhydride Grafted Fischer–Tropsch Paraffin Wax

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ABSTRACT: The modification of the polarity and adhesive properties of linear low-density polyethylene, low-density polyethylene, and isotactic polypropylene through blending with paraffin wax (Fischer–Tropsch synthesis), grafted by maleic anhydride, was investigated. Maleic anhydride grafted paraffin wax significantly increased the polar component of the total surface free energy of polyolefins. Modified polyolefins also had significantly higher adhesion to the polar substrate, a crosslinked, epoxy-based resin. The

conservation of the good mechanical properties of the blends was observed up to 10 wt % wax, except for isotactic polypropylene blends, for which there was a reduction in the stress and strain at break at wax concentrations higher than 5%. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3069–3074, 2006

Key words: adhesion; isotactic; mechanical properties; polyethylene (PE); poly(propylene) (PP)

INTRODUCTION

Polyolefins are the most frequently used polymers in industry because of their excellent properties, low price, and easy processing. They have limitations in their adhesion because of their nonpolar nature, which leads to low surface free energy (SFE) and consequently poor adhesive properties. To obtain a plausible value of adhesion, it is necessary to introduce some polar groups into the macromolecules of polyolefins with a convenient modification method. For this reason, different methods for the modification of the polarity of polyolefins have been investigated, mainly for the introduction of suitable polar sites into and/or onto the chains of the polymers.^{1,2} A number of methods for isotactic polypropylene (iPP) modification have recently been developed, and some of them have been successfully used for the surface modification of iPP. These include electric discharge plasma at atmospheric pressure^{3,4} and at reduced pressure,^{5,6} various chemical methods,^{7,8} and grafting by some organic acids and/or anhydrides.^{9–12} During iPP modification, a chemical pretreatment, which introduces

specific functional groups, plays an important role, resulting in strong adhesive bonds. One of the most frequently used modification methods is the modification of iPP in the bulk by the addition of low-molecular-weight compounds or polar polymers.¹³ The diffusion of the modifier to the iPP surface plays a fundamental role in the increase in iPP adhesion.

Various methods have also been used to improve polyethylene (PE) adhesive properties, such as corona-discharge¹⁴ and plasma-surface modification^{15,16} and chemical surface etching.^{17–20} Such types of surface modification 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 increasing the adhesive properties of PE is its modification in the bulk by the addition of small amounts of polar polymers or low-molecular-weight additives.²¹

Recently, we investigated the influence of oxidized wax on the polarity, adhesion, and mechanical properties of low-density polyethylene (LDPE) and high-density polyethylene (HDPE).²² The wax improved the polarity of the blends. The increase in the polar component of the total SFE in particular was exceptionally pronounced, especially for the LDPE matrix, in which the polar component increased 10 times in comparison with unmodified PE. The modification of LDPE with oxidized paraffin wax also significantly improved the strength of the adhesive joint between LDPE and a cured epoxy-based substrate. In the case of HDPE, even though the polar component of the

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total SFE significantly increased, an improvement in the adhesion to the epoxy substrate was not observed. The conservation of the good mechanical properties was observed for LDPE, linear low-density polyethylene (LLDPE), and HDPE as a result of the miscibility of PE and wax, as discussed in our previous articles.^{23–25} We also showed that an oxidized Fischer–Tropsch wax could be effectively used as an agent for the improvement of the polarity of iPP. Ten weight percent oxidized wax increased the polar component of the total SFE of iPP 11 times and the polar ratio 14 times. Modified iPP had a significantly higher adhesion to the more polar substrate, which was represented by a crosslinked, epoxy-based resin. The strength of the adhesive joint between the cured epoxy resin and iPP increased by about 62% when it was modified by 10 wt % oxidized wax. The conservation of the good mechanical properties of iPP blended with wax was observed for samples containing up to 6 wt % oxidized wax.²⁶

The modification of the polarity of LDPE, LLDPE, and iPP through blending with Fischer–Tropsch paraffin wax, grafted with maleic anhydride (MA), was investigated in this study. The adhesion of modified polyolefins to the metallic substrate and their mechanical properties were also investigated.

