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Comparison of LDPE, LLDPE and HDPE as matrices for phase change materials based on a soft Fischer–Tropsch paraffin wax

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ABSTRACT

Phase change materials based on LDPE, LLDPE and HDPE blended with soft paraffin wax were studied in this work. The purpose of this study was to compare the influence of wax content on the thermal and tensile properties of PE/wax blends. It was found that the different polyethylene/wax blends were immiscible for the samples containing 30–50% wax. The presence of wax influenced the melting and crystallization behaviour of the different polyethylenes in different ways, and the thermal analysis results show that the waxes were evenly distributed in the polymer matrices and that there was no wax leaking during sample preparation. For all the blends the thermal stability decreased with an increase in wax content, and the PE/wax blends degraded in two clearly distinguishable steps. The presence of wax generally caused a reduction in tensile properties, but the extent of the wax' influence depended upon the morphology of the polyethylene.

1. Introduction

Phase change materials (PCMs) are substances with a high heat of fusion which, through melting and solidifying at certain temperatures, are capable of storing or releasing large amounts of energy [1]. Phase change materials received great interest in many applications such as energy storage and thermal protection systems as well as in active and passive cooling of electronic devices [2]. Different inorganic ($CaCl_2{\cdot}6H_2O$, $MgCl_2{\cdot}6H_2O$) as well as organic (lauric, palmitic, stearic acids, polyethyleneglycol) substances were already employed for the creation of phase change materials; paraffin waxes belong to the most prospective ones [3] due to their exceptional properties such as high latent heat of fusion, negligible super-cooling, low vapor pressure in the melt, chemical inertness and stability, no phase segregation and commercial availability at relatively low cost. The carbon atom chain lengths for paraffin waxes with a melting temperature between 30 and 90 °C usually range from 18 to 50 (C18–C50). Increased length of the carbon atom chains increases molecular weight and results in a higher melting temperature of the material. The specific heat capacity of latent heat paraffin waxes is about 2.1 J g^{-1} K^{-1}. Their melting enthalpy lies between 180 and 230 J g^{-1} which is very high for organic materials. The combination of these two values results in an excellent energy storage density.

Molten paraffin wax has to be kept in a closed tank or container to suppress leaching. This aim can, however, be achieved through microencapsulation or blending of the paraffin waxes with convenient polymers [4–6]. A polymeric matrix fixes a phase change material in compact form, even after its melting, and suppresses leaching. Such materials are easily shaped and the polymeric phase provides its own specific properties [2,6]. A variety of polymer matrices, based on both thermoplastics and thermosetting resins, are available with a large range of chemical and mechanical properties [7–9]. However, polyethylene seems to be the most frequently used polymer for blending with paraffin waxes to obtain PCM [3,10–14] due to its chemical and structural similarity with paraffin wax that ensures a good compatibility of the two components. However, our previous results indicated that compatibility between polyethylene and wax depends on the types of polyethylene and wax. The degree of crystallinity, molecular weight and extent of branching should be taken into account [15–17]. In this paper we present the results on the thermal and mechanical properties of PCMs based on the three types of polyethylene (low-density polyethylene, linear low-density polyethylene and high-density polyethylene) blended with a soft Fischer–Tropsch paraffin wax.

2. Experimental

LDPE and LLDPE were supplied in pellet form by Sasol Polymers. LDPE has an MFI of 7.0 g/10 min (ASTM D-1238), a melting point of 106 °C, a molecular weight of 96 000 g mol^{-1}, and a density of

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0.918 g cm^{-3}. LLDPE has an MFI of 1.0 g/10 min (ASTM D-1238), a molecular weight of 191 600 g mol^{-1}, a melting point of 124 °C, and a density of 0.924 g cm^{-3}. HDPE was supplied in pellet form by DOW Chemicals. It has an MFI of 8 g/10 min (ASTM D-1238), a molecular weight of 168 000 g mol^{-1}, a melting point of 130 °C, and a density of 0.954 g cm^{-3}. Soft paraffin wax (M3 wax) was supplied in powder form by Sasol Wax. It is a paraffin wax consisting of approximately 99% of straight chain hydrocarbons and few branched chains, and it is primarily used in the candle-making industry. It has an average molar mass of 440 g mol^{-1} and a carbon distribution between C15 and C78. Its density is 0.90 g cm^{-3} and it has a melting point range around 40–60 °C.

