

Influence of Different Waxes on the Physical Properties of Linear Low-density Polyethylene

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ABSTRACT

The influence of three different waxes on the thermal and mechanical properties of linear low-density polyethylene (LLDPE) 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 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. H1 wax and M3 wax (which are both Fischer-Tropsch paraffin waxes produced by Sasol Wax) both reduce the apparent viscosity of LLDPE more than EnHance (a Fischer-Tropsch paraffin wax produced by Sasol Wax as a polyethylene processing lubricant). M3 wax had the strongest influence on the melt flow rates (MFI) of the blends, and it had the least influence on the tensile properties of LLDPE. It did, however, strongly reduce its thermal stability. H1 wax, on the other hand, had only a small influence on the thermal stability of LLDPE, but like EnHance it strongly increased the modulus.

KEY WORDS

LLDPE, paraffin wax, melt flow, thermal stability, tensile properties.

1. Introduction

Lubricants are mixed with polymers to modify the apparent viscosity of a polymer melt. In many instances it is a problem to process polyethylenes, especially when it comes to recycling. A number of studies have been performed on the blending of different types of polyethylene, as well as on the use of processing aids, in order to improve processing.^{1–7} These include various references to the use of a variety of waxes as processing aids (lubricants) in polyethylene processing, but we could not find any reference to a systematic study of the influence of small amounts of different waxes on the viscosity (melt flow) of polyethylenes. Typically one would expect a lubricant 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 has conducted several studies on LLDPE/wax blends,^{8–13} but in all cases high (up to 50%) wax contents were mixed into the polymer, which greatly reduced the melt flow and most other physical properties of the blends. In this work we concentrated on LLDPE blends containing 1–10 mass% wax contents, and we investigated the influence of different types of wax on the melt flow, thermal stability and tensile properties of the blends. We tried to identify a wax that would 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

All the waxes were obtained from Sasol Wax (SA), Sasolburg, South Africa, and according to their specification sheets,

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 drop melting point of 117°C. H1 wax has a drop melting point of 112°C, an average molar mass of 785 g mol⁻¹, and a density of 0.94 g cm⁻³. It has a carbon distribution between C33 and C128. M3 wax has a drop melting point of 73°C, an average molar mass of 440 g mol⁻¹, and a density of 0.90 g cm⁻³. It has a carbon distribution between C15 and C78.

LLDPE was supplied in powder form by Sasol Polymers, Johannesburg, South Africa. It has a density of 0.938 g cm⁻³, an MFI of 3.5 g (10 min)⁻¹, a melting point of 127°C and an average molar mass of 191 600 g mol⁻¹.

2.2. Methods

The blends were prepared by melt mixing in a Brabender Plastograph (Brabender GmbH, Duisberg, Germany) at a set temperature of 150°C and a rotation speed of 30 rpm for 10 min, after which they were compression-moulded into 1 mm thick slabs.

TGA analyses were carried out using a Perkin-Elmer TGA7 thermogravimetric analyser (Perkin-Elmer, Wellesley, MA, USA) in a nitrogen atmosphere. Samples of 5–10 mg were heated from 25 to 600°C at 20°C min⁻¹.

DSC analyses were carried out using a Perkin-Elmer DSC7 thermal analyser in a 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. Enthalpy values were determined by using a sigmoidal baseline in the Pyris DSC analysis software (Perkin-Elmer, Wellesley, MA, USA). In the DSC curves

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the endothermic direction is upwards.

The flow rates of the samples were determined using a Ceast Melt Flow Junior apparatus (Ceast SpA, Pianezza, Italy) at 150°C and under a 1 kg mass.

A Hounsfield H5KS tensile tester (Hounsfield Test Equipment, London) was used for the determination of the mechanical properties. The speed of deformation was 50 mm min⁻¹. The final mechanical properties were evaluated from at least five 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 (peak shoulder) and 102°C, and M3 wax at 56 and 66°C (peak shoulder). The temperatures for all the waxes are lower than the specified drop melting points because of the difference in analysis techniques. The narrower peak and higher peak temperatures of EnHance indicates that it has a higher average molar mass and a narrower crystal distribution than H1 wax. M3 wax clearly has a much lower molar mass and a narrower crystal distribution than both EnHance and H1 wax, and this is clear from its peak width and temperature.