EXPERIMENTAL

Polymers and chemicals

The following materials were used: LDPE (Bralen RA 2-19; MFI (Melt flow index) = 1.7 g/10 min, density = 0.916 g/cm³, particle size < 50 μm, specific enthalpy of melting = 109.8 J/g, melting temperature = 107°C) from Slovnaft (Bratislava, Slovakia); LLDPE (MFI = 3.5 g/10 min, density = 0.938 g/cm³, 90% of particles are smaller than 600 μm, specific enthalpy of melting = 155.9 J/g, melting temperature = 130°C) from Sasol Polymers (Johannesburg, South Africa); iPP Tatren FF 500 (MFI = 10 g/10 min, density = 0.901 g/cm³, particle size < 30 μm, specific enthalpy of melting = 58.6 g/cm³, melting temperature = 164°C) from Slovnaft; and hard, brittle, straight-hydrocarbon-chain paraffin wax (average molar mass = 785 g/mol, density = 0.940 g/cm³) from Sasol Wax (Sasolburg, South Africa).

Methods

The grafted paraffin wax was prepared as follows: the paraffin wax was mechanically ground with MA and dibenzoyl peroxide (both obtained from Sigma–Aldrich, Taufkirchen, Germany). The composition of the mechanical blend was 85/10/5 (w/w/w) paraffin wax/MA/dibenzoyl peroxide (DBP) because this composition ensured an appropriate modification of

the polarity of the wax.²⁷ This was followed by the heating of the mixture in an oil bath at 140°C for 10 min in a nitrogen atmosphere, cooling and grinding of the sample, washing in boiling water to dissolve any unreacted MA, filtering, and drying in an oven at 50°C.²⁷

The efficiency of the grafting of MA onto paraffin wax chains was determined according to a titration method reported by Gaylord and Mishra.²⁸ Grafted wax (1 g) was extracted in distilled water under reflux for 2 h. The solution was cooled and filtered. The solid fraction was put into a beaker. Distilled water and a few droplets of a 1% ethanol solution of phenolphthalein were added. The concentration of maleic groups was determined by titration with a 0.2N solution of KOH in *n*-butanol. The real concentration of grafted maleic groups was 3.6 wt %, which represented 36% efficiency of grafting.

Unmodified and grafted wax was examined with Fourier transform infrared (FTIR; Fig. 1). For the maleated Fischer–Tropsch wax, the wavelengths of interest were 1713 cm⁻¹ (characteristic of carbonyls from carboxylic dimer acids) and 1790 cm⁻¹ (characteristic of five-membered cyclic anhydride carbonyls).^{29,30}

The blends were prepared via the mixing of the components in a 50-mL mixing chamber of a Brabender (Duisberg, Germany) PLE 331 plasticorder at 180°C for 10 min at a mixing speed of 35 rpm. Slabs (1-mm-thick) were prepared by compression molding of the mixed composite with a Fontijne (Vlaardingen, The Netherlands) SR-100 laboratory hydraulic press at 180°C for 3 min. Dog-bone-shaped specimens with a working area of 35 × 3.6 × 1 mm³ were cut from the slabs. The mechanical properties were measured at room temperature with an Instron (High Wycombe, England) 4301 5-kN universal testing machine at a deformation rate of 10 mm/min.

The SFE of the samples was carried out by the measurement of the contact angles [θ (°)] of a set of testing liquids with various polarities with an Amplival Pol contact-angle meter (Zeiss, Jena, Germany). For the determination of the SFE of the polymers, the testing liquids listed in Table I were used. The testing liquids were glycerin, formamide, and 1-bromonaphthalene (Merck, Darmstadt, Germany); methylene iodide (Fluka, Buchs, Switzerland); and thiodiglycol, ethyl 2-aminobenzoate, and ethylene glycol (Serva, Heidelberg, Germany).

The relationship between θ and 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 a least-squares method by the minimization of the following relation:⁹

