



ORIGINAL ARTICLE

Effect of waste wax and chain structure on the mechanical and physical properties of polyethylene



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Abstract The influence of adding waste wax, produced as a by-product of the low density polyethylene manufacturing process, on the thermal and mechanical properties of three types of polyethylene (PE), high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE) and low-density polyethylene (LDPE), with 10, 20, 30 and 40 wt.% was investigated. Polymer-wax mixing was effective with no apparent leakage of the wax during sample preparation, which was evident from the agreement between the theoretical and experimental values of enthalpy for all types of PE.

The wax dispersion in the matrix strongly depends on the percentage of wax added to the polymer and the molecular structure of the polymer. It was found that increasing the wax content enhances the phase separation. LDPE undergoes less phase separation due to its highly branched structure composed of a network of short and long chain branches. The wax has no pronounced plasticising effect on the polymer. This is clearly manifested in LDPE as no change in the melting temperature occurred. LLDPE and HDPE were slightly affected by a high concentration of wax (30% and 40%). This is due to the non-uniform distribution of short chain branching along the LLDPE and HDPE main chains, which can interact with the wax structure.

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1. Introduction

Environmental protection and energy conservation represent two main challenges facing the world in the 21st century. Waste wax from Polyethylene plants has only found commercial use in limited applications. Developing new uses for it, especially in energy saving applications, should make significant contributions to meet the above challenges. Paraffin wax is a by-product of the high-pressure olefin polymerisation process (Pladis et al., 2006). It is a very low molecular weight

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polyethylene with a melting point ranging from 80 to 100 °C, depending on the average number of carbon atoms in the chains. As the mixture of polymer and unreacted ethylene gas exits the reactor and enters the separator, the solubility of the polymer in the unreacted ethylene is still high. The low molecular weight polymer chains are especially soluble in the unreacted ethylene gas at high pressure. As the regular polymer is separated from the unreacted gas, the low-molecular-weight polymer (wax) passes through the gas phase and is later separated and collected in metal drums as a by-product of the LDPE manufacturing process. This phenomenon is common in both autoclave and tubular technologies, but it is more common in autoclaves due, in part, to the short residence times in the reactor (Peacock, 2000).

Polyolefins have been extensively studied in combination with wax (Mpanza and Luyt, 2006). Several researchers have focused on the performance of these blends to act as phase change materials (PCM) (Molefi et al., 2010; Peng et al., 2004; Krupa et al., 2007a,b; Luyt and Krupa, 2009; Salyer, 1996). The interest in the use of wax is due to its many advantages, such as the possibility of high thermal energy storage and cost effectiveness in producing materials with new properties.

The carbon chain lengths of paraffin waxes with melting points between 30 and 90 °C usually range between 18 and 50 carbons. An increase in the length of the carbon chains increases the melting point of these waxes. Moreover, the melting enthalpy lies between 180 and 230 J/g, which is very high for organic materials (Molefi et al., 2010).

Wax/polymer blends can be used in many applications such as hot melt adhesives, coatings and phase change materials (Peng et al., 2004; Krupa et al., 2007a; Luyt and Krupa, 2009). The most common matrix used for blending paraffin waxes is polyethylene (Krupa et al., 2007b; Salyer, 1996; Xiao et al., 2001; Inaba and Tu, 1997; Sari, 2004). This is due to the chemical and structural similarities between polyethylene and paraffin wax, which ensure good compatibility between the two components.

Polyethylene (PE) is a commercially available low-cost polymer with excellent physical and mechanical properties. There are many types of PEs: high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE) and low-density polyethylene (LDPE). The main difference between them is the degree of branching they exhibit at the microstructural level. HDPE has the lowest degree of branching; LLDPE features short chain branches at regular intervals and LDPE is composed of both short and long, irregularly distributed branches. Changes in microstructure and the degree of branching result in several changes in properties such as the degree of crystallinity, morphology and lamellar thickness (Inaba and Tu, 1997; Sari, 2004).

AlMaadeed et al. (2012) showed that the properties of PE reinforced with glass fibres depend on chain branching. The stiffening effect of glass fibres was more pronounced in the case of LDPE due to the formation of a network between the filler and the long chain branching structure. This was clear from the significant increase in modulus of elasticity and storage modulus upon addition of glass fibres. Crystallinity also plays an important factor, as explained by the same authors. Molefi et al. (2010) studied three types of polyethylene (LDPE, LLDPE, and HDPE) with Fischer–Tropsch paraffin wax. They explained the immiscibility of the PE and wax as well as the plasticising effect of the molten wax on the PE matrix;

the authors mentioned that the wax affected the crystallisation behaviour of PE in terms of crystallinity and morphology without explaining the effect of structure and branching on the properties of the new material.

