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Material Properties

Comparison of different waxes as processing agents for low-density polyethylene

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Abstract

The influence of three different waxes on the thermal and mechanical properties of low-density polyethylene (LDPE) was investigated. The samples were prepared through melt blending in a Brabender mixer. The thermal properties of the samples were determined using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The tensile and flow properties of all the samples were determined and compared. The observations are discussed in terms of possible morphological changes when wax is mixed with LDPE. The polymer-wax miscibilities differed with the type of wax used and with the amount of wax mixed into the polymer. These miscibilities, and accompanying morphologies, had a strong influence on the flow properties, thermal stabilities and tensile properties of the corresponding blends. Based on our observations, H1 wax may be regarded as the best processing agent for LDPE. Both EnHance and H1 wax had a similar influence on the tensile properties of LDPE, but H1 wax increased the melt flow rate more than EnHance, which was specifically designed as a polyethylene processing agent. The blends seemed to be thermally more stable in the presence of EnHance than with H1 wax. Although M3 wax improved the melt flow rate in a similar way to H1 wax, it had a strong negative impact on the tensile properties of LDPE.

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1. Introduction

In many instances it is difficult to process polyethylenes, especially where it comes to recycling. A number of studies were performed on the blending of different types of polyethylene in order to improve processing [1-5]. There are various references to the use of a variety of waxes as processing agents in polyethylene processing, but we could not find any reference to a systematic study of

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the influence of small amounts of different waxes on the viscosity (melt flow) of polyethylenes. Typically, one would expect a processing agent (wax) to improve the melt flow of the polymer to be processed, without having a detrimental influence on the mechanical properties and thermal stability of that polymer.

Our group conducted several studies on lowdensity polyethylene (LDPE)/wax blends [6–12], but in all cases high wax contents were mixed into the polymer, which drastically reduced the melt flow and most other physical properties of the blends. In this work we concentrated on LDPE blends

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containing fairly low wax contents, and we investigated the influence of different types of waxes on the melt flow, thermal stability and tensile properties of the blends. We tried to identify a wax that will improve the melt flow of the blends, without having a detrimental effect on the thermal stability and tensile properties of the blends.

2. Experimental

2.1. Materials

We compared the influence of three different types of Fischer–Tropsch paraffin waxes (supplied by Sasol Wax, South Africa) on the thermal, tensile and melt flow properties of LDPE.

EnHance is a highly crystalline Fischer–Tropsch hydrocarbon designed to improve the processability of polyolefins during injection moulding. It is claimed that it is highly compatible with polyolefins, and at the recommended loadings is dissolved in the polymer matrix. It has a melting point of $117 \,^{\circ}$ C.

H1 wax is a hard, brittle, crystalline, straight hydrocarbon chain paraffin wax. It has a melting point of 90 °C, decomposes at 250 °C and has an average molar mass of $785 \,\mathrm{g \, mol^{-1}}$. It is white with exceptional opacity and has a carbon distribution between C33 and C128. It has an iso-paraffin content of approximately 10%, is chemically inert, inhibited against oxidation and free of aromatics.

M3 wax is a paraffin wax consisting of approximately 99% of straight chain hydrocarbons and very few branched chains, and it is primarily used in the candle-making industry. It has an average molar mass of $440 \text{ g} \text{ mol}^{-1}$ and a carbon distribution between C15 and C78. Its density is $0.90 \text{ g} \text{ cm}^{-3}$ and its melting point is $72 \degree \text{C}$.

LDPE was supplied in powder form by Sasol Polymers. It has a melting point of $103 \,^{\circ}$ C, a density of $0.91 \,\text{g cm}^{-3}$, an MFI of $20 \,\text{g}/10 \,\text{min}$ and an average molecular weight of $96000 \,\text{g mol}^{-1}$.

2.2. Methods

The blends were prepared by melt mixing in a Brabender Plastograph at a set temperature of $150 \,^{\circ}$ C and a rotation speed of $30 \, \text{rev/min}$ for $10 \, \text{min}$, after which they were compression moulded into 1 mm thick slabs.

Thermogravimetric analysis (TGA) analyses were carried out in a Perkin Elmer TGA7 thermogravimetric analyzer in nitrogen atmosphere. Samples of 5–10 mg were heated from 25 to $600 \,^{\circ}\text{C}$ at $20 \,^{\circ}\text{C} \,\text{min}^{-1}$.