LLDPE/EnHance blends show one melting peak for the low wax content blends, but for the blends containing 5 and 10% wax, the DSC curves show a second peak at the wax melting temperature (Fig. 2). LLDPE and EnHance are therefore only partially miscible at higher wax contents. LLDPE and H1 wax are miscible up to 3% wax content (Fig. 3). There is a clearly observable second peak at about 117°C for the blends containing 5 and 10% wax. They are therefore only partially miscible at these wax contents. From previous work^{10,14–16} it was clear that mechanically mixed LLDPE and H1 wax interacted in a totally different way. DSC curves showed only one melting peak in the temperature range of LLDPE melting, even for blends containing up to 20% wax. The miscibility of LLDPE with paraffin wax is obviously affected by the mode of sample preparation. The LLDPE/M3 wax blends show one peak, indicating miscibility of LLDPE and M3 wax, for the blends containing up to 5% wax (Fig. 4). For the

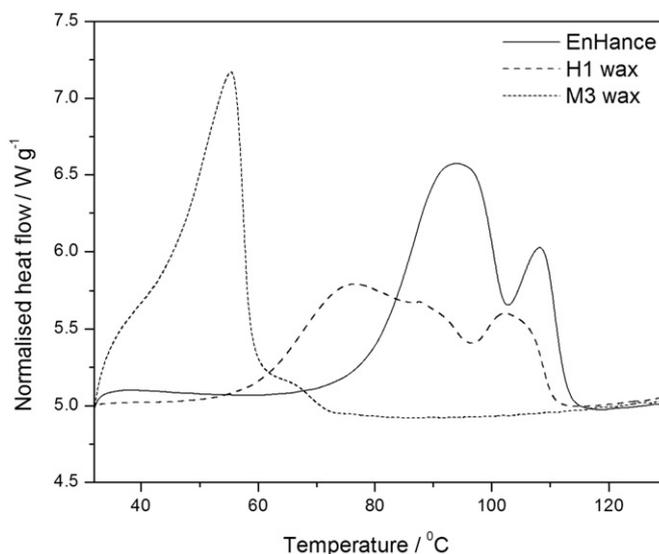


Figure 1 DSC heating curves of pure waxes.

90/10 m/m LLDPE/M3 wax blend, a second peak can be seen at a lower temperature of about 44°C, indicating only partial miscibility. Since the crystallization temperature of M3 wax is much lower than that of LLDPE (29°C compared with 110°C), it is possible that at higher wax contents, the larger part of the wax does not co-crystallize with LLDPE. This wax will then crystallize in the amorphous part of LLDPE. On heating, these wax crystallites will then melt separately from the LLDPE/wax co-crystals.

The melting enthalpy of the LLDPE/EnHance blends increases with increasing wax content, indicating increasing crystallinity of the material (Table 1). This behaviour is expected, since EnHance has a higher melting enthalpy (and crystallinity, if it can be assumed that the LLDPE and wax have similar structures) than LLDPE, which explains the increased melting enthalpy (crystallinity) of these blends. The EnHance chains probably co-crystallize with the linear sequences of the LLDPE chains, giving rise to improved crystallinity. The peak temperatures of

Table 1 DSC onset and peak temperatures, and enthalpies of melting and crystallization of the investigated samples.^a