All the blends were prepared by mixing the polymer and wax in the 50 mL mixer of a Brabender Plastograph at 160 °C and a speed of 70 rpm for 15 min. After the preparation, the samples were melt pressed at the same temperature and for the same period of time. Blends with wax concentrations ranging between 0 and 50% by weight were prepared.

DSC analyses were done in a Perkin-Elmer Pyris-1 differential scanning calorimeter under flowing nitrogen (flow rate 20 mL min^{-1}). The instrument was computer controlled and the peak analyses were done using Pyris software. The instrument was calibrated using the onset temperatures of melting of indium and zinc standards, as well as the melting enthalpy of indium. Samples (5–10 mg) were sealed in aluminium pans and heated from −40 to 160 °C at a heating rate of 10 °C min^{-1}, and cooled at the same rate. For the second scan, the samples were heated and cooled under the same conditions. The peak temperatures of melting and crystallization, as well as melting and crystallization enthalpies, were determined from the second scan. All DSC measurements were repeated three times for each sample. The temperatures and enthalpies are reported as average values with standard deviations.

TGA analysis was carried out in a Perkin-Elmer TGA7 thermogravimetric analyser. Samples ranging between 5 and 10 mg were heated from 30 to 650 °C at a heating rate of 20 °C min^{-1} under flowing nitrogen (flow rate 20 mL min^{-1}).

A Hounsfield H5KS universal testing machine was used for the tensile analysis of the samples. The dumbbell samples were stretched at a speed of 50 mm min^{-1} under a cell load of 250 N. About nine dumbbell samples per composition were analysed. Stress–strain curves that indicated sample deficiencies were ignored during the final calculations of the tensile properties.

3. Results and discussion

The DSC heating curves for the different PE/wax blends are shown in Figs. 1–3. The melting peak temperatures, as well as the melting and crystallization enthalpies are summarized in Table 1. The wax shows a melting peak at 58 °C, with a peak shoulder at 33 °C, that are the result of the melting of different molecular weight fractions in the wax [18]. The DSC heating curves of the LDPE/wax blends show two clearly defined endothermic events (Fig. 1). The first event between 30 and 70 °C consists of a peak shoulder at about 33 °C and two overlapping peaks between 45 and 70 °C. This event is in the same temperature region as the melting peak of pure wax, but its shape is different. When the wax content in the blend is lower, the peaks between 45 and 70 °C show clearly defined peak maxima. However, at higher wax contents, the lower temperature peak becomes more dominant, reducing the higher temperature peak to a peak shoulder. This indicates that the shorter LDPE chains and/or branches probably co-crystallized with the wax, but that this effect became less pronounced with increasing wax content. The melting enthalpy values of the LDPE/wax blends are

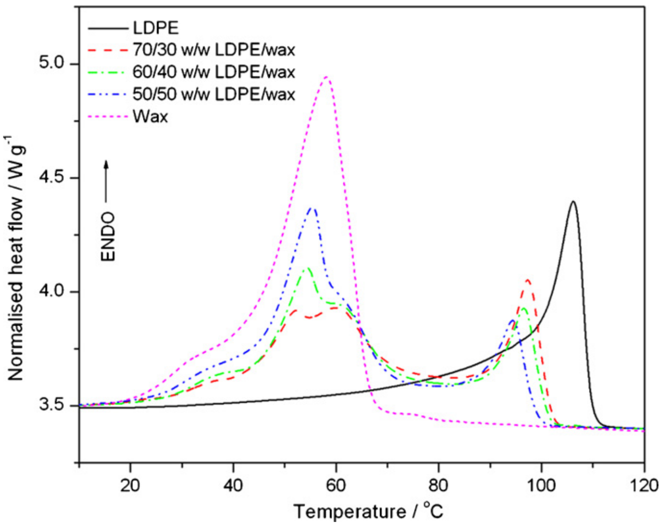

Fig. 1. DSC heating curves of LDPE, wax and LDPE/wax blends.