The properties of polymer-additive blends depend on the structure and degree of branching of the polymer (AlMaadeed et al., 2012), and in the case of adding wax to polyethylene, crystallinity plays an important role (Molefi et al., 2010).

The focus of this study was to understand the influence of the chain structure of polyethylene on the morphological, mechanical and thermal properties of new blends based on waste wax fillers.

2. Experimental

2.1. Materials

Three different types of polyethylene were used as a matrix: HDPE (MFI 0.35 g/10 min, density 0.955 g/cm³), LDPE (MFI 2.4 g/10 min, density 0.923 g/cm³) and LLDPE (MFI 2 g/10 min, density 0.918 g/cm³). They were graciously provided by QChem (Qatar) and QAPCO (Qatar). The waste wax, Q wax, was obtained from QAPCO (Qatar) and exhibited a density of 0.88 g/cm³. It is considered to be a high melting point paraffin wax. The Q wax exhibited one endothermic peak at 102 °C and a corresponding melting enthalpy of 20 J/g. This wax has a high average molecular weight (carbon chain lengths can be expected to be between C33 and C128). The very low degree of crystallinity indicates that the chains are highly branched, presenting obstacles for the regular folding of chains. This wax also has a wide molecular weight distribution resulting from the polymerisation process.

2.2. Preparation of PE- wax blend matrix

Blends were fabricated using a lab-scale twin screw extruder. Twin screw compounding is known to result in good dispersion in the polymer matrix. The throughput of the extruder and the screw speed were 0.7 kg/h and 110 rpm, respectively.

The blends were then dried for approximately 30 min at 70 °C before being fed into the injection moulding machine at 180 °C to make the final samples.

2.3. Characterisation

2.3.1. Scanning electron microscope (SEM)

The morphology of the PE/wax blends was characterised using a FEI Quanta 200 environmental scanning electron microscope (ESEM) at 2.0 keV. The samples were fractured perpendicular to the injection moulding direction in liquid nitrogen.

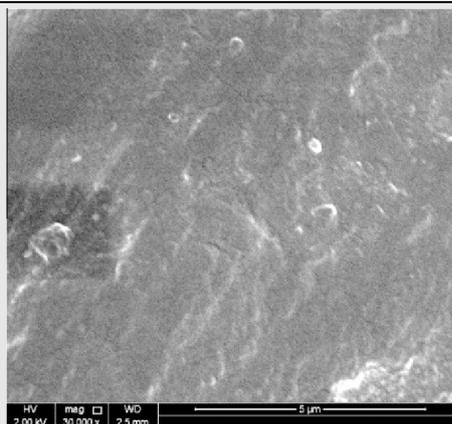
2.3.2. Atomic force microscopy (AFM)

The morphology of the samples was also studied by using AFM equipped with a Nanoscope IIIa controller (Digital Instruments, Santa Barbara, CA). All results were obtained in the tapping mode. A vertical engage scanner and Si probes were applied. The resonant frequency of the free-oscillating cantilever adjacent to the surface of the samples in the tapping mode was set as the driving frequency. The roughness of the samples was calculated from AFM images.

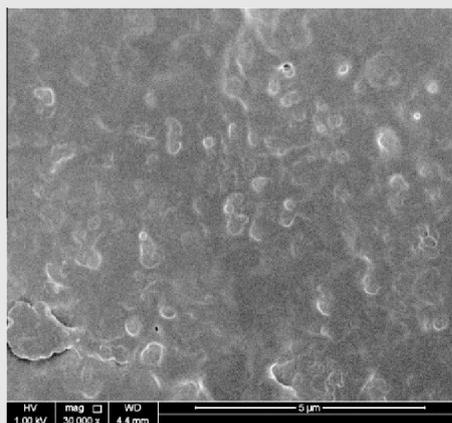
Table 1 SEM micrographs of the HDPE/wax, LLDPE/wax and LDPE/wax blends.