Sample	T _{o,m} /°C	T _{p,m} /°C	ΔH _m /J g ⁻¹	T _{o,c} /°C	T _{p,c} /°C	ΔH _c /J g ⁻¹
EnHance	70.5	94.2/108.1	215	65.4	95.2/88.0	-208
H1 wax	54.4	102.4/88.3/77.1	205	50.1	90.1/65.2	-191
M3 wax	30.1	56.0/66.1	168	29.2	60.3/50.1	-149
LLDPE/EnHance						
100/0	119.3	127.0	82	110.8	107.2	-56
99/1	118.9	127.0	90	110.4	107.5	-63
97/3	119.9	125.2	94	110.2	108.1	-56
95/5	120.1	109/125	10/96	110.2	108.3	-50
90/10	119.9	110/124	14/105	110.1	108.3	-51
LLDPE/H1 wax						
99/1	119.9	128.0	82	109.5	106.8	-56
97/3	118.8	127.2	92	110.2	107.6	-56
95/5	119.9	113/126	11/86	110.1	107.6	-50
90/10	118.6	117/127	15/87	109.8	107.3	-45
LLDPE/M3 wax						
99/1	119.2	126.0	85	110.9	108.5	-55
97/3	119.4	125.7	81	109.9	107.6	-56
95/5	119.5	124.5	80	109.8	107.8	-56
90/10	118.7	44/125	11/71	109.2	106.8	-46

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

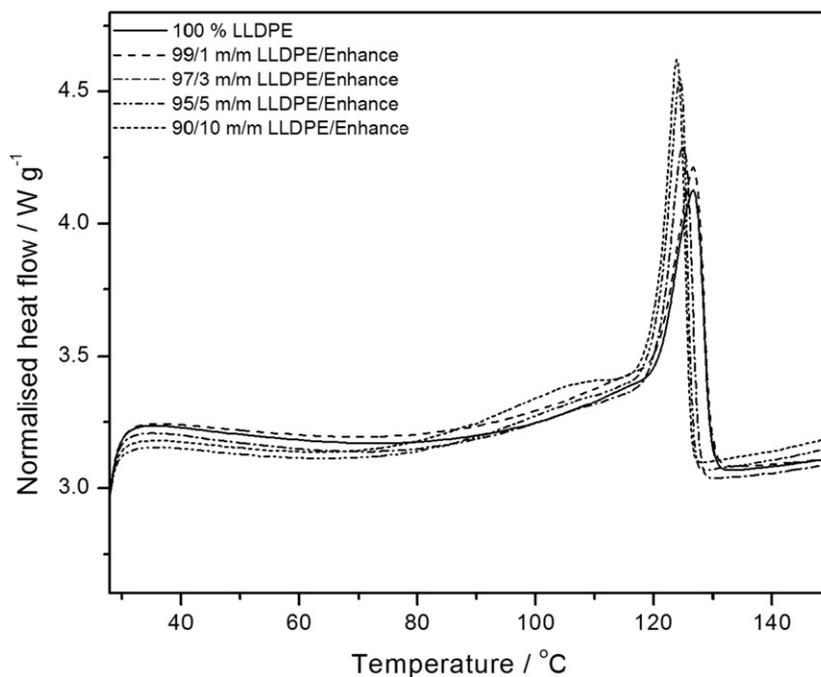


Figure 2 DSC heating curves for LLDPE and different LLDPE/Enhance blends.

melting decrease slightly as the wax content increases, suggesting a decrease in the average lamellar thickness. Co-crystallization of the wax with LLDPE somehow causes the blend to form thinner lamellae, although it causes a higher extent of crystallization. The H1 wax content shows little influence on the specific enthalpies of melting of LLDPE. This is probably due to the specific melting enthalpy of H1 wax and LLDPE being the same. There is very little change in the onset and peak temperatures of melting. The melting behaviour of the blends is similar to that of pure LLDPE. For the LLDPE/M3 wax blends both the melting temperature and enthalpy show a decrease with increasing wax content. The decrease in the peak temperature of melting suggests a decrease in the average lamellar thickness.

