

Modification of the Polarity of Isotactic Polypropylene through Blending with Oxidized Paraffin Wax

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ABSTRACT: The modification of the polarity of isotactic polypropylene (iPP) through blending with oxidized paraffin wax (Fischer–Tropsch synthesis) was investigated. The oxidized paraffin wax significantly increased the polar component of the total surface free energy of polypropylene. Modified iPP also showed significantly higher adhesion to the polar substrate, as represented by a crosslinked epoxy-

based resin. The conservation of the good mechanical properties of the blends was observed up to 6 wt % wax. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 529–533, 2004

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

INTRODUCTION

Polypropylene is synthesized entirely by a low-pressure process with Ziegler–Natta catalysts. Usually, 90% or more of the polymer is in the isotactic form. Major markets for homopolymers are filaments and fibers, automotive and appliance components, packaging materials, furniture, and so forth. Isotactic polypropylene (iPP) has limitations in its adhesion because of its nonpolar nature, which leads to its low surface free energy (SFE) and consequently to its poor adhesive properties. For obtaining a plausible value of adhesion, it is necessary to introduce some polar groups into the macromolecules of iPP with a convenient modification method. For this reason, different methods for the modification of the polarity of iPP were investigated, mainly aimed at the addition of suitable polar sites into or onto the chains of the polymer.^{1,2} A number of modification methods for iPP modification have recently been developed, and some of them have been successfully used for the surface modification of iPP (e.g., electric discharge plasma at atmospheric^{3,4} and reduced pressures,⁵ by various chemical methods,^{7,8} and grafting with some organic acids and their anhydrides^{9–12}). In all these methods, a chemical pretreatment, which adds specific functional groups, plays an important role, providing strong adhesive bonds. One of the most frequently used modifica-

tion methods is the modification of iPP in bulk by the addition of some 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.

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).¹⁴ Wax improved the polarity of the blends. The increase in the polar component of the total SFE (γ) in particular was exceptionally pronounced, especially for the LDPE matrix: the polar component increased 10-fold, in comparison with that of unmodified polyethylene (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. On the other hand, in the case of HDPE, even though the polar component of γ significantly increased, an improvement in the adhesion to the epoxy substrate was not observed. The conservation of good mechanical properties was observed for LDPE, linear LDPE, and HDPE because of the miscibility of PE and wax, as discussed in our previous articles.^{15,16}

The modification of the polarity of iPP through blending with wax was investigated in this study. The adhesion of iPP/oxidized wax blends to an epoxy-based cured substrate, as well as the mechanical properties of the blends, was also investigated.

EXPERIMENTAL

Polymers and chemicals

The following materials were used: iPP Tatren FF 500 R (melt-flow index = g/10 min, density = 0.901 g

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cm⁻³, particle size < 30 μm) from Slovnaft (Slovakia); hard, 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 Sasol Waxes (South Africa), and a set of testing liquids [twice distilled water; glycerine (p.a.), formamide (p.a.), and 1-chloronaphthalene from Merck, Germany; methylene iodide (p.a.) from Fluka Germany; and thiodiglycol, ethyl 2-aminobenzoate (p.a.), and ethylene glycol (p.a.) from Serva, Germany].

Methods

The blends were prepared through the mixing of the components in a 50-mL mixing chamber of a PLE 331 plasticorder (Brabender, Germany) at 190°C for 10 min at a mixing speed of 35 rpm. Slabs (1-mm-thick) were prepared by the compression molding of the mixed composite with an SR-100 laboratory hydraulic press (Fontijne, The Netherlands) 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 model 4301 5 kN universal testing machine (Instron, England) at a deformation rate of 10 mm min⁻¹. The SFE determination of the samples was carried out through the measurement of the contact angles (θ ; °) of a set of testing liquids with different polarities with a contact-angle meter (Zeiss, Germany). The relationship of 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 the minimization of the relation:⁹

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

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

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

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

$$x_s^p = \frac{\gamma_s^p}{\gamma_s(\text{Total})} \quad (3)$$

The mechanical work of adhesion (A_m) to the crosslinked epoxy resin (Epoxy 341, Spolchemie, Czech Republic) was measured by a peel test of the