Differential scanning calorimetry (DSC) analyses were carried out in a Perkin Elmer DSC7 thermal analyzer in nitrogen atmosphere. The samples were heated from 25 to 160 °C at 10 °C min⁻¹, cooled to 25 °C at the same rate, and re-heated and cooled under the same conditions. Melting and crystallization temperatures and enthalpies were determined from the second scan.

The flow rates (MFI) of the samples were determined using a Ceast Melt Flow Junior apparatus at $150 \,^{\circ}$ C and under a 1 kg mass.

A Hounsfield H5KS tensile tester was used for determination of the mechanical properties. The speed of deformation was 50 mm min^{-1} . The final mechanical properties were evaluated from at least 5 different measurements.

3. Results and discussion

The DSC curves of the pure waxes are presented in Fig. 1 and the melting and crystallization data are summarized in Table 1. EnHance shows melting peak temperatures at 94 and 108 °C, H1 wax at 77, 88 °C (peak shoulder) and 102 °C, and M3 wax at 56 and 66 °C (peak shoulder). It is clear that EnHance has a higher average molecular weight and a narrower crystal distribution than H1 wax, while M3 wax clearly has a much lower molecular weight and a narrower crystal distribution than both EnHance and H1 waxes.

The DSC curves for the different blends are shown in Figs. 2–4. Only one endothermic peak was



Fig. 1. DSC heating curves of pure waxes.

Table 1 DSC onset and peak temperatures, as well as enthalpies, of melting and crystallization of the investigated samples

Sample	$T_{o,m}$ (°C)	$T_{\mathrm{p,m}}$ (°C)	$\Delta H_{\rm m}~({\rm J~g^{-1}})$	$T_{\rm o,c}$ (°C)	$T_{\rm p,c}$ (°C)	$\Delta H_{\rm c} ({\rm J g^{-1}})$
EnHance	70.5	94.2/108.1	214.5	65.4	95.2/88.0	-208.0
H1 wax	54.4	102.4/88.3/77.1	205.4	50.1	90.1/65.2	-191.4
M3 wax	30.1	56.0/66.1	168.2	29.2	60.3/50.1	-148.5
LDPE/EnHar	nce					
100/0	96.1	103.2	55.1	89.9	86.5	-55.2
99/1	95.8	103.2	59.7	90.3	86.9	-55.2
97/3	95.9	103.7	62.6	90.4	87.0	-56.0
95/5	96.3	104.4	64.5	91.8	88.0	-53.7
90/10	97.1	104.0	74.0	92.4	89.3	-62.7
LDPE/H1 wa	X					
99/1	93.4	102.5	60.3	89.2	85.8	-55.5
97/3	94.3	103.0	59.4	90.4	86.9	-56.9
95/5	95.8	103.2	69.9	91.5	87.9	-56.3
		88.2	11.5			
90/10	96.1	90/103	13.6/69.8	91.7	88.6	-58.7
LDPE/M3 wa	ax					
99/1	95.9	102.5	51.9	89.9	86.6	-52.0
97/3	95.6	101.7	49.9	89.3	86.6	-52.7
95/5	95.5	101.9	43.6	88.8	85.8	-59.6
90/10	95.0	54/101	10.6/42.5	88.5	85.5	-55.3

 $T_{o,m}$, $T_{p,m}$, $T_{o,c}$, $T_{p,c}$, ΔH_m and ΔH_c are, respectively, the onset temperature of melting, peak temperature of melting, onset temperature of crystallization, peak temperature of crystallization, melting enthalpy and crystallization enthalpy.



Fig. 2. DSC heating curves for LDPE and different LDPE/ $\ensuremath{\mathsf{EnHance}}$ blends.

observed for all the LDPE/EnHance blends, indicating that LDPE and EnHance are miscible in the crystalline phase up to 10% wax content and probably co-crystallize. LDPE and H1 wax are miscible up to 3% wax content. For 5 and 10% wax, a second peak at 90 °C can be seen, indicating that LDPE and H1 wax are only partially miscible at



Fig. 3. DSC heating curves for LDPE and different LDPE/H1 wax blends.

these wax contents. One endothermic peak is seen for the LDPE/M3 wax blends up to 5% wax content. For 10% wax, a second peak at 54 $^{\circ}$ C can be seen. This behaviour shows that LDPE and M3 wax are partially immiscible, and that a fraction of M3 wax probably crystallizes in the amorphous phase of LDPE.





Fig. 4. DSC heating curves for LDPE and different LDPE/M3 wax blends.

