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Physical properties of blends of LLDPE and an oxidized paraffin wax

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Abstract

The thermal, tensile and flow properties, as well as the surface tension, of blends of linear low-density polyethylene (LLDPE) and oxidized hard paraffin wax were determined. DSC analysis showed only one endothermic peak, despite the fact that pure wax shows two significant peaks. An increase in wax content of the blends hardly changes the onset and peak temperatures, or the specific enthalpies of melting of the blends. The TGA analyses of the blends show that the thermal stability of blends decreases with an increase in wax content, particularly after the 50% stage, since the thermal stability of the wax is much lower than the thermal stability of LLDPE. A small increase in Young's modulus of the blends with an increase in wax content was observed. Wax content was found to have no influence on the yield point (elongation at yield and yield stress) of the blends. An increase in wax content decreases both stress and elongation at break. An increase in flow rate with an increase in wax content of the blends was observed. We also observed that our wax slightly improves the polarity of the blends. There is, however, no direct correlation between the surface tension and wax content in the blends. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: LLDPE/oxidized wax blends; Thermal analysis; Tensile properties

1. Introduction

Blending of different polymers is regarded as an economical alternative to the development of new polymers. Materials with improved properties can be obtained by blending two or more polymers having different chemical compositions and physical properties [1]. In this paper we investigate some thermal and mechanical properties, as well as flow rate and polarity, of linear low-density polyethylene (LLDPE)/oxidized Fischer–Tropsch wax blends.

LLDPE has good mechanical properties and is often used in industry. Grocery bags, heavy duty shipping sacks, agricultural films, pipes, liners for consumers, landfills and waste ponds are only a few examples [2–4].

Paraffins are a class of aliphatic hydrocarbons, characterized by straight or branched carbon chains, generic formula C_nH_{2n+2}. Paraffin waxes (Fischer–Tropsch synthesis) are white, translucent, tasteless and odorless solids consisting of a mixture of solid hydrocarbons of high molecular weight. Common properties are water repellency, smooth texture, low toxicity, freedom from objectionable odor and color. They are combustible and have good dielectric properties. They are used for preparation of candles, paper coating, protective sealant for food products and beverages, glass-cleaning preparations, hot-melt carpet backing, biodegradable mulch, lubricants, stoppers for acid bottles, electrical insulation and others [5].

In our previous studies we devoted attention to the preparation and characterization of cross-linked and uncross-linked LLDPE/wax and LDPE/wax blends [6–9]. In these cases, blends were either mechanically mixed or blended in an industrial extruder. Very different behavior was observed for all physical properties, since the morphology of the blends strongly influences the final properties [1]. This also depends on processing conditions.

2. Experimental

The following materials were used: LLDPE (MFI = 3.5 g/10 min, density = 0.938 g cm^{-3}, particle size — 90% less than 600 μm); hard, brittle, oxidized straight-hydrocarbon chain paraffin wax, (average molar mass 785 g mol^{-1}, density = 0.94 g cm^{-3}, C/O ratio 18.8/1 [10]) from Sasol Ltd.

The wax and LLDPE were powders and all blends were at first mechanically mixed for a few minutes in a coffee mill and then pressed for 3 min at 160°C. Thermogravimetric analysis was carried out on a Perkin Elmer TGA7 thermal

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Table 1
Parameters obtained from DSC measurements for LLDPE/wax blends ('T' is temperature, 'ΔH' specific enthalpy, 'm' melting, 'c' cooling, 'o' onset, and 'p' peak. Notation *x*/*y* means LLDPE/wax m/m ratio)

Sample	$T_{o,m}$ (°C)	$T_{p,m} = T_m$ (°C)	ΔH_m (J g^{-1})	$T_{o,c} = T_c$ (°C)	$T_{p,c}$ (°C)	ΔH_c (J g^{-1})
LLDPE	120.2	127.5	161.66	112.8	110.8	168.92
95/5	120.6	126.7	159.18	111.6	109.5	171.39
90/10	119.9	126.5	161.79	111.4	109.1	168.04
85/15	120.6	126.5	162.34	111.2	108.6	167.74
80/20	120.9	126.1	161.52	111.2	109.0	167.33
75/25	120.6	126.2	160.93	111.2	108.8	168.65
70/30	120.0	126.5	159.22	111.0	108.8	168.65
60/40	120.0	126.2	159.94	110.9	108.5	168.93
50/50	120.0	125.9	158.01	111.0	108.8	168.39
Oxid. wax	40.9	70.5[a]	174.03	87.1	65.5[b]	–