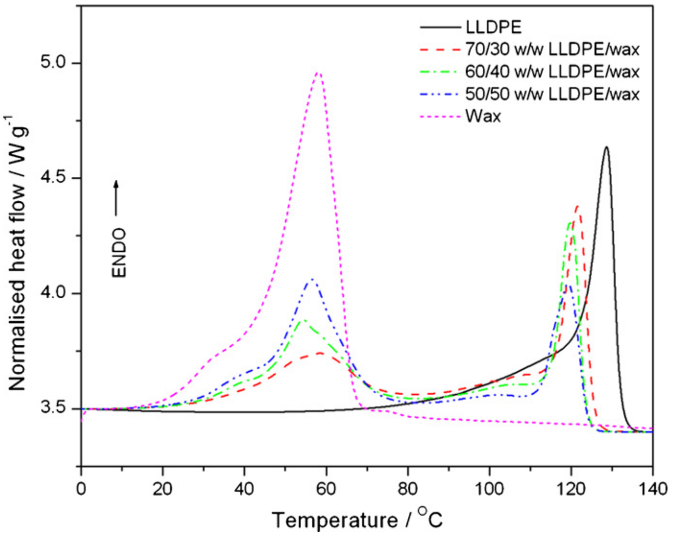

Fig. 2. DSC heating curves of LLDPE, wax and LLDPE/wax blends.

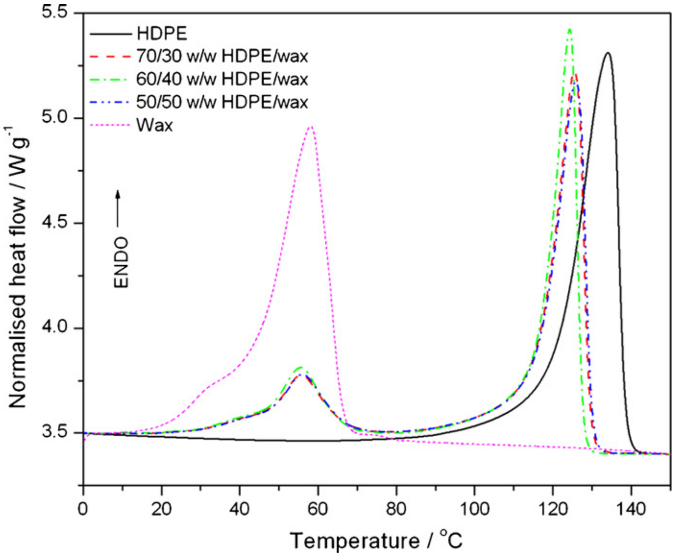

Fig. 3. DSC heating curves of HDPE, wax and HDPE/wax blends.

the same within experimental error than those calculated using the additive rule in Eq. (1):

$$\Delta H_m^{add} = \Delta H_{m,PE} w_{PE} + \Delta H_{m,w} w_w \qquad (1)$$

where $\Delta H_{m,PE}$, $\Delta H_{m,w}$, ΔH_m^{add} are the specific enthalpies of melting of PE, wax and blends, and w_{PE}, w_w are the weight fractions of PE and wax in the blends. This confirms that there was no wax leakage from the LDPE matrix, which is a good observation for shape-stabilized phase change materials. The explanation of the DSC results in terms of co-crystallization of LDPE/wax blends, at low wax contents, is in line with that given by Hato and Luyt [19]. They envisaged co-crystallization of LDPE with both un-oxidized and oxidized hard paraffin wax in their study of the thermal fractionation of PE/wax blends. The second thermal event in Fig. 1 is associated with the melting of LDPE crystallites. The melting peak temperatures of LDPE in the blends are significantly lower than that of pure LDPE (Table 1 and Fig. 1), and the temperatures further decrease with increasing wax content. This behaviour is probably the result of the molten wax which acts as a plasticizer in the LDPE matrix. Another possible reason is that the LDPE crystallization is disrupted by the wax, which is less miscible and therefore forms a more segregated morphology with the wax dispersed in the polymer matrix.