The TGA curves of LLDPE/Enhance blends show a decrease in

onset temperatures of decomposition with increasing wax content (Fig. 5), although for 1 and 3% Enhance the thermal stability of LLDPE does not seem to change significantly. This is probably the result of the better miscibility at these wax contents, as a result of which the wax vapour pressure was depressed. The values are somewhere between those of pure wax and pure LLDPE. The short chains of the wax, as well as fragments formed by chain scission, will have sufficient energy to escape from the matrix at lower temperatures. Thus, introducing more of the low molar mass material induces a gradual decrease in the temperature at which decomposition starts. Figure 6 shows that the thermal stabilities of LLDPE/H1 wax blends are between those of LLDPE and H1 wax, with no specific trend for the blends themselves. The vaporization of H1 wax starts at a much lower

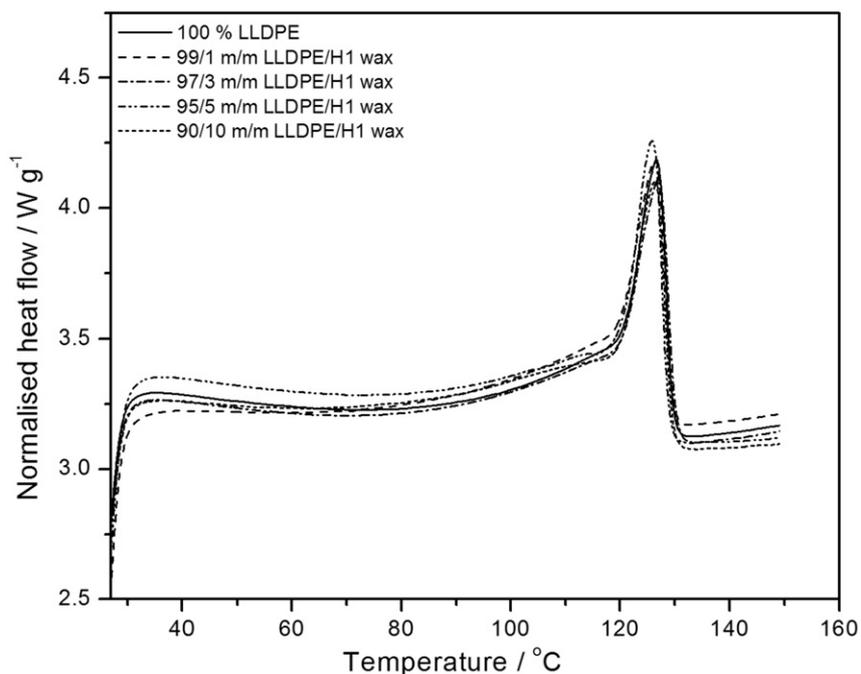


Figure 3 DSC heating curves for LLDPE and different LLDPE/H1 wax blends.

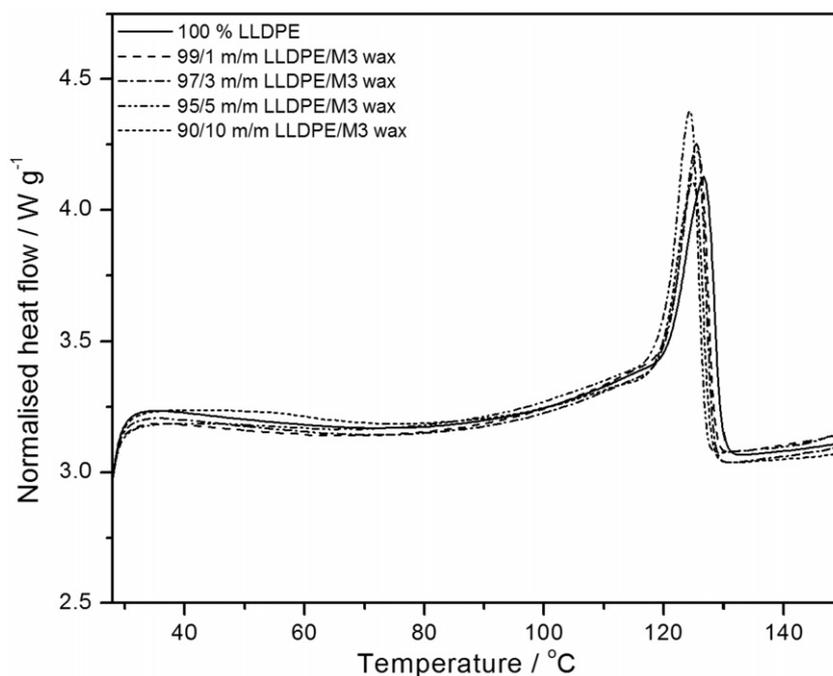


Figure 4 DSC heating curves for LLDPE and different LLDPE/M3 wax blends.