[a] The DSC heating curve of pure wax shows two endothermic peaks. This one is the main peak. The other one is at 93.7°C. See Fig. 1.
[b] The DSC cooling curve of pure wax shows two exothermic peaks. This one is the main peak. The other one is at 82.6°C. See Fig. 2.

analyzer from 25 to 560°C at a heating rate of 10°C min^{-1} in a nitrogen atmosphere. Differential scanning calorimetry was performed with a Perkin Elmer DSC7 thermal analyzer in a nitrogen atmosphere. Samples were heated from 25 to 140°C at a heating rate of 10°C min^{-1} and then cooled at the same rate. Thermal properties, like melting and crystallization temperatures and enthalpy, were determined from the second scan.

A common tensile tester (Hounsfield W5K ROM rev M73) was used to determine the mechanical properties. The speed of deformation was 50 mm min^{-1}. Measurements were made at room temperature. The final mechanical properties were evaluated from at least 6 different measurements. The flow rates of the molten blends were determined in a Ceast Melt Flow Junior apparatus at 190°C and under a 1 kg mass.

The surface tension was determined from contact angle measurements by using a Cahn recording electro-microbalance (so called Wilhelmy balance method [11]). All measurements were performed at 20°C. Bromonaphthalene and water were used as test liquids. The harmonic-mean method [12] was used for the surface tension calculations.

3. Results and discussion

3.1. Differential scanning calorimetry

Parameters obtained from the DSC measurements are summarized in Table 1. Fig. 1 shows the DSC heating curves for the blends. Only one endothermic peak is observed despite the fact that pure wax shows two significant peaks. One possible explanation of this is that LLDPE and wax are miscible in the crystalline phase [13]. Another explanation may be that the components are not miscible on the microscopic level, but shows homogeneity (miscibility) on a macroscopic scale in the concentration region under investigation.

An increase in the wax content of the blends does not influence T_o and T_m (Table 1, Fig. 1). In our previous work, where we used un-oxidized wax [6], we observed similar behavior.

The wax content also does not have a big influence on the specific enthalpies of melting (ΔH_m). This is probably due to the specific enthalpies of the wax and the LLDPE melting being very similar.

The DSC cooling curves for the samples are shown in Fig. 2 and the results are summarized in Table 1. It is clear that the wax content has no influence on the crystallization temperature or on the specific enthalpy of crystallization. The DSC cooling curves for all the samples, both pure LLDPE and blends show, beside the main exothermic peak, another very small peak at about 70°C (Fig. 2 — the peak at about 70°C is obvious and reproducible in the original curves). Since this peak was observed for both pure LLDPE and the blends, it is probable that its origin is in the LLDPE structure. The characteristic peaks for the pure wax are not observable.

The behavior of the investigated systems during melting and crystallization indicates mutual miscibility of LLDPE

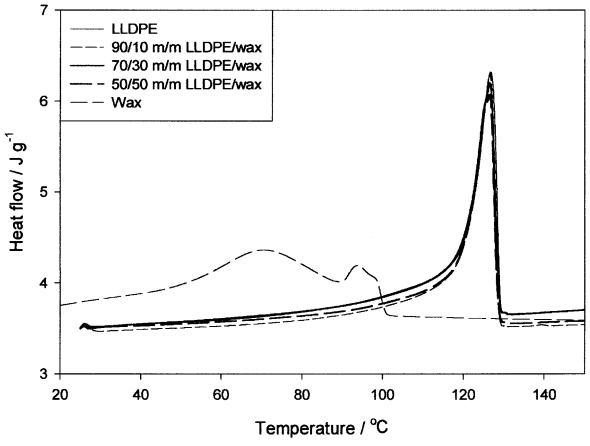

Fig. 1. DSC heating curves of LLDPE, wax and different LLDPE/wax blends.