The results of the DSC analyses of LLDPE/wax blends are summarized in Table 1 and presented in Fig. 2. The DSC heating curves of the blends show two clearly defined endothermic events. The first event consists of a peak shoulder at about 33 °C and a single peak at about 58 °C. In this case there is no development of a double peak in this temperature region, as was the case for the LDPE/wax blends, which suggests that the wax co-crystallized with LLDPE and/or crystallized separately in the amorphous phase of LLDPE. The extent of separate and/or co-crystallization of the wax could, however, not be established through separate analysis of the wax and LLDPE melting peaks. The second event is associated with the melting of the LLDPE crystallites. The melting peak temperatures of LLDPE in the blends are lower than that of pure LLDPE (Table 1 and Fig. 2), and the temperatures further decrease with increasing wax content. Similar to the LDPE/wax blends, this behaviour indicates the plasticizing behaviour of the molten wax. When Figs. 1 and 2 are compared, it seems as if there are smaller decreases in the melting temperatures of LLDPE compared to LDPE. The reason is most probably that the paraffin wax, which was found to have a much lower miscibility with LDPE than with LLDPE [19–21], crystallizes separately in the amorphous phase of LDPE, while part of the wax may co-crystallize with the LLDPE chains. The wax that crystallizes separately will melt before the polyethylene, and the molten wax will act as a plasticizer. However, the wax that is co-crystallized with the polyethylene chains will melt at the same temperature as the polyethylene, and can therefore not contribute to the plasticizing effect of the wax. Since the wax seems to have a higher miscibility (more co-crystallization) with LLDPE than with LDPE, there will be less crystalline wax in the amorphous regions of LLDPE and therefore the plasticizing effect and reduction in melting temperature of the polymer will be less obvious. There is also, in the case of the LLDPE/wax blends, a good correlation between the experimental and calculated melting enthalpy values, which confirms that there was no wax leakage from the LLDPE matrix during sample preparation.

Table 1
DSC results for polyethylene/wax blends.

v/v	$T_{p,m}$ (°C)	ΔH_m^{obs} (J g^{-1})	ΔH_m^{calc} (J g^{-1})	$T_{p,c}$ (°C)
LDPE/wax				
100/0	106.8 ± 1.5	75.4 ± 6.2	75.4	91.7 ± 0.6
70/30	$58.2^{a} \pm 5.0$ $59.7^{b} \pm 1.2$ $100.4^{c} \pm 2.8$	104.7 ± 3.7	104.4	$55.6^{a} \pm 0.9$ $87.4^{b} \pm 0.9$
60/40	$55.5^{a} \pm 0.7$ $96.9^{b} \pm 3.2$	114.0 ± 10.9	113.6	$55.8^{a} \pm 0.2$ $87.8^{b} \pm 1.8$
50/50	$55.0^{a} \pm 0.6$ $97.6^{b} \pm 2.1$	111.0 ± 8.6	106.3	$56.0^{a} \pm 0.6$ $86.0^{b} \pm 0.5$
0/100	$58.4^{a} \pm 1.2$	172.2 ± 0.1	172.2	53.1 ± 0.4
LLDPE/wax				
100/0	126.7 ± 2.1	86.9 ± 1.0	86.9	109.6 ± 0.9
70/30	$57.3^{a} \pm 1.6$ $121.8^{b} \pm 0.9$	108.5 ± 10.3	111.7	$53.2^{a} \pm 0.9$ $105.7^{b} \pm 0.9$
60/40	$54.5^{a} \pm 1.1$ $119.8^{b} \pm 1.1$	104.9 ± 15	120.6	$49.8^{a} \pm 0.7$ $105.2^{b} \pm 1.1$
50/50	$57.2^{a} \pm 0.6$ $120.8^{b} \pm 1.1$	130.3 ± 8.2	130.0	$49.8^{a} \pm 0.9$ $103.8^{b} \pm 0.6$
0/100	$58.4^{a} \pm 1.2$	172.2 ± 0.1	172.2	53.1 ± 0.4
HDPE/wax				
100/0	134.7 ± 0.5	149.3 ± 9.7	149.3	113.9 ± 1.1
70/30	$56.1^{a} \pm 0.1$ $124.6^{b} \pm 1.8$	150.9 ± 15	156.2	$51.1^{a} \pm 0.1$ $110.2^{b} \pm 1.8$
60/40	$56.4^{a} \pm 0.4$ $124.1^{b} \pm 2.3$	153.2 ± 9.9	158.5	$51.1^{a} \pm 0.6$ $110.2^{b} \pm 0.4$
50/50	$57.1^{a} \pm 0.1$ $124.1^{b} \pm 0.3$	148.4 ± 8.9	160.8	$50.8^{a} \pm 0.9$ $109.6^{b} \pm 1.1$
0/100	$58.4^{a} \pm 1.2$	172.2 ± 0.1	172.2	53.1 ± 0.4

$T_{p,m}$, ΔH_m^{obs}, ΔH_m^{calc}, $T_{p,c}$ are melting peak temperature, observed melting enthalpy, calculated melting enthalpy, and crystallization peak temperature, while a and b indicate the first and second peak maxima in the wax melting peak.