Blend

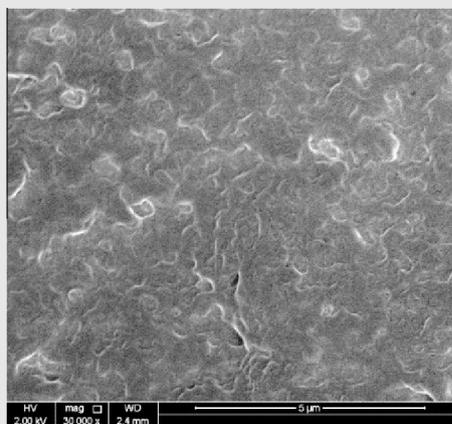
HDPE/wax blends, 10% of wax



HDPE/wax blends, 20% of wax



HDPE/wax blends, 30% of wax



HDPE/wax blends, 40% of wax

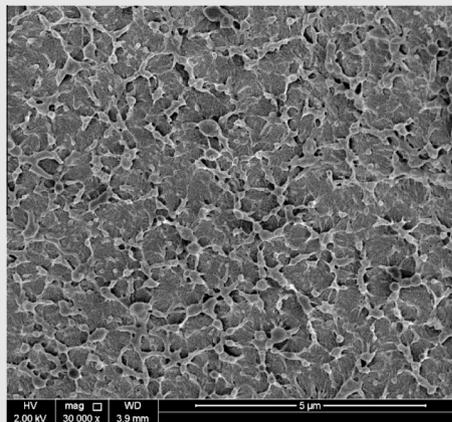
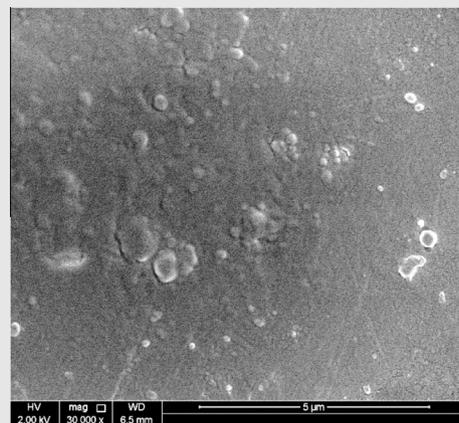
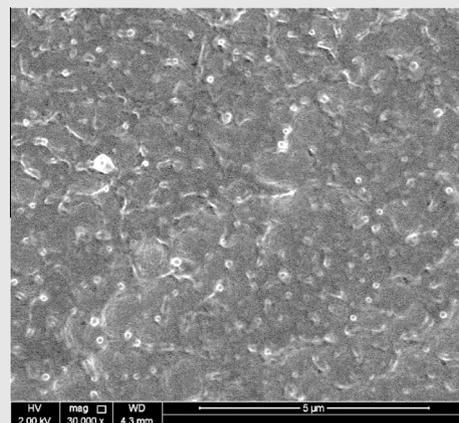


Table 1 (continued)