temperature than the decomposition of LLDPE, with an almost 180°C difference between the temperatures. The TGA curves of LLDPE/M3 wax blends show that their thermal stabilities fall between those of pure wax and pure LLDPE (Fig. 7). The vaporization of M3 wax starts at a much lower temperature than the decomposition of LLDPE, with an almost 182°C difference between the temperatures. A possible reason for the poor resistance of LLDPE/wax blends to thermal degradation is the low molar mass of the wax. In all the LLDPE/wax blends there is a substantial difference in onset temperature of decomposition between that of pure LLDPE and that of the 99/1 m/m LLDPE/wax blend. This temperature increases with increasing wax content in the blend up to 95/5 m/m LLDPE/wax. For all three waxes the 90/10 m/m LLDPE/wax blend, however, shows a

lower onset temperature of decomposition than the 95/5 m/m LLDPE/wax sample. Another interesting observation is the absence of a two-stage decomposition process for LLDPE/wax blends, which can also be explained by the good polymer/wax miscibility, which results in the suppression of the wax vapour pressure.

For all the blends the flow rate increases with an increase in wax content (Fig. 8). Since the MFI is a direct measure of the viscosity of a material, these results indicate that the presence of wax reduces the viscosity of LLDPE. Lower viscosity (higher flow rate) may improve the processability of LLDPE. LLDPE/wax blends have higher MFI values than pure LLDPE. All waxes have a similar influence on the MFI of LLDPE at lower contents, while M3 wax has the largest influence at higher wax

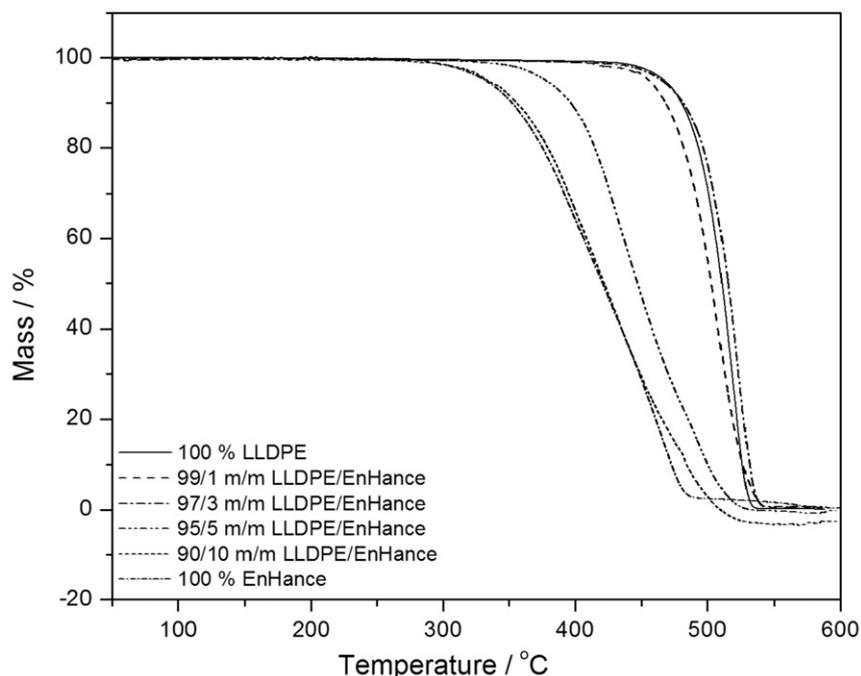


Figure 5 TGA curves of LLDPE, EnHance and different LLDPE/EnHance blends.