In the case of the LDPE/EnHance blends, the enthalpy increases with increasing wax content and, since enthalpy is proportional to crystallinity, this also indicates an increase in crystallinity of the material. Since the wax is more crystalline than LDPE ($\Delta H = 214.5 \text{ J g}^{-1}$ for EnHance and $\Delta H = 55 \text{ J g}^{-1}$ for LDPE, and assuming that 100% crystalline wax and LDPE have the same melting enthalpies, since they have a similar chemical structure), this observation can be expected. The peak temperature of melting slightly increases with increasing wax content, possibly indicating a small increase in lamellar thickness (Fig. 2).

The presence of H1 wax slightly increases the enthalpy of its blends with LDPE (Fig. 3, Table 1). This indicates an increase in the crystallinity of the material. This increase in crystallinity is less than that of the LDPE/EnHance blends. The reason is that EnHance is more crystalline than H1 wax. An increase in wax content slightly increases the peak temperature of melting up to 5% wax content, after which the temperature remains fairly constant. This behaviour indicates a small increase in lamellar thickness. Higher wax contents, however, do not seem to have an observable influence on the lamellar thickness during crystallization. For LDPE/M3 wax blends, the onset and peak temperatures of melting very slightly decrease, and the melting enthalpy observably decreases, as the M3 wax content increases in the blends (Fig. 4, Table 1). This behaviour indicates a decrease in the crystallinity of the material. Since M3 wax has a higher crystallinity than LDPE, the only possible reason is that Wax 3

does not co-crystallize with LDPE and inhibits LDPE crystallization by acting as a plasticizer.

Fig. 5 shows the TGA curves of pure LDPE, pure EnHance and their blends. It is clear that the wax starts decomposing at a much lower temperature than LDPE. It is, however, interesting that the presence of small amounts of wax improves the thermal stability of LDPE. The sample containing 1% wax is the most stable, and the stability decreases with increasing wax content. Up to 10% wax the stability, however, does not fall below that of pure LDPE. The more crystalline a polymer sample, the higher is its thermal stability. From Table 1 it is clear that the crystallinities of the samples substantially increase with increasing wax content. However, since wax itself is thermally less stable than LDPE, the two effects will balance out. and therefore the thermal stability does not generally increase with increasing wax content.

Fig. 6 shows the TGA curves of pure LDPE, pure H1 wax and their blends. H1 wax is clearly less thermally stable than LDPE, with almost a 90 °C difference between their respective onset temperatures of decomposition. The blends show a shift in the onset of decomposition to higher temperatures compared to the pure materials. Since thermal degradation starts at weak bonds or chain ends, it is possible that the less thermally stable wax chains are somehow protected in the thicker PE lamellae. At the same time, the wax chains improve the stability of the blend by increasing its crystallinity. The 99/1 w/w LDPE/H1 wax sample, however, has a lower onset of decomposition temperature than



Fig. 5. TGA curves of LDPE, EnHance and different LDPE/ EnHance blends.



Fig. 6. TGA curves of LDPE, H1 wax and different LDPE/H1 wax blends.



Fig. 7. TGA curves of LDPE, M3 wax and different LDPE/M3 wax blends.

pure LDPE. The reason for this behaviour is not clear.

M3 wax is clearly much less thermally stable than LDPE, with almost a 91 °C difference between their respective onset temperatures of decomposition (Fig. 7). The blends have higher onset of decomposition temperatures compared to the pure materials, except for the $90/10 \, w/w$ blend. The decomposition temperatures increase for low M3 wax content, despite the lower thermal stability of the wax. In the case of 1% M3 wax, the thermal stability improved by more than 30 °C. This sample is the most stable, and the stability decreases with increasing wax content. For 10% wax, however, the stability falls below that of pure LDPE. This is



Fig. 8. Melt flow rates of LDPE blended with three different types of wax.

because Wax 3 has much shorter chains and is thermally less stable than LDPE, and because it probably crystallizes in the amorphous part of LDPE.

The MFI values for the different LDPE/wax blends are plotted in Fig. 8 as a function of wax content. For all the blends, the flow rate increases with an increase in wax content. Since the MFI is a direct measure of a material's viscosity, these results indicate that the presence of wax reduces the viscosity of the polyethylenes. Lower viscosity (higher flow rate) will improve the processability of LDPE. M3 wax has the largest influence on the MFI of LDPE at lower wax contents, while H1 wax has a larger influence at higher wax contents. EnHance is inferior to both H1 wax and M3 wax in improving the melt flow properties. Low melt flow rates are associated with higher molecular weights, while higher melt-flow rates indicate a lower average molecular weight. EnHance is inferior because of its higher molecular weight, followed by H1 wax. M3 wax has the lowest molecular weight, which is why it has the strongest influence on the flow properties of LDPE. It was not possible to determine the MFI of the pure waxes with the available equipment, because their MFI is too high at the analysis temperature.