TABLE I
 γ , γ^p , γ^d , and x_s^p of the iPP/Wax Blends

iPP/wax (mol/mol)	γ (mJ/m ²)	γ^p (mJ/m ²)	γ^d (mJ/m ²)	x_s^p
100/0	30.5	0.4	30.1	0.01
98/2	31	1.3	28.7	0.04
96/4	32.3	2.7	29.6	0.08
94/6	33.5	3.4	30.1	0.10
92/8	34.6	4.0	30.6	0.12
90/10	34.8	4.3	30.5	0.14
				0.23
0/100	35.1	7.9	27.2	

adhesive joint at a constant angle of 90°. The peel test was performed with the Instron 4301 with an additive aluminum peeling wheel at a crosshead speed of 10 mm min⁻¹ and at a joint length of 100 mm. The laminates of the iPP/oxidized wax blends with epoxy crosslinked with diethylene triamine as a hardener for the peeling tests were prepared after the deposition of epoxy on the cotton technical fabric (Molino, Slovakia) with a laboratory coating ruler (Druopta, Czech Republic). The width of the deposited epoxy layer was 0.2 mm. The adhesive joints were made by the application of pressure with a rubber cylinder. Then, the epoxy resin was crosslinked for 48 h at room temperature and cut into strips (25 mm × 150 mm). The 180° peeling of the adhesive joints was performed along the length of the adhesive joint. The values of A_m were calculated according to the following equation:

$$A_m = \frac{P}{b} \quad (4)$$

where P is the mean force of delamination (N) and b is the width of the adhesive joint.

Differential scanning calorimetry (DSC) was carried out on a PerkinElmer DSC7 thermal analyzer under a nitrogen atmosphere. The samples were heated from 25 to 180°C at a heating rate of 10°C min⁻¹ and then cooled down at the same rate. The thermal properties, such as the melting and crystallization temperatures and enthalpies, were determined from the second heating scan.

RESULTS AND DISCUSSION

SFE measurements

γ , its polar and dispersive components, and the polar fraction of the SFE of iPP/wax blends are summarized in Table I. The oxidized wax improved the polarity of the blends: for all the blends, both the SFE values and the polar components were higher than the values for unmodified iPP. The increase in the polar component in particular was exceptionally pronounced: 10 wt %

TABLE II
***P* Values Obtained from the Peel Tests of the iPP/Wax Blends to Crosslinked Epoxy Resin**

iPP/wax (w/w)	$P \pm S_p$ (J/m ²)
100/0	145.6 ± 18.2
98/2	160.8 ± 18.9
96/4	189.3 ± 24.3
94/6	207.3 ± 26.2
92/8	216.2 ± 23.2
90/10	236.9 ± 26.4

S_p standard deviation of the strength of the adhesive joint.

oxidized wax increased the polar component of SFE of iPP 11 times and its polar ratio 14 times. Similar behavior was observed for both LDPE and HDPE,¹⁶ for which 10 wt % oxidized wax increased the polar component of SFE of LDPE 10 times and that of HDPE 4.5 times. The oxygenic groups in the Fischer–Tropsch wax improved the surface as well as the adhesive properties of the polyolefin with which it was blended. The increase in the polar component of SFE of iPP was almost the same as that for LDPE. This was caused by the similar degree of crystallinity. The degrees of crystallinity were as follows: 33% for iPP, 37% for LDPE, and 74% for HDPE. Because the wax chains, containing oxidized groups, were localized primarily in the amorphous part of the semicrystalline matrix of the polymers consisting of more amorphous phase, the oxidized groups were distributed over a larger area and modified the final polarity more effectively.

Strength of the adhesive joint

The strength of the adhesive joint of the iPP/oxidized wax blend to the crosslinked epoxy resin, determined by 180° peeling tests, was investigated (Table II). The strength of the adhesive joint for all the iPP/oxidized wax blends was higher than that for the nonmodified polymer (145.6 N m⁻¹). The strength of the adhesive joint for iPP/oxidized wax blends increased signifi-

cantly with an increase in the oxidized wax content, from 160.8 N m⁻¹ (for 2 wt % oxidized wax in the blend) to 236.9 N m⁻¹ (for 10 wt % oxidized wax).

These observations agreed with previous results obtained from surface energy measurements that showed an increase in the surface energy and its polar component with an increase in the oxidized wax content in the blend.

DSC

The results obtained from the DSC analyses are summarized in Table III. The DSC heating and cooling curves for both the pure components and some selected blends are shown in Figures 1 and 2. Only one endothermic peak was observed for all the investigated blends, even though the DSC curve of wax has two endothermic peaks lying at different temperatures than that of pure iPP. Because iPP and wax can in principle not be miscible on account of the different morphologies of the crystallites (iPP crystallizes in a helical form and wax crystallizes in a planar zigzag form, similarly to PE), a probable explanation is that iPP and wax show macroscopic homogeneity at these concentrations. This fact probably also results in the relatively good conservation of the mechanical properties of the blends, as discussed.