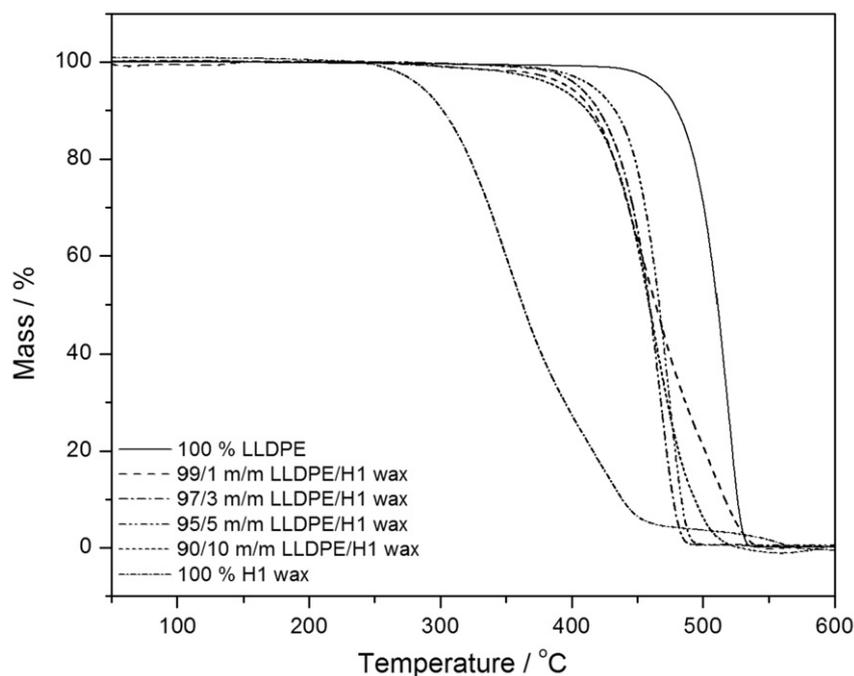


Figure 6 TGA curves of LLDPE, H1 wax and different LLDPE/H1 wax blends.

contents, followed by H1 wax and EnHance.

The tensile properties of the different LLDPE/wax blends are summarized in Table 2. The yield stress increases slightly 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.*¹⁷ 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. Although EnHance has a higher melting enthalpy (crystallinity) than H1 wax, there is very little difference in the yield stress values between LLDPE/EnHance and LLDPE/H1 wax blends. The increase in yield stress in the case of LLDPE/M3 wax blends is, however, not in line with the

decrease in melting enthalpy (crystallinity) of these blends with increasing wax content. In this case a possible reason is the formation of wax crystals in the amorphous phase which may influence the chain mobility.

An increase in wax content causes a decrease in elongation at yield for all the blends. The decrease is more pronounced in the case of the 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 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

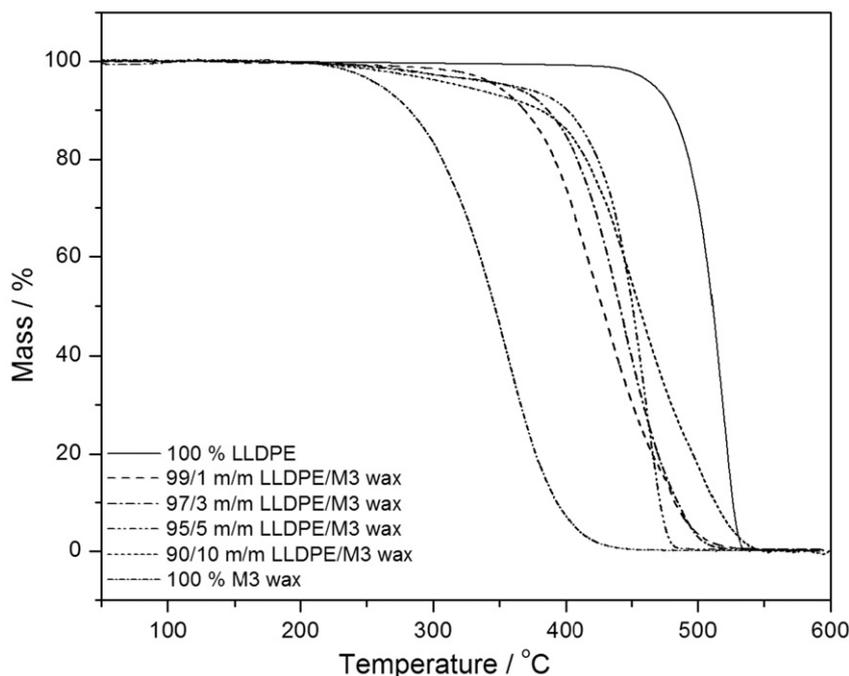


Figure 7 TGA curves of LLDPE, M3 wax and different LLDPE/M3 wax blends.