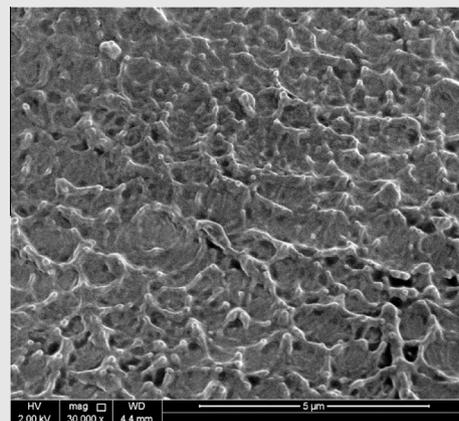
LLDPE/wax blends, 10% of wax



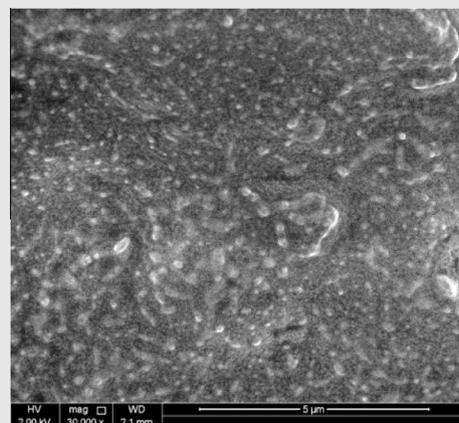
LLDPE/wax blends, 20 % of wax



LLDPE/wax blends, 30% of wax



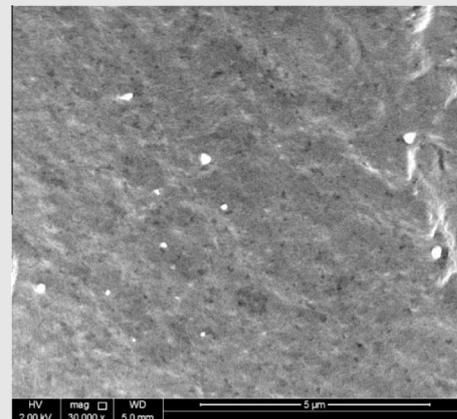
LLDPE/wax blends, 40% of wax



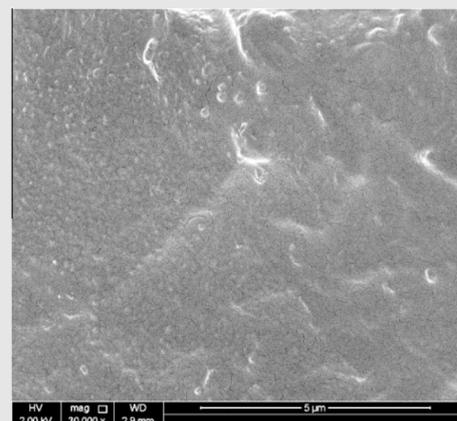
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Table 1 (continued)

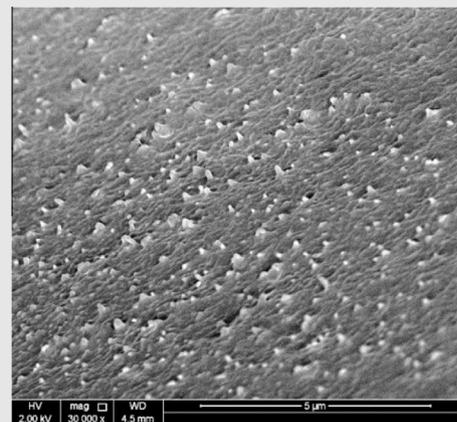
LDPE/wax blends, 10%, of wax



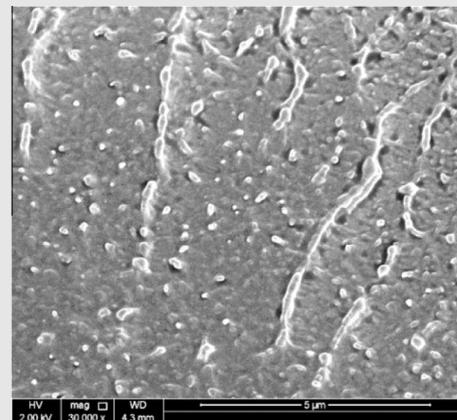
LDPE/wax blends, 20%, of wax



LDPE/wax blends, 30%, of wax



LDPE/wax blends, 40%, of wax



The root mean square (rms) roughness parameter is a statistical measure of the relative roughness of a surface and is essentially the standard deviation of the heights indicated by all pixels from the arithmetic mean in Eq. (1):

$$\text{rms} = \frac{\sqrt{(Z_i - Z_{av})^2}}{N} \quad (1)$$

where Z_i is the height at a particular point on an image (nm), Z_{av} is the mean height of all pixels in the image (nm) and N is the total number of pixels in the image. The maximum range is the height difference between the lowest and highest pixels in the image.

2.3.3. Thermal measurements

Differential scanning calorimetry (DSC) analysis was carried out using a Perkin Elmer DSC8500 under nitrogen gas. DSC results were collected during the second heating cycle from 20 to 170 °C at 10 °C/min.

The theoretical enthalpy ΔH^{theo} at the melting point is calculated by Eq. (2):

$$\Delta H^{\text{theo}} = w \times \Delta H_{\text{PE}} \quad (2)$$

where ΔH_{PE} is the melting enthalpy of the pristine PE matrix and w is the fraction of the PE matrix in the blend. The degree of crystallinity X (%) is calculated via Eq. (3):

$$X (\%) = \Delta H_m \times w / \Delta H_0 \quad (3)$$

where ΔH_m is the melting enthalpy and ΔH_0 is the enthalpy of 100% PE (Brandrup and Immergut, 1988; Zarandi et al., 2012; Moly et al., 2005).