As far as the onset and peak temperatures of melting are concerned, an increase in the wax content slightly decreased these temperatures, as shown in Table III and Figure 1. The specific enthalpy of melting slightly increased with an increase in the wax content because this value was bigger for wax than for iPP. Similar trends were also observed during the crystallization of the blends. The explanation of this fact can be the same as that discussed previously: iPP and wax are not miscible in the molten state and just exhibit macroscopic homogeneity. On the other hand, it can also mean that iPP and wax are really miscible in the melt, but upon cooling, each component separates and forms its own unique crystal structure.

TABLE III
Parameters Obtained from DSC Measurements for the iPP/Wax Blends

Sample	Wax	iPP	98/2 w/w iPP/wax	96/4 w/w iPP/wax	94/6 w/w iPP/wax	92/8 w/w iPP/wax	90/10 w/w iPP/wax
$T_{o,m}$ (°C)	40.9	154.8	152.5	153.4	151.9	151.0	150.0
$T_{p,m}$ (°C)	70.5 ^a	161.7	161.7	159.4	157.4	159.9	161.9
ΔH_m (J/g)	174.0	57.6	63.9	58.3	60.6	60.4	58.8
$T_{o,c}$ (°C)	87.1	117.2	115.7	114.2	112.6	113.3	112.7
$T_{p,c}$ (°C)	65.5 ^b	110.8	110.1	108.5	108.0	108.0	107.0
ΔH_c (J/g)	172.1	-69.2	-75.2	-71.4	-70.3	-71.7	-72.5

T = temperature; ΔH = specific enthalpy. The subscripts m , c , and o refer to melting, cooling, and onset, respectively.

^a The DSC heating curve of pure wax showed two endothermic peaks. This one was the main peak. The other one was at 93.7°C.

^b The DSC cooling curve of pure wax showed two exothermic peaks. This one was the main peak. The other one was at 82.6°C.

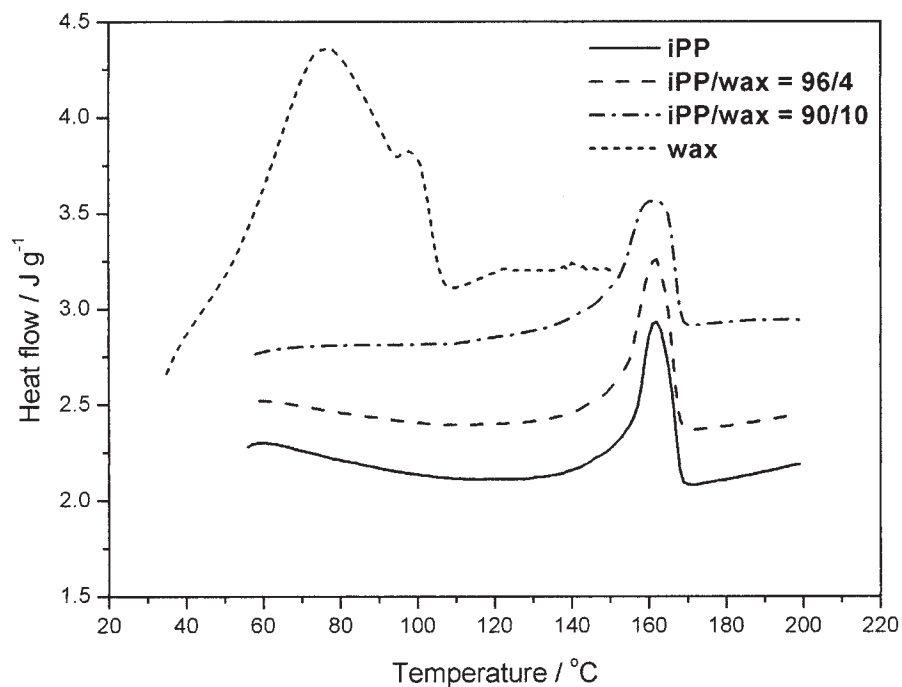


Figure 1 DSC heating curves of iPP, wax, and different iPP/wax blends.

Mechanical properties

The mechanical properties of the investigated blends are summarized in Table IV. All the mechanical properties of the blends (Young's modulus, elongation at break, and stress at break) decreased with an increase in the wax content. 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, elongation at break, and stress at break of wax are much lower than those of iPP, this decrease could be expected. IPP crystallizes in a helical form in which there are three monomer units