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

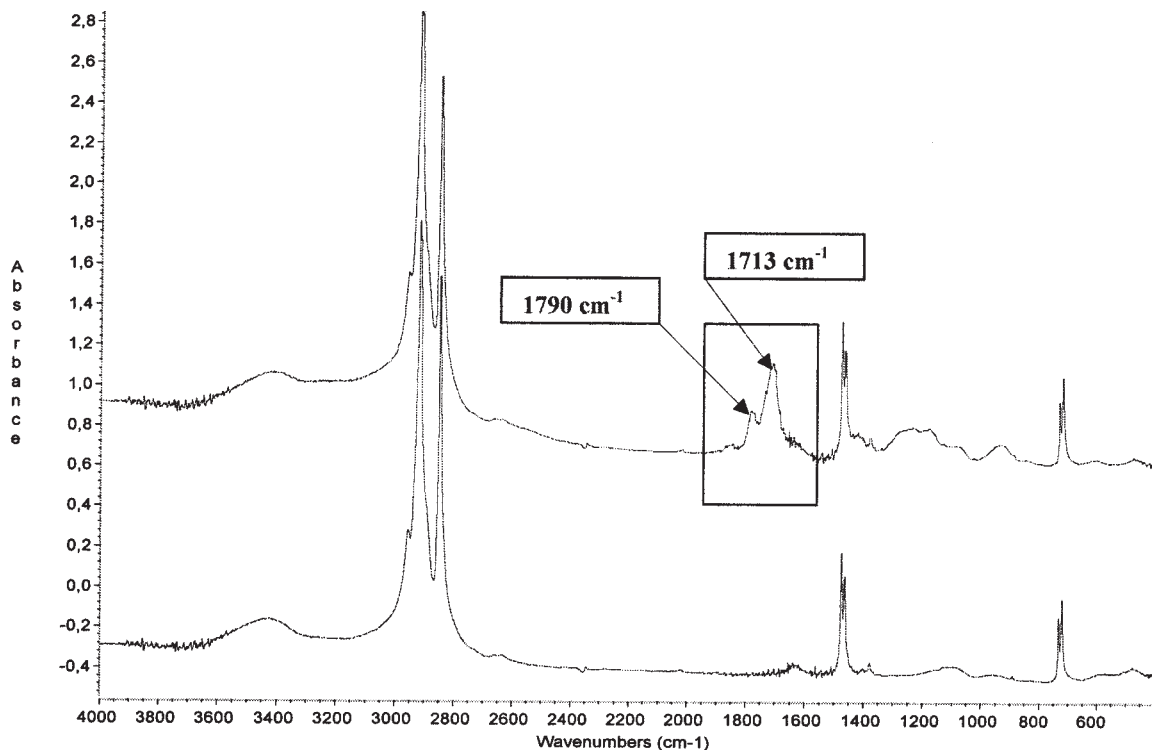


Figure 1 FTIR spectra for an unmodified Fischer-Tropsch wax (bottom) and the same wax grafted with 3.6 wt % MA (top).

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^d and γ_s^p are the dispersive and polar components of the SFE of the polymer (mJ/m^2), respectively. Moreover,

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

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 peel strength [P (J/m^2)] of the adhesive joint at a constant angle of 180° was measured after the creation of adhesive joints with two aluminum foils (the dimensions of the joints were $150 \times 20 \times 0.2 \text{ mm}^3$) bonded together with molten blends of the polyolefin and grafted wax in a Fontijne SR-100 laboratory hydraulic press at a temperature of 200°C and a pressure of 300 kPa. The thickness of the adhesive layer was 0.1 mm, and the length of peeling was 100 mm. The 180° peel test of the adhesive joints was performed along the length of the adhesive joint. The values of P of the adhesive joints were calculated as follows:

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

TABLE I
Surface Free Energy, Its Polar Component, and Polar Fraction of the Testing Liquids Used for the Measurement of the Surface Energies of the Polymers

| Testing liquid (23°C) | γ_L^{total} (mJ/m^2) | γ_L^p (mJ/m^2) | X_L^p |
|----------------------------|---|--|---------|
| Redistilled water | 72.8 | 51.0 | 0.701 |
| Glycerine | 63.4 | 26.4 | 0.416 |
| Ethylene glycol | 48.5 | 19.1 | 0.394 |
| Formamide | 58.2 | 18.7 | 0.321 |
| Thiodiglycol | 54.2 | 17.3 | 0.319 |
| α -Bromonaphthalene | 45.3 | 0 | 0 |
| Methylene iodide | 50.8 | 2.3 | 0.045 |
| Ethyl 2-aminobenzoate | 39.3 | 7.9 | 0.201 |

It holds for the polar fraction of the testing liquid

$$X_L^p = \gamma_L^p / \gamma_L^{\text{total}}$$

where γ_L^{total} is the total surface free energy of the testing liquids, γ_L^p is the polar component of the surface free energy, and X_L^p is the polar fraction of the testing liquid.