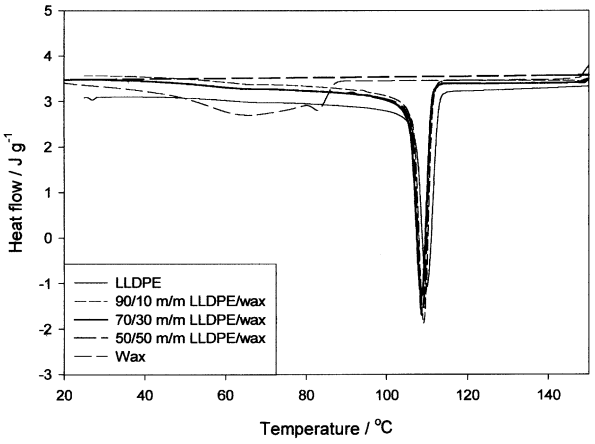

Fig. 2. DSC cooling curves of LLDPE, wax and different LLDPE/wax blends.

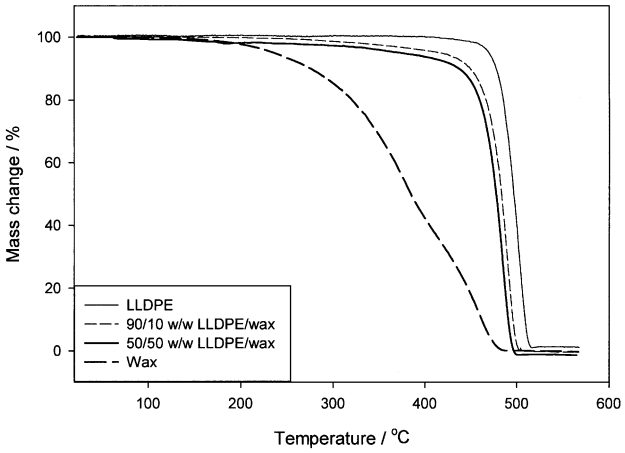

Fig. 3. TGA curves of LLDPE, wax and different LLDPE/wax blends.

and oxidized wax in the solid as well as in the molten state, since (according to general experience) the characteristic melting and crystallization peaks for non-miscible components would have been observed. On the other hand, the sample preparation was such that homogeneity on a molecular level could not be guaranteed.

3.2. Thermogravimetric analysis

The thermal stability of the blends was characterized in terms of the temperatures of 5 and 10% degradation. The results are summarized in Table 2. The results show that the thermal stability of blends decreases with an increase in wax content, since the thermal stability of the wax is much lower than the thermal stability of LLDPE (Table 2, Fig. 3). It is further clear that LLDPE, presumably by encouraging a solid state, remarkably increases the stability of the blends above that of the wax, even if the wax is as much as 50% by mass.

3.3. Mechanical properties

The mechanical properties of the studied blends are summarized in Table 3. Young's modulus of the blends slightly increases with an increase in wax content. It seems as if the modulus of the wax is a little bit higher than that of LLDPE.

The wax content also has no influence on the yield point (elongation at yield and yield stress). The values for pure LLDPE and for all the blends are very similar. What is important, is that most of the blends are ductile and show yield points.

The ultimate properties, like elongation and stress at break, very strongly depend 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 prior to failure. Materials that undergo strain (orientation) hardening during stretching, have higher strength at break than materials which do not undergo strain hardening. In our case, only the pure LLDPE undergoes significant strain hardening before stretching. For blends, which consist of 5 and 10% of wax, a small strain hardening is also observed. In this case, however, stress at break is lower than yield stress. For all the other samples, no orientation hardening was observed. On the other hand, all samples (except a few samples containing 30, 40 and 50% of wax) showed cold drawing. In the exceptions, the samples broke close to their yield point. A consequence of this is that the values for elongation at break are highly scattered.