The tensile properties of the different PE/wax blends are summarized in Table 2. The yield stress slightly increases with increasing wax content in the blends. This behaviour is expected, since wax increases the crystallinity of the blend (see DSC results), and yield stress depends on crystallinity. This is in line with results obtained by Mtshali et al.

Table 2 Tensile properties of LDPE/wax blends

Sample	$\sigma_{\rm y} \pm S \sigma_{\rm y}$ (MPa)	$\varepsilon_{\rm y} \pm S \varepsilon_{\rm y}$ (%)	$\varepsilon_{\rm b} \pm S \varepsilon_{\rm b}$ (%)	$\sigma_{\rm b} \pm S \sigma_{\rm b}$ (MPa)	$E \pm S_E (MPa)$
LDPE/EnHa	nce				
100/0	71.6 ± 2.1	119.4 ± 4.0	272.8 ± 14.5	78.8 ± 1.6	748.6 ± 19.4
99/1	73.4 ± 2.1	96.3 ± 4.1	225.0 ± 14.2	74.4 ± 1.2	746.4 ± 18.2
97/3	76.0 ± 2.4	93.8 ± 5.0	165.0 ± 14.4	72.3 ± 1.5	732 ± 17.9
95/5	79.5 ± 2.1	79.5 ± 4.6	156.3 ± 14.2	70.3 ± 1.6	816 ± 17.6
90/10	86.6 ± 2.2	66.5 ± 4.3	145.0 ± 14.3	66.8 ± 1.5	898.8 ± 17.9
LDPE/H1 wa	IX				
99/1	72.5 ± 2.1	90.2 ± 4.2	223.8 ± 14.2	65.4 ± 1.6	616.2 ± 16.0
97/3	75.4 ± 2.1	87.8 ± 4.1	191.3 ± 14.0	64.8 ± 1.9	702.0 ± 18.6
95/5	78.2 ± 2.1	78.2 ± 5.1	119.2 ± 14.0	63.7 ± 1.5	735.0 ± 18.8
90/10	85.1 ± 2.1	66.2 ± 4.6	107.2 ± 14.1	60.2 ± 1.7	933.8 ± 18.0
LDPE/M3 wa	ax				
99/1	72.5 ± 2.1	95.0 ± 4.1	220.0 ± 13.8	73.9 ± 1.4	678.2 ± 19.8
97/3	76.2 ± 2.2	74.8 ± 4.3	162.8 ± 14.5	70.8 ± 1.6	808.8 ± 17.0
95/5	79.5 ± 2.1	31.5 ± 5.0	116.7 ± 15.0	67.8 ± 1.5	833.4 ± 18.1
90/10	82.5 ± 2.2	27.3 ± 5.0	86.3 ± 15.0	64.8 ± 1.6	866.8 ± 16.1

 σ_y , ε_y , ε_b , σ_b , E are yield stress, elongation at yield, elongation at break, stress at break and Young's modulus— $S\sigma_y$, $S\varepsilon_y$, $S\varepsilon_b$, $S\sigma_b$ and S_E are their standard deviations.

[6]. Changes in the yield stress with increasing wax content are within experimental uncertainty and in agreement with small changes in melting enthalpies, as shown in Table 1. EnHance has a higher enthalpy (crystallinity) than H1 wax, and so do its blends, and this is reflected in the differences in yield stress between LDPE/EnHance and LDPE/H1 wax blends. The increase in yield stress in the case of LDPE/M3 wax blends is, however, not in line with the decrease in enthalpy (crystallinity) of these blends with increasing wax content. A possible reason for this is the probable crystallization of M3 wax in the amorphous part of LDPE, and the influence of such crystallites on the chain mobility.

An increase in wax content causes a decrease in elongation at yield for all the LDPE/wax blends. The decrease is more pronounced in the case of M3 wax blends. Elongation at yield is the onset of strain value at which plastic deformation takes place, i.e. the material starts to flow. This decrease is the result of a decrease in the amorphous content with increasing wax content. This will lead to a decrease in the strain at which the plastic deformation starts. The reason that the wax content gives low elongation at yield values is related to (i) an increase in crystallinity or (ii) wax crystallization in the amorphous phase, both of which reduce chain mobility.