TABLE II
Total Surface Free Energy (γ_s), Its Polar Component (γ_s^p), Its Dispersive Component (γ_s^d), and Polar Fraction (X_s^p) of LDPE Bralen RA 2-19/MA-Wax Blends

| LDPE/MA-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 | 32.0 | 0.4 | 31.6 | 0.01 |
| 98/3 | 32.5 | 1.2 | 31.3 | 0.04 |
| 94/5 | 34.5 | 3.3 | 31.2 | 0.10 |
| 92/7 | 35.6 | 4.5 | 31.1 | 0.13 |
| 90/10 | 36.2 | 5.5 | 30.7 | 0.15 |
| 0/100 | 36.6 | 6.2 | 30.4 | 0.17 |

TABLE III
Total Surface Free Energy (γ_s), Its Polar Component (γ_s^p)
Its Dispersive Component (γ_s^d), and Polar Fraction (X_s^p)
of LLDPE/MA-Wax Blends

| LLDPE/MA-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 | 31.2 | 0.6 | 29.2 | 0.03 |
| 98/3 | 33.4 | 1.2 | 32.1 | 0.04 |
| 94/5 | 35.8 | 3.1 | 32.7 | 0.09 |
| 92/7 | 36.2 | 4.2 | 32.0 | 0.12 |
| 90/10 | 36.2 | 5.0 | 31.2 | 0.14 |
| 0/100 | 36.6 | 6.2 | 30.4 | 0.17 |

where F_s is the mean force of peeling (N) and b is the width of the adhesive joint. The peel tests of the adhesive joints were carried out with an Instron 4301 universal testing machine at a constant crosshead speed of 10 mm/min.

The shear strengths of the adhesive joint (MPa) were measured by the tensile testing of the singly overlapped adhesive joints. The adhesive joints were prepared with two aluminum slabs with dimensions of $60 \times 10 \times 2$ mm³. The thickness of the adhesive layer was 0.1 mm, the length of the overlap was 10 mm, and the bonded area was 1 cm². The aluminum slabs were bonded together at 200°C in a laboratory press with a molten modified polyolefin. The adhesive joints were tested in shear with an Instron 4301 universal testing machine at a constant crosshead speed of 10 mm/min.

Differential scanning calorimetry was carried out on a PerkinElmer (Wellesley, Massachusetts) DSC7 thermal analyzer in a nitrogen atmosphere. Samples were heated from 25 to 180°C at a heating rate of 10°C/min and then cooled at the same rate. Thermal properties, such as the melting and crystallization temperatures and enthalpies, were determined from the second scan.

Infrared analyses were performed on a Nicolet (Waltham, Massachusetts) Impact 410 FTIR spectrometer connected to a photoacoustic cell. A carbon disk was used to obtain a baseline under a helium atmosphere. A resolution of 8 cm⁻¹, a scan range of 4000–500 cm⁻¹, and a total of 200 scans per analysis were used.

TABLE IV
Total Surface Free Energy (γ_s), Its Polar Component (γ_s^p)
Its Dispersive Component (γ_s^d), and Polar Fraction (X_s^p)
of iPP Tatren FF 500/MA-Wax Blends

| iPP/MA-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 | 30.2 | 0.3 | 29.9 | 0.01 |
| 98/3 | 31.2 | 1.2 | 30.0 | 0.04 |
| 94/5 | 33.8 | 2.6 | 31.2 | 0.08 |
| 92/7 | 34.2 | 3.2 | 31.0 | 0.09 |
| 90/10 | 34.6 | 3.6 | 31.0 | 0.10 |
| 0/100 | 36.6 | 6.2 | 30.4 | 0.17 |

TABLE V
Peel Strength of the Adhesive Joints (P) Obtained
from 180° Peel Tests of LDPE, LLDPE, and iPP Blends
with MA-Wax

| Polyolefin/ MA-wax (w/w) | $P \pm S_p$ (J/m ²) | | |
|--------------------------------|---------------------------------|----------|----------|
| | LDPE | LLDPE | iPP |
| 100/0 | 166 ± 17 | 120 ± 21 | 140 ± 10 |
| 97/3 | 178 ± 14 | 132 ± 18 | 155 ± 16 |
| 95/5 | 196 ± 12 | 158 ± 14 | 188 ± 18 |
| 93/7 | 255 ± 26 | 198 ± 24 | 196 ± 20 |
| 90/10 | 299 ± 29 | 239 ± 32 | 220 ± 21 |

S_p = standard deviation of the strength of the adhesive joint.

RESULTS AND DISCUSSION

Total SFE measurements

The total SFE, its polar and dispersive components, and the polar fraction of the SFE of all the investigated blends are summarized in Tables II–IV. The grafted wax improves the polarity of all the blends; for all the blends, both the SFE values and their polar components are higher than the values for the unmodified polyolefins. The increase in the polar component (γ_s^p) of the SFE and the polar fraction (x_s^p) in particular is exceptionally pronounced: 10 wt % grafted paraffin wax increases the polar component of the SFE of LDPE 13.8 times and the polar fraction 15 times. For LLDPE, 10 wt % grafted paraffin wax increases the polar component of the SFE 6.2 times and the polar fraction 5.7 times. For iPP, a similar improvement can be observed: 10 wt % grafted paraffin wax increases the polar component of its SFE 10.7 times and the polar fraction 10 times.