The melting peak temperatures, as well as the melting and crystallization enthalpies of the HDPE/wax blends are shown in Fig. 3 and summarized in Table 1. The DSC heating curves of the HDPE/wax blends show two clearly defined endothermic events. The first event consists of a peak shoulder at about 33 °C, and a single peak at about 58 °C. The second event is associated with the melting of the HDPE crystallites. In this case the decrease in melting peak temperature is higher than in the case of LDPE and LLDPE. According to Hato and Luyt [19] paraffin wax has the lowest miscibility with HDPE, and it will therefore have the strongest influence on the melting temperature of the polymer. As in the case of LDPE and LLDPE the observed and calculated (according to Eq. (1)) melting enthalpies are the same within experimental error, indicating that no wax leakage occurred during sample preparation.

The TGA curves of the LDPE/wax blends are shown in Fig. 4, and the degradation results for the LDPE/wax, LLDPE/wax and HDPE/wax blends are summarized in Table 2. Since the TGA curves of the LLDPE/wax and HDPE/wax blends were very similar to those of the LDPE/wax blends, they are not presented here. For all the blends the thermal stability decreases with an increase in wax content, and the PE/wax blends degrade in two clearly distinguishable steps. Such degradation behaviour is typical for immiscible blends in which the constituents have different degradation temperatures. The first degradation step is that of wax, which has a lower thermal stability than any of the polymers. For all the samples the percentage mass loss during the first degradation step correlated well with the amount of wax initially mixed into the sample. The second step is associated with the polymer degradation. The short-chain fractions of the wax, as well as the fragments formed by chain scission, will have enough energy to leave the matrix at a lower temperature [8,10,20,22]. Thus, introducing more of the low molecular weight wax induces a gradual decrease in the temperatures at which the degradation starts. For example, when 10% mass loss was selected as point of comparison, the thermal degradations of LDPE/wax samples with 30, 40, and 50 vol.% of wax were determined as 292, 282, and 271 °C respectively, that are 150, 161, and 172 °C lower than

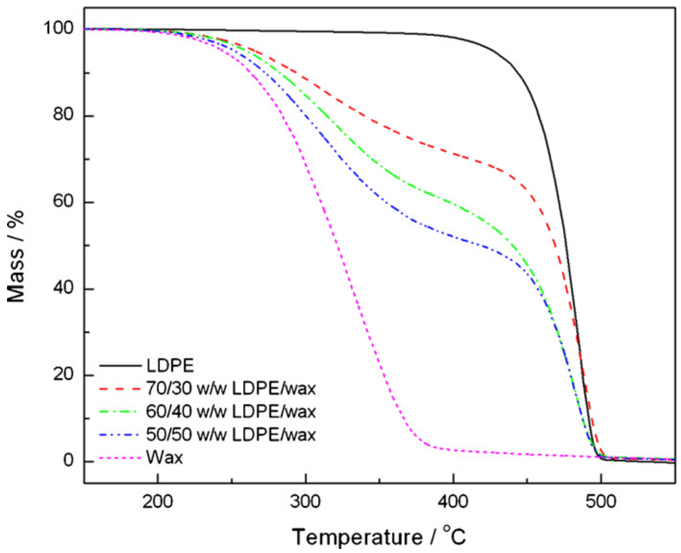

Fig. 4. DSC heating curves of HDPE, wax and HDPE/wax blends.

the 443 °C of pure LDPE. At the same level of mass loss the thermal degradation temperatures for the LLDPE/wax blends were determined as 172, 182, and 192 °C lower than the 464 °C of pure LLDPE. The same is true for the HDPE/wax blends, with thermal degradation temperatures for the HDPE/wax blends 176, 171 and 195 °C lower than that of pure HDPE. No char yield was observed at temperatures higher than 500 °C for all the PE/wax blends. The thermal stabilities of all the PE/wax blends therefore fall below those of the pure PEs, and gradually decrease with increasing wax content. This is because the soft paraffin wax has much shorter chains and is thermally less stable than the pure polyethylenes.