Table 2
Temperatures of 5 and 10% degradation of LLDPE/wax blends in nitrogen atmosphere (notation *x*/*y* means LLDPE/wax m/m ratios)

Sample	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)
LLDPE	453.4	462.4
95/5	427.4	452.1
90/10	416.8	449.3
85/15	396.1	446.5
80/20	395.7	448.4
75/25	389.5	444.4
70/30	351.4	434.9
60/40	350.7	433.9
50/50	346.8	430.8
Wax	234.4	273.8

3.4. Surface tension measurements

The improvement of the polarity of generally non-polar polyolefins has significant practical importance. Surface tension must be taken into account when investigating interactions with solid and liquid materials, for example coating or inking of final products.

Generally the surface tension for unmodified PEs ranges between 31 and 34 mJ m^{-2}. It depends on the degree of crystallinity, antistatics, additives during the polymerization process and so on. There is only a significant improvement

Table 3
Mechanical properties of LLDPE/wax blends (notation *x/y* means LLDPE/wax m/m ratios). ϵ_y, σ_y, ϵ_b, σ_b, E are, respectively, elongation at yield, yield stress, elongation at break, stress at break, Young's modulus of elasticity, $S\epsilon_y$, $S\sigma_y$, $S\epsilon_b$, $S\sigma_b$, S_E are their standard deviations

Sample	$\epsilon_y \pm S\epsilon_y$ (%)	$\sigma_y \pm S\sigma_y$ (MPa)	$\epsilon_b \pm S\epsilon_b$ (%)	$\sigma_b \pm S\sigma_b$ (MPa)	$E \pm S_E$ (MPa)
LLDPE	22.4 ± 1.8	16.7 ± 0.6	1154 ± 72	21.2 ± 1.6	138 ± 7
95/5	20.5 ± 1.3	17.6 ± 0.2	956 ± 57	18.6 ± 0.6	145 ± 17
90/10	21.3 ± 2.0	17.6 ± 0.2	922 ± 92	16.8 ± 0.7	142 ± 24
85/15	20.4 ± 1.3	18.3 ± 0.3	805 ± 54	14.3 ± 1.0	130 ± 15
80/20	20.5 ± 1.5	16.8 ± 0.3	890 ± 51	16.5 ± 0.7	150 ± 19
75/25	20.3 ± 0.4	17.5 ± 0.6	687 ± 175	12.5 ± 3.3	142 ± 26
70/30	20.7 ± 1.3	16.8 ± 0.6	630 ± 213	13.4 ± 2.5	148 ± 9
60/40	20.4 ± 1.0	15.8 ± 0.5	637 ± 274	13.1 ± 3.2	145 ± 25
50/50	20.2 ± 1.3	16.1 ± 0.3	287 ± 246	11.3 ± 1.5	136 ± 18

Table 4
The surface free energy (γ), its polar (γ^p) and dispersive (γ^d) components, and contact angles (degrees) in distilled water (Θ_1) and bromonaphtalene (Θ_2), of LLDPE/wax blends (notation *x/y* means LLDPE/wax m/m ratios)

Sample	Θ_1	Θ_2	γ^p (mJ m^{-2})	γ^d (mJ m^{-2})	γ (mJ m^{-2})
LLDPE	101.17	55.67	2.10	28.89	30.99
95/5	78.89	45.73	11.12	28.23	39.35
90/10	88.81	49.65	6.75	28.71	35.46
85/15	100.03	48.25	1.21	36.49	37.70
80/20	98.51	45.94	1.68	36.67	38.35
70/30	93.36	53.21	5.05	28.35	33.40
60/40	87.93	52.98	7.64	26.65	34.29
50/50	92.00	53.50	5.74	27.65	33.39

in polarity if the values of the surface tension are approximately 42–44 mJ m^{-2} [14].

The polar and dispersive components, as well as the contact angles in distilled water and bromonaphthalene, of the surface tension measurements are summarized in Table 4. We can see that our wax slightly improves the polarity of the blends — for all the blends, both the surface tension values and their polar components are higher than the surface tension of LLDPE. There is, however, no direct correlation between the surface tension values and the wax content. This fact is probably due to insufficient homogeneity of the surface, which is the result of sample preparation.