Elongation at break of LDPE decreases with increasing wax content. Up to 3 wt% wax, all three

waxes have a similar influence on the elongation at break. At higher wax contents, M3 wax reduces the elongation at break more than H1 wax, and H1 wax more than EnHance. Pure LDPE has enough space and time to orientate when force is applied to the polymer chains. When chains are oriented, they start to form orientation crystallinity, which increases the sample strength. Since wax molecules are too short to form tie chains, the number of chain ends, i.e. the number of dislocations, will increase with an increase in wax content. This will induce a decrease in the strain at break.

Stress at break decreases with increasing wax content. The influence is not so pronounced, probably because the wax preferentially crystallizes in the amorphous part of LDPE, having much less influence on its tie chain concentration. For the material to break, many of the tie-molecules should be tightly stretched, and the tightly stretched tiemolecules should be drawn out of the lamellae. During stretching of the blends less force is needed to draw out the stretched tie-molecules from the lamellae. If wax co-crystallizes with the polymer, the number of tie chains is reduced, because wax chains are too short to form tie chains [8]. A reduction in the number of tie chains reduces the ultimate strength of the polymer. H1 wax has the largest influence, followed by M3 wax and then EnHance.

Young's modulus increases as the wax content increases. This behaviour is expected, since Young's

modulus depends on crystallinity, which increases with increasing wax content. Young's modulus depends on the interaction between the crystalline and amorphous regions, due to the elongation energy transmitted from the amorphous to the crystalline phase. The interaction between the wax chains, some crystallized in the amorphous phase of the polymer, and the polyethylene chains affects the transfer of energy to the crystalline phase, and is responsible for the increase in stiffness of the blends. The three waxes have a similar influence on Young's modulus. The influence of Wax 3 is restricted to very low wax contents-Young's modulus remained fairly constant at wax contents higher than 1%. The increase in modulus is the result of increasing crystallinity (see DSC results). Since the crystallinity does not increase with increasing wax content for the LDPE/M3 wax blend, the smaller influence of M3 wax on Young's modulus can be understood.

4. Conclusions

The DSC curves for LDPE with EnHance showed one endothermic peak for all the blends. The enthalpy was found to increase with increasing wax content, and the peak temperature of melting slightly increased. The TGA results showed that the sample containing 1% wax was the most stable, and that the stability decreased with increasing wax content. Up to 10% wax the stability did not, however, fall below that of pure LDPE. At all concentrations EnHance, which was developed to improve processability, had a small influence on the melt flow properties. The presence of EnHance gave rise to an increase in yield stress and Young's modulus, while the elongation at yield and the stress and elongation at break decreased.

The DSC curves for LDPE and H1 wax showed that they were miscible up to 3% wax content. For 5% and 10% wax, LDPE and H1 wax were only partially miscible. The presence of H1 wax slightly increased the enthalpy of its blends with LDPE, and the peak temperature of melting slightly increased up to 5% wax content. The TGA results showed that H1 wax is clearly less thermally stable than LDPE, but that the blends were more stable, except for the sample containing 1% wax. H1 wax generally improved the flow rate of LDPE. The presence of H1 wax gave rise to an increase in yield stress and Young's modulus. Elongation at yield, as well as stress and strain at break, decreased in the presence of H1 wax.

LDPE/M3 wax blends showed one DSC melting peak up to 5% wax content. For 10% wax, a second peak was seen. The peak temperatures of melting very slightly decreased, and the melting enthalpies observably decreased, as the M3 wax content increased. The TGA results showed an increase in onset temperature of degradation for low M3 wax contents, despite the lower thermal stability of the wax, but the stability decreased with increasing wax content. M3 wax has the lowest molecular weight, which is why it had the strongest influence on the flow properties of LDPE. The increase in yield stress and Young's modulus (the values tended to be constant at higher Wax 3 contents) was, however, not in line with the decrease in enthalpy of these blends with increasing wax content. M3 wax had a more pronounced influence on elongation at yield. Stress and elongation at break decreased with increasing wax content.

Based on the observations summarized above, H1 wax may be regarded as the best processing agent for LDPE. Both EnHance and H1 wax had a similar influence on the tensile properties of LDPE, but H1 wax increased the melt flow rate more than EnHance, which was specifically designed as a polyethylene processing agent. As far as thermal stability is concerned, the blends seemed to be thermally more stable in the presence of EnHance than in that of H1 wax. Although M3 wax improved the melt flow rate in a similar way to H1 wax, it had a strong negative impact on the tensile properties of LDPE.

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