Thermogravimetric analysis (TGA) was carried out on a Perkin Elmer TGA7 analyser (USA) thermal analyser from 50 °C to 600 °C at a heating rate of 10 °C/min in a nitrogen atmosphere (20 ml/min).

2.3.4. Mechanical properties measurements

A tensile analyser (LLOYD Instruments, UK) was used to measure the mechanical properties of the materials at room temperature. Tensile testing was performed at a rate of 50 mm/min according to the ASTM D638 standard. The average values and standard deviations were obtained from the analysis of at least five measurements. Mechanical properties such as tensile strength, Young's modulus and elongation at break were evaluated directly from the stress-strain curves.

3. Results and discussion

The SEM micrographs of the HDPE/wax, LLDPE/wax and LDPE/wax blends are shown in Table 1. Different morphologies were observed and depended on the polyethylene structure.

For the morphology of the HDPE blends. At a low content of 10% wax, a homogeneous surface and good dispersion of the wax was observed. Then, the miscibility of the wax within the HDPE matrix became poor, and an agglomeration of the wax was observed at contents of 20%, 30% and 40%, as shown in Table 1.

As in the HDPE blends, the wax showed good dispersion in the LLDPE blends at a low content (10%). Higher contents of

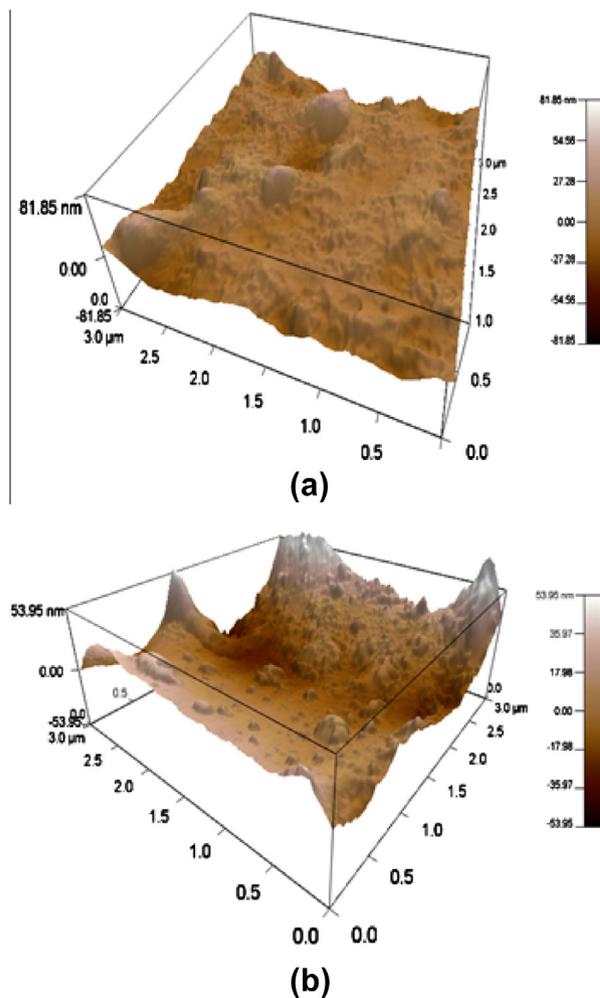


Figure 1 AFM surface of 10% wax in (a) HDPE, and (b) LDPE.

wax (20%, 30% and 40%) led to more agglomeration at the sample surface, as shown in Table 1.

For the LDPE blends, the dispersion of the wax was well noted, as observed Table 1; at 20% wax content, a heterogeneous surface was observed, indicating the immiscibility of the Q wax within the LDPE matrix. The agglomeration of the wax continued at contents of 30% and 40%. The amorphous structure of the polymer allows the wax to disperse easily between the chains.

Although the blends were prepared under the same conditions, the wax dispersion in the matrix strongly depends on (1) the percentage of wax added to the polymer and (2) the morphology of the polymer. Increasing the wax content causes an increase in phase separation and miscibility. LDPE shows less phase separation because it is composed of a network of long chain branches with the wax, and it has larger open amorphous areas due to its low crystallinity, similar to the behaviour observed when the PE was filled with fibreglass (AlMaadeed et al., 2012). The amorphous structure of the polymer means less packing of the polymer chains which allows the low molecular weight wax chains to penetrate easily in the LDPE chain network. This phenomenon is in agreement with the generally held view that lower crystallinity polyolefins have relatively lower chemical resistance due to penetration.