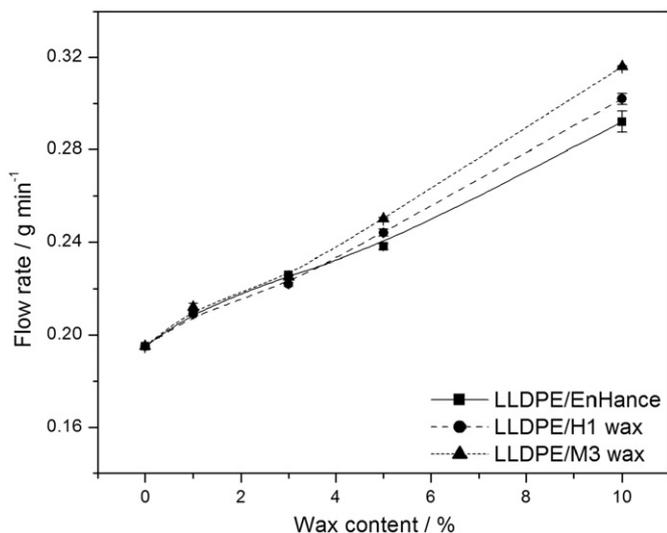


Figure 8 Melt flow rates of LLDPE blended with three different types of wax.

chain mobility. EnHance and H1 wax have the same influence on the elongation at yield, while M3 wax reduces this property as a function of wax content much more.

Elongation at break of LLDPE decreases with increasing wax content (Table 2). 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. EnHance has a much larger influence on the elongation at break than the other two waxes. A possible reason is the higher extent of co-crystallization of EnHance with LLDPE, reducing the number and length of tie chains between the LLDPE lamellae.

Stress at break decreases with increasing wax content. The influence is much more pronounced in the case of LLDPE/EnHance blends, probably because of a higher extent of co-crystallization. For the material to break, many of the tie-molecules should be tightly stretched, and the tightly stretched tie-molecules 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.¹⁸ A reduction in the number of tie chains reduces the ultimate strength of the polymer.

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 to be transmitted from the amorphous to the crystalline phase. The interaction between the wax (partially crystallized in the amorphous phase of the polymer) and polyethylene chains affects the transfer of energy to the crystalline phase, and is responsible for the increase in stiffness of the blends. EnHance and H1 wax have a much greater influence than M3 wax on the Young's modulus of LLDPE, especially at higher wax contents. The influence of M3 wax is restricted to very low wax contents – Young's modulus remained fairly constant at wax contents higher than 1%. An increase in modulus is normally the result of increasing crystallinity. Since the crystallinity does not increase with increasing wax content for LLDPE/M3 wax blends, the smaller influence of M3 wax on Young's modulus can be understood.

4. Conclusions

The DSC results for the LLDPE/EnHance blends show one melting peak for the low wax content blends, but for the blends containing 5 and 10% wax a second peak was seen. LLDPE and EnHance were therefore only partially miscible at higher wax contents. The melting enthalpy increased with increasing wax content, while the peak temperatures of melting slightly decreased as the wax content increased, suggesting a decrease in the average lamellar thickness. The TGA curves show a decrease in onset temperatures of decomposition with increasing wax content. The values were somewhere between those of pure wax and pure LLDPE. The melt flow index increased with increasing amounts of EnHance in the blends. There was an increase in yield stress and Young's modulus with increasing wax content, while elongation at yield decreased because of reduced chain mobility. Stress and elongation at break decreased with increasing wax content.