Similar behavior has been observed for both LDPE and HDPE,²² for which 10 wt % oxidized wax increases the polar component of the SFE of LDPE 10 times and that of HDPE 4.5 times. The oxygenic groups in the Fischer–Tropsch wax (whether it is an oxidized or MA-grafted wax) improve the surface as well as adhesive properties of the polyolefin with

TABLE VI
Shear Strength of the Adhesive Joints (P) Obtained
from Shear Tests of LDPE, LLDPE,
and iPP Blends with MA-Wax

| Polyolefin/ MA-wax (w/w) | $P \pm S_p$ (J/m ²) | | |
|--------------------------------|---------------------------------|------------|-----------|
| | LDPE | LLDPE | iPP |
| 100/0 | 0.6 ± 0.1 | 0.5 ± 0.04 | 0.6 ± 0.1 |
| 97/3 | 0.7 ± 0.1 | 0.6 ± 0.04 | 0.7 ± 0.1 |
| 95/5 | 0.9 ± 0.1 | 0.7 ± 0.06 | 0.8 ± 0.1 |
| 93/7 | 1.1 ± 0.1 | 0.9 ± 0.09 | 1.1 ± 0.1 |
| 90/10 | 1.3 ± 0.1 | 1.1 ± 0.1 | 1.2 ± 0.1 |

S_p = standard deviation of the strength of the adhesive joint.

TABLE VII
Mechanical Properties of the LDPE (Bralen RA 2-19)/MA-Wax Blends

| LDPE/MA-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 | 21.5 ± 1.6 | 8.1 ± 0.4 | 396 ± 41 | 10.9 ± 1.8 | 129 ± 16 |
| 97/3 | 20.1 ± 1.3 | 8.7 ± 0.4 | 437 ± 51 | 11.9 ± 1.1 | 139 ± 11 |
| 95/5 | 16.3 ± 1.7 | 8.5 ± 0.4 | 476 ± 42 | 9.5 ± 1.7 | 160 ± 19 |
| 93/7 | 15.7 ± 1.8 | 9.4 ± 0.5 | 483 ± 64 | 12.5 ± 2.1 | 147 ± 20 |
| 90/10 | 16.2 ± 0.8 | 9.4 ± 0.5 | 415 ± 56 | 11.7 ± 1.6 | 141 ± 17 |

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

which it is blended. The increase in the polar component of the SFE of iPP is almost the same as in the case of LDPE. This is probably the result of a similar degree of crystallinity. The values of the degree of crystallinity are as follows: 33% for iPP, 37% for LDPE, and 74% for HDPE. Because the wax chains, containing oxidized groups, are localized primarily in the amorphous part of the semicrystalline matrix in the polymers consisting of more amorphous phase, the oxidized groups are distributed over a larger area and modify the final polarity more effectively.

Strength of the adhesive joint

The P value of the adhesive joints of LDPE, LLDPE, and iPP, blended with MA-grafted wax, to aluminum was determined by 180° peel tests. The results are summarized in Table V. The P value of the adhesive joint increases with an increase in the grafted wax content in all the investigated cases. The strength of the adhesive joint for polyolefin/grafted wax blends increases 1.8 times for the LDPE matrix, 2 times for the LLDPE matrix, and 1.6 times for the iPP matrix, when blended with 10 wt % grafted wax. These observations correspond to the results obtained from SFE measurements, which show an increase in the surface energy and its polar component with an increase in the grafted wax content in the blend.

The same trend has been observed for the dependence of the shear strength of the adhesive joints to aluminum of LDPE, LLDPE, and iPP blended with MA-grafted wax, obtained from shear tests, on the

MA-grafted wax content. These results are summarized in Table VI. The shear strength of the adhesive joint for polyolefin/grafted wax blends increases 2.2 times for the LDPE and LLDPE matrices and 2 times for the iPP matrix, with an increase in the grafted wax content when they are blended with 10 wt % grafted wax. The failures of the adhesive joints tested by peeling took place at the interface of the polymer blend/aluminum system for all the investigated samples.