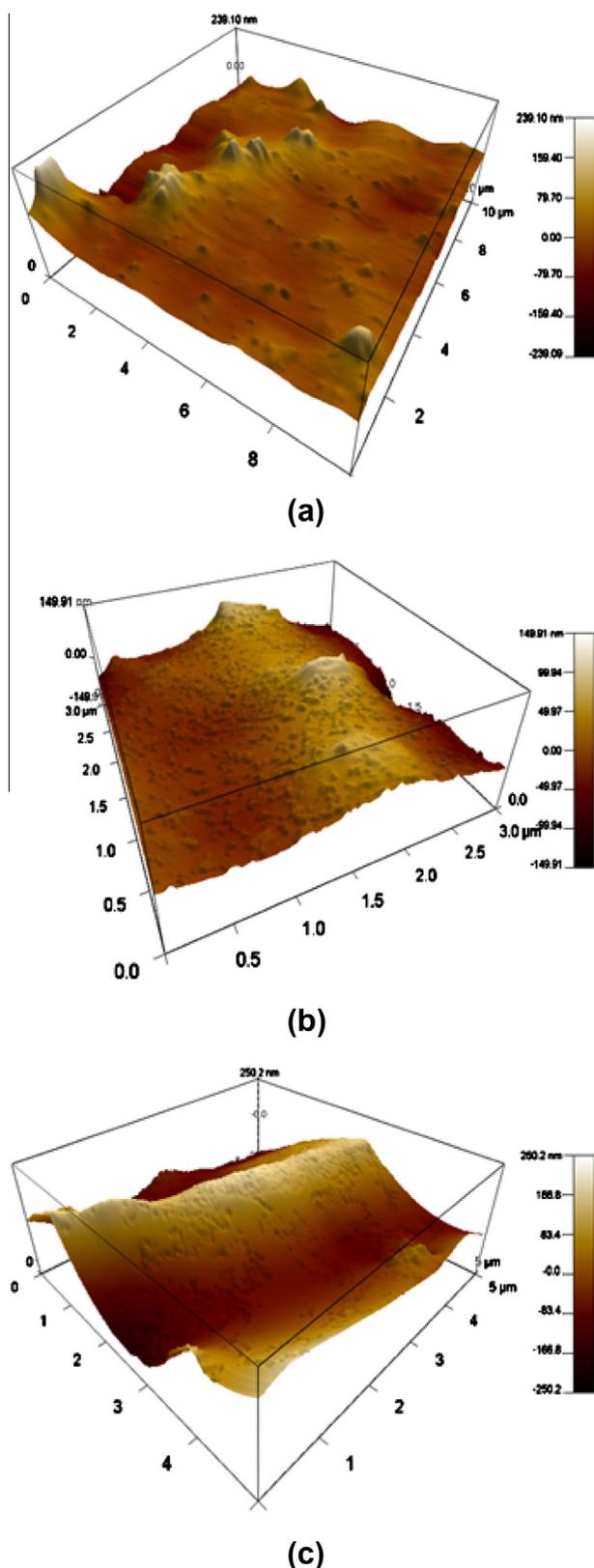


Figure 2 AFM surface of 30% wax in (a) HDPE, (b) LLDPE and (c) LDPE.

The higher degree of crystallinity of the polymer hinders the additive dispersion and causes aggregation as reported in the literature (Kaur et al., 2011).

Cohesion of wax occurs due to intermolecular attraction forces at high wax content during the melt processing in the extruder. Shear stresses provide energy for the dispersion which cannot be achieved for higher concentrations of wax contents.

If the wax content is very high (above 20%), even the open areas in the low density PE are not enough to accommodate the wax chains and the phenomenon of agglomeration is seen with all types of PE densities. In other words, the LDPE amorphous regions become saturated with wax chains and agglomeration starts to occur like in the other two types of PE (LLDPE and HDPE).

AFM photos in Fig. 1(a and b) for HDPE and LDPE 10% wax show the surface of the composites with a roughness of 12.81 and 16.82 nm, respectively.

The AFM images in Fig. 2(a–c) for HDPE, LLDPE and LDPE with 30% wax, show the surfaces of the composites with a roughness of 25.476, 40.087 and 57.048 nm, respectively.

The AFM results again show that the wax loading affects the surface morphology. The roughness increases due to the restriction of the free flow of the resin and the increase in contact area. Regarding the effect of the structure, it is noticed that the roughness increases with the degree of branching because flow decreases in networks of long chain branches.