LLDPE and H1 wax were miscible up to 3% wax content. There was a clearly observable second peak for the blends contain-

Table 2 Tensile properties of LLDPE/wax blends.^a

Sample	$\sigma_y \pm s_{\sigma_y}$ / MPa	$\epsilon_y \pm s_{\epsilon_y}$ / %	$\epsilon_b \pm s_{\epsilon_b}$ / %	$\sigma_b \pm s_{\sigma_b}$ / MPa	$E \pm s_E$ / MPa
LLDPE/EnHance					
100/0	50.7 ± 1.0	25.0 ± 0.6	1029 ± 25	141.7 ± 6.3	454 ± 38
99/1	51.1 ± 1.1	24.2 ± 0.5	904 ± 25	110.5 ± 5.9	617 ± 31
97/3	52.8 ± 1.1	24.0 ± 0.5	863 ± 25	86.7 ± 6.0	620 ± 35
95/5	59.9 ± 1.2	21.9 ± 0.5	829 ± 25	83.9 ± 6.1	695 ± 30
90/10	67.1 ± 1.3	19.8 ± 0.6	810 ± 25	82.0 ± 5.8	809 ± 29
LLDPE/H1 wax					
99/1	51.8 ± 1.1	25.0 ± 0.5	1017 ± 25	122.3 ± 5.4	460 ± 25
97/3	57.1 ± 1.2	24.0 ± 0.6	954 ± 25	120.6 ± 6.2	557 ± 25
95/5	60.5 ± 1.1	23.0 ± 0.5	933 ± 25	115.6 ± 6.0	697 ± 25
90/10	71.2 ± 1.4	21.0 ± 0.4	896 ± 25	106.7 ± 6.1	758 ± 24
LLDPE/M3 wax					
99/1	51.9 ± 1.1	23.3 ± 0.4	1021 ± 25	127.4 ± 5.9	562 ± 35
97/3	53.5 ± 1.1	23.0 ± 0.4	996 ± 25	122.1 ± 6.0	569 ± 37
95/5	58.9 ± 1.1	21.0 ± 0.5	950 ± 25	114.7 ± 5.8	550 ± 35
90/10	65.4 ± 1.1	18.0 ± 0.4	917 ± 25	99.2 ± 6.1	604 ± 35

^a σ_y , ϵ_y , ϵ_b , σ_b and E are yield stress, elongation at yield, elongation at break, stress at break and Young's modulus s_{σ_y} , s_{ϵ_y} , s_{ϵ_b} , s_{σ_b} and s_E are their standard deviations.

ing 5 and 10% wax. The presence of H1 wax did not change the melting enthalpies of the blends, probably due to the crystallinity of H1 wax and LLDPE being similar. There was very little change in the peak temperatures of melting with increasing wax content. The presence of wax substantially reduced the thermal stabilities of the LLDPE/H1 wax blends, with the onset temperatures of decomposition of the blends about 50°C lower than that of pure LLDPE. H1 wax improved the melt flow of LLDPE. Yield stress and Young's modulus increased with increasing wax content. Elongation at yield decreased because of the reduced chain mobility. Both stress and elongation at break decreased with increasing wax content.

The LLDPE/M3 wax blends showed one DSC melting peak, indicating miscibility of LLDPE and M3 wax, for the blends containing up to 5% wax. It is possible that at higher wax contents, some of the wax was forced out of the LLDPE crystallites during LLDPE crystallization. Both the melting temperatures and enthalpies showed a decrease with increasing wax content. The TGA curves showed that the thermal stabilities of the LLDPE/M3 wax blends fell between those of pure wax and pure LLDPE. M3 wax had a slightly larger influence on the melt flow properties of the blends than the other two waxes, with the melt flow index increasing with increasing wax content. There was no correlation between the decreasing crystallinity (melting enthalpy), with increasing wax content, and increasing yield stress and Young's modulus of the blends. In this case a possible reason was the formation of wax crystals in the amorphous phase, which may have influenced the chain mobility. Elonga-

tion at yield, as well as stress and elongation at break, decreased with increasing wax content.

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