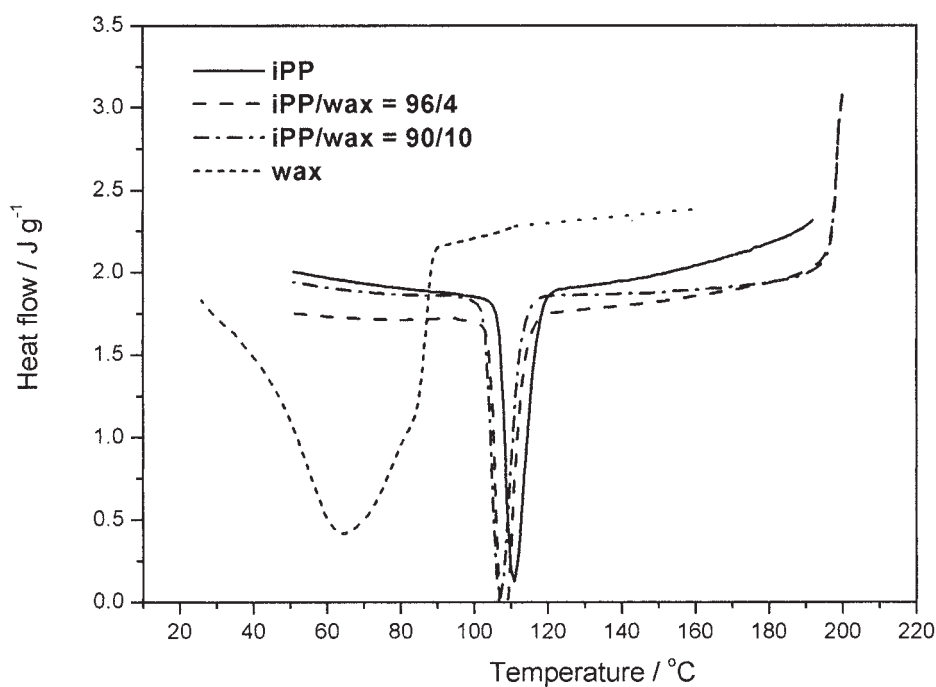


Figure 2 DSC cooling curves of iPP, wax, and different iPP/wax blends.

TABLE IV
Mechanical Properties of the iPP/Wax Blends

iPP/wax (w/w)	$\epsilon_y \pm S_{\epsilon_y}$ (%)	$\epsilon_b \pm S_{\epsilon_b}$ (%)	$\sigma_y \pm S_{\sigma_y}$ (MPa)	$\sigma_b \pm S_{\sigma_b}$ (MPa)	$E \pm S_E$ (MPa)
100/0	10.5 ± 0.7	731 ± 92	34.3 ± 1.9	34.9 ± 5.5	805 ± 44
98/2	11.1 ± 1.3	710 ± 98	28.6 ± 0.8	32.2 ± 3.7	661 ± 50
96/4	10.8 ± 0.6	761 ± 106	29.5 ± 0.9	33.3 ± 5.6	695 ± 28
94/6	11.8 ± 0.7	764 ± 22	28.2 ± 1.2	28.3 ± 7.7	661 ± 28
92/8	11.6 ± 0.2	466 ± 35	28.5 ± 0.9	16.0 ± 3.3	677 ± 56
90/10	12.7 ± 0.4	462 ± 23	27.7 ± 0.8	19.5 ± 3.8	651 ± 23

ϵ_y , σ_y , ϵ_b , σ_b , and E are the elongation at yield, yield stress, elongation at break, stress at break, and Young's modulus of elasticity; S_{ϵ_y} , S_{σ_y} , S_{ϵ_b} , S_{σ_b} , and S_E are the standard deviations of these values, respectively.

per turn of the helix,¹⁷ and the 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.

A slight increase in the elongation at yield and a decrease in the stress at yield were observed. This could have been caused by a relative decrease in iPP in the blends (only iPP exhibited yielding). On the other hand, the stress-strain curves indicated that virgin iPP and its blends, consisting of 2, 4, and 6 wt % wax, showed cold drawing followed by strain (orientation) hardening before breaking. No brittle rupture was observed in any of the samples. Therefore, it seems that the mechanical properties of iPP were not very much deteriorated by the presence of the wax. The samples with 8 and 10 wt % wax showed cold drawing but did not undergo orientation hardening. These materials had significantly lower values of the elongation at break and stress at break.

Total torque moment

The values of the total torque moment of all the iPP/wax blends are summarized in Table V. 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 iPP.

TABLE V
Total Torque Moment (TM) of the iPP/Wax Blends

iPP/wax (w/w)	TM (Nm)
100/0	5.3
98/2	4.8
96/4	4.3
94/6	4.0
92/8	3.3
90/10	2.8

CONCLUSIONS

The γ measurements have shown that oxidized Fischer-Tropsch wax can be effectively used as an agent for the improvement of the polarity of iPP. Ten weight percent oxidized wax increased the polar component of γ of iPP 11 times and the polar ratio 14 times. The modified iPP showed significantly more 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 the wax was observed up to 6 wt % oxidized wax. The wax modified the viscosity of the blends. The torque moment of the blends decreased with an increase in the wax content over the whole concentration range.

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