3.5. Flow rate measurements

The flow rates of the molten blends were also investigated. Lower viscosity (higher flow rate) can improve processibility and also reduce shear forces during processing (e.g. extrusion), which are often responsible for breaking polymer chains. If we plot the normalized flow rate of the blends (FR/FR_{LLDPE}) as function of the mass ratio of wax in the blends, we see an exponential increase indicating the appreciable influence of the wax on the flow properties of the blends (Fig. 4).

If the log of the flow rate is plotted as function of the mass ratio of wax in the blends (Fig. 4), a perfectly straight line is obtained. It was reported [15] that, if the viscosity of the blends in the melt behaves according to the log-additive rule, the components are miscible with each other. If the components are not miscible, the experimental data will show a negative deviation from this rule. We could not determine the real viscosity values for the blends, but the log-additive rule can be rewritten for the flow rates (FR) — Eq. (1)

$$\log(FR_{blend}) = w_w \log(FR_{wax}) + w_{LLDPE} \log(FR_{LLDPE}) \quad (1)$$

It can be seen in Fig. 4 that the experimental data are excellently linear over the investigated concentration range. This confirms the conclusion from the DSC data that the LLDPE and the oxidized wax are miscible in the molten state. The flow rate of a 100% wax sample could not be measured, because it flowed too rapidly. From the slope of this graph, however, the flow rate of wax is calculated as 65 g/10 min.

4. Conclusions

DSC analyses showed only one endothermic peak, despite the fact that pure wax shows two significant peaks. This is possibly the result of the LLDPE and the wax being

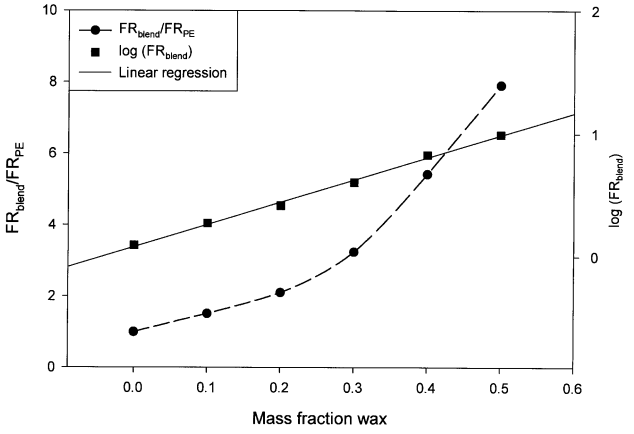

Fig. 4. Normalized flow rate and log (flow rate) as function of wax content in LLDPE/wax blends.

miscible in the crystalline phase, despite the method used in the preparation of the blends. An increase in wax content of the blends does not appreciably influence either the onset and peak temperatures of melting, or the specific enthalpies of melting of the blends. The same is true for the crystallization temperatures and specific enthalpies of crystallization. The DSC cooling curves of the samples show that wax has no influence on the crystallization temperatures and specific enthalpies of crystallization. Only one exothermic peak is observed. This indicates that the components are miscible with each other.

The trends are similar to those observed for LLDPE/normal wax blends [6]. It therefore does not seem as if the oxygen-containing groups cause the wax to interact any differently with the LLDPE.

The TGA analyses of the blends show that the thermal stability of blends decreases with an increase in wax content, since the thermal stability of the wax is much lower than the thermal stability of LLDPE. The blends are, however, appreciably more stable than pure wax, even at wax concentrations as high as 50%.

A small increase in Young's modulus of the blends with an increase in wax content was observed. Wax content was found to have no influence on the yield point (elongation at yield and yield stress) of the blends. An increase in wax content decreases both stress and elongation at break.

An increase in flow rate with an increase in wax content of the blends was observed. When these data were tested against the log-additive rule, it gave a straight line indicating miscibility of the components in the molten state.

We also observed that our wax slightly improves the polarity of the blends. There is, however, no direct correlation between the surface tension and wax content in the blends.

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