The results presented in Figs. 5–7 show that blending wax with PE significantly influences the mechanical properties of the materials. In all the investigated PE/wax blends, the stress at break decreased with an increase in wax content (Fig. 5). The main reason for this decrease is the increased amount of low molecular weight wax, which deteriorates the tensile strength of the blend. Wax itself has very poor tensile properties and the wax crystals in the amorphous phase of the respective polymers act as defect points for the initiation and propagation of stress cracking. Increasing wax content had a more significant influence on the tensile strength of LDPE, probably because of the higher amorphous content in this

Table 2
Temperatures of 10 and 50% degradation of PE/wax blends.

v/v	T_{10} (°C)	T_{50} (°C)
LDPE/wax		
100/0	443.3	476.3
70/30	292.9	468.8
60/40	282.4	439.4
50/50	271.1	–
100/0	262.4	341.4
LLDPE/wax		
100/0	464.6	486.1
70/30	292.9	479.4
60/40	282.4	469.1
50/50	271.1	–
100/0	262.4	341.4
HDPE/wax		
100/0	467.0	493.0
70/30	290.8	478.8
60/40	294.8	478.8
50/50	271.9	–
100/0	262.4	341.4

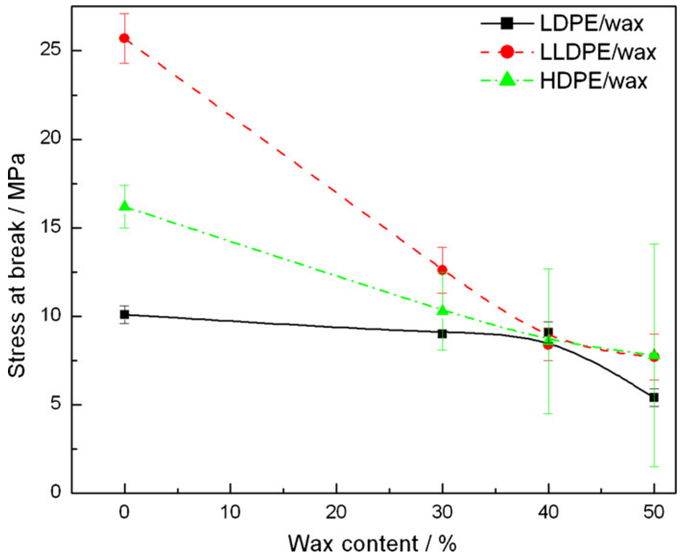

Fig. 5. Tensile strength as function of wax content in the blends.

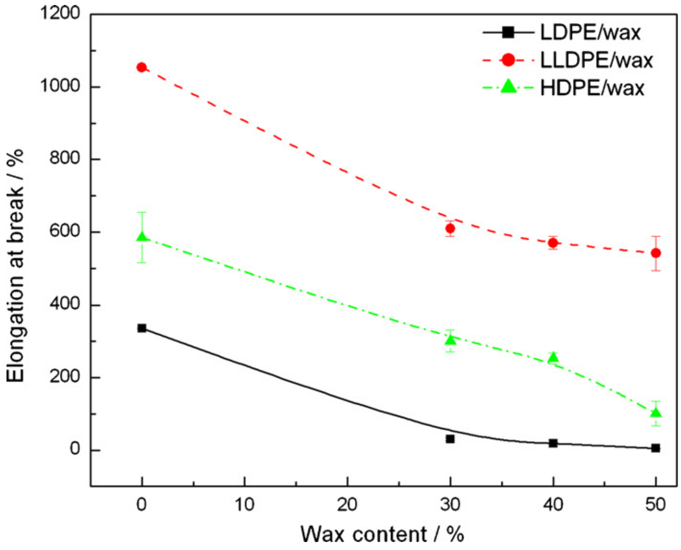

Fig. 6. Elongation at break as function of wax content in the blends.