Mechanical properties

The mechanical properties of all the investigated blends are summarized in Tables VII–IX. The mechanical properties of the blends differ, depending on the polymer matrix used. Young's modulus of the LDPE/grafted wax blends slightly increases with an increase in the wax content, most likely because of an increase in the crystalline fraction in the blend, because the degree of crystallinity of the wax is significantly higher than that of LDPE. For LLDPE/grafted wax blends, no statistically significant influence of the wax content on Young's modulus has been observed. Although the degree of crystallinity of wax is higher than that of LLDPE, the increase in the total degree of crystallinity of the blends has a marginal influence on Young's modulus, probably because of the low wax content. However, if more wax is incorporated into the LLDPE matrix (ca. 20–30%), an increase in Young's modulus is observed. This is probably due to cocrystallization of the wax with LLDPE at higher wax contents.³¹

TABLE VIII
Mechanical Properties of the LLDPE/MA-Wax Blends

| LLDPE/MA-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 | 19.2 ± 2.3 | 16.3 ± 0.5 | 1120 ± 82 | 21.7 ± 1.6 | 160 ± 19 |
| 97/3 | 16.1 ± 1.0 | 16.7 ± 0.2 | 926 ± 88 | 18.3 ± 2.2 | 169 ± 22 |
| 95/5 | 14.7 ± 1.6 | 17.3 ± 1.3 | 941 ± 62 | 17.8 ± 2.4 | 166 ± 17 |
| 93/7 | 14.9 ± 0.6 | 16.9 ± 0.7 | 962 ± 70 | 17.2 ± 1.4 | 162 ± 14 |
| 0/10 | 14.9 ± 0.3 | 16.2 ± 1.2 | 952 ± 32 | 15.6 ± 2.5 | 154 ± 21 |

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

TABLE IX
Mechanical Properties of the iPP (Tatren FF 500)/MA–Wax Blends

| iPP/MA–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 | 9.6 ± 1.2 | 29.4 ± 3.6 | 769 ± 71 | 30.9 ± 3.8 | 862 ± 67 |
| 97/3 | 10.3 ± 1.1 | 27.4 ± 2.1 | 737 ± 51 | 27.8 ± 3.9 | 699 ± 46 |
| 95/5 | 9.7 ± 1.1 | 29.2 ± 2.7 | 716 ± 62 | 29.5 ± 1.7 | 660 ± 59 |
| 93/7 | 10.6 ± 1.4 | 24.2 ± 1.8 | 483 ± 44 | 17.5 ± 2.1 | 746 ± 72 |
| 90/10 | 11.0 ± 1.4 | 23.8 ± 2.8 | 415 ± 33 | 16.7 ± 2.4 | 707 ± 112 |

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

In the case of the iPP matrix, the presence of wax deteriorates Young's modulus as well as the stress and elongation at break of the blends. Because iPP and wax are not miscible in the solid phase on account of the different morphologies of the crystallites, and because the values of Young's modulus, the elongation at break, and the stress at break of wax are much lower than those of iPP, this decrease can be expected. IPP crystallizes in a helical form in which there are three monomer units per turn of the helix,³² and wax, similarly to PE, crystallizes in a planar zigzag form. For this reason, the chains of both iPP and wax crystallize separately, and this has a negative influence on the final mechanical properties.

The stress at break of the LLDPE/grafted wax blend slightly decreases with an increase in the wax content. For the LDPE matrix, no significant influence on the stress at break has been observed. It is associated with the partial miscibility of PE with wax, as discussed in our previous articles.^{23–25} The same tendency has been observed for the elongation at break of the blends.

The stress–strain curves indicate that virgin iPP and its blends consisting of 2, 4, and 6 wt % wax show cold drawing followed by strain (orientation) hardening, before breaking. No brittle rupture has been observed. This indicates that the mechanical properties of iPP are not very much deteriorated by the presence of the wax. The samples having 8 and 10 wt % wax showed cold drawing but did not undergo orientation hardening. These materials have significantly lower values of elongation and stress at break.

CONCLUSIONS

MA-grafted paraffin wax, blended with LDPE, LLDPE, and iPP, causes a pronounced increase in the SFE and particularly its polar fraction of the investigated polyolefins. This has an influence on the adhesion of the blends to a metallic (aluminum) substrate, for which the strengths of the adhesive joints increase markedly. Adhesive failure occurred at the adhesive joints between the modified polyolefin and aluminum for all the samples. As far as mechanical properties are concerned, Young's modulus and the stress and strain at break are conserved for LLDPE and iPP blends

containing up to 5% MA-grafted wax and for LDPE blends containing up to 10% (the maximum amount of MA-grafted wax used in this investigation).

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