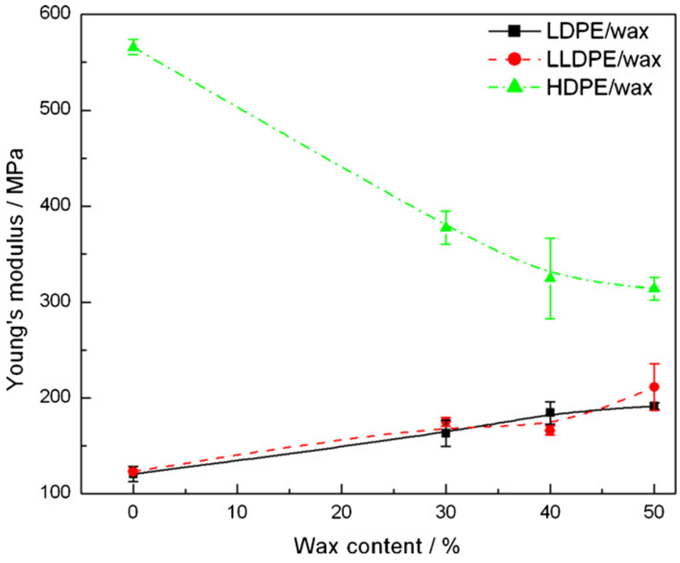

Fig. 7. Young's modulus as function of wax content in the blends.

polymer. Lower values of stress at break were also observed by Mtshali et al. [16], after blending LDPE with wax. They showed that the changes at lower wax concentrations are within experimental error, but at higher wax concentrations significant deterioration of the basic properties of the materials were observed.

An increase in wax content resulted in a decrease in elongation at break of all the investigated blends (Fig. 6). This can also be explained by the wax crystals acting as defect points for the initiation and propagation of stress cracking. Elongation at break is also influenced by the immiscibility of the components. Since there is phase separation in all the blends, the materials loses drawability and elongation at break strongly decreases. An increase in Young's modulus with an increase in wax content was observed for the LDPE and LLDPE blends, indicating that the modulus of the wax is higher than those of both polymers (Fig. 7). This is associated with its higher degree of crystallinity. The degree of crystallinity of wax, LDPE and LLDPE are 58.9, 25.7 and 29.7%. These values were calculated according to Eq. (2):

$$X_c\,(\%) = \frac{\Delta H_m}{\Delta H_m^+} \times 100 \qquad (2)$$

where X_c is the degree of crystallinity, ΔH_m is the specific melting enthalpy of the sample and ΔH_m^+ is the specific melting enthalpy for 100% crystalline polyethylene. In this study we used $\Delta H_m^+ = 293\,\mathrm{J\,g^{-1}}$ [23] for the polyethylenes, and we assumed that 100% crystalline wax has the same melting enthalpy. There is an interaction between the crystalline and amorphous regions of the polyethylenes, giving rise to the elongation energy being transmitted from the amorphous to the crystalline phase. The presence of the wax seems to affect this energy transfer, which may be responsible for the increase in stiffness of the polyethylene/wax blends. In contrast with the observations on LDPE/wax and LLDPE/wax blends, the moduli of the HDPE/wax blends decreased with increasing wax content (Fig. 7). Since the wax has a lower crystallinity than HDPE, the modulus (which depends on the sample crystallinity) decreases with increasing wax content.

4. Conclusions

When soft Fischer–Tropsch paraffin wax was mixed with LDPE, LLDPE and HDPE, a two-phase morphology was observed in all cases, implying the immiscibility of the PEs and wax at wax contents of 30, 40 and 50%. This showed that phase change materials were successfully formed. The presence of wax in PE/wax blends reduced the melting temperatures of all three polyethylenes, indicating the plasticizing effect of the molten wax in the PE matrix. The DSC results further indicated that the extent to which the wax influenced the melting and crystallization behaviour of a particular polyethylene, depended on the morphology and crystallinity of the polyethylene matrix. The DSC results further showed that the wax molecules were evenly distributed in the PE matrix for all three types of polyethylene, and that there was no wax leakage from the matrix. The TGA results showed a definite influence of the wax on the degradation behaviour of the different samples, and this influence was similar for the different types of polyethylene. The tensile strength and elongation of the samples generally decreased with increasing wax content, but the extent of decrease was different for the different polyethylenes. The tensile modulus increased with increasing wax content in the case of LDPE and LLDPE, while it decreased in the case of HDPE.

Acknowledgements

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