The DSC results of the blends are presented in Table 2. For HDPE/Q wax composites, there is only one endothermic peak, which indicates that HDPE and Q wax are miscible in the crystalline phase up to 30 wt.% wax and might co-crystallise (Molefi et al., 2010).

For 40% wax, a second narrow peak was observed at 100 °C, indicating that HDPE and Q wax are partially miscible at this wax content (Table 2). The melting point of the HDPE matrix was slightly affected by the addition of the wax (Table 2), decreasing from 134 to 131 °C. This indicates a small decrease in lamellar thickness (Plaza et al., 1997). Nevertheless, the enthalpy decreased significantly from 170 to 101 J/g, and because enthalpy is proportional to percent crystallinity, this also indicates a decrease in the percent crystallinity of the blend. This decrease will affect the mechanical properties and the thermal stability of the HDPE matrix, as will be discussed later.

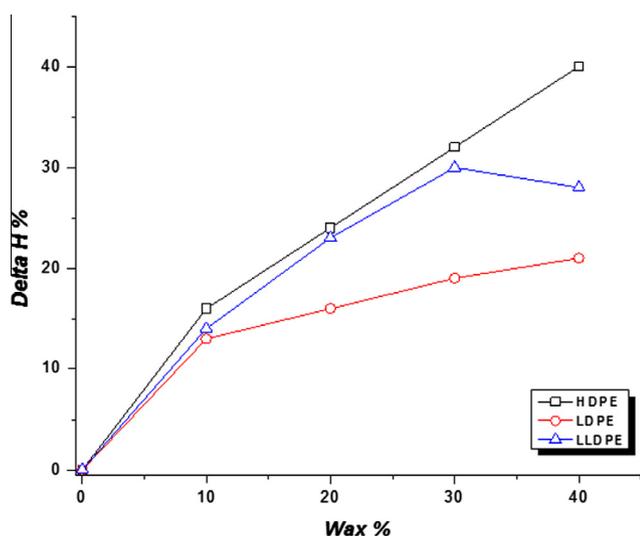
For the virgin LLDPE matrix, two peaks were observed. The first one appears at approximately 109 °C and the second at 123 °C. The first peak in the virgin polymer may be due to the distribution of the short chain branches along the main chains in the polymer; a common phenomenon in LLDPE (Shanks and Amarasinghe, 2000). This is due to the fact that the short chain branches (SCB) are not equally distributed along the LLDPE main chains.

According to Table 2, the enthalpy of this phase related to the side chains increases with the wax content from 1.2 J/g for the virgin polymer to 4.5 J/g at 40% wax content, which means that there is an affinity between this short-side-chain phase and the short molecules of wax. In addition, the melting point of the first peak is affected by the addition of the wax. The temperature decreased from 109 to 106 °C at 40% wax content. Thus, the melting point of this phase shifts to the melting temperature of the wax, which again indicates that the side chains of the polymer co-crystallise with the wax.

Melting temperature can be related to the size and perfection of the crystalline regions in the polymer (Da Costa and Ramos, 2008). Reduction in melting point with the increase

Table 2 DSC results of the investigated samples.

Sample	T_m (°C)	ΔH_m (J/g)	ΔH^{theo} (J/g)	X (%)	T_c (°C)	ΔH_c (J/g)
Q wax	103	20	20		84	-25
<i>HDPE/Q wax</i>						
HDPE	134	170	170	58.6	120	-167
HDPE/10%	133	143	153	44.3	120	-136
HDPE/20%	133	130	136	35.8	119	-130
HDPE/30%	131	115	119	27.7	119	-109
HDPE/40%	100/131	-/101	102	20.9	92/119	-/ -110
<i>LLDPE/Q wax</i>						
LLDPE	109.4/123.4	1.2/33	33	23.5	108	-46
LLDPE/10%	108.5/123.5	2.7/28.4	29.7	18.2	109.9	-37
LLDPE/20%	106.7/122.9	3.3/25.4	26.4	14.5	108.8	-28.9
LLDPE/30%	106.8/122.9	3.9/23	23.1	11.5	109	-28.9
LLDPE/40%	106.3/122.6	4.5/25	19.8	10.7	108.9	-31.6
<i>LDPE/Q wax</i>						
LDPE	110	70	70	24.3	96	-70
LDPE/10%	111	61	63	19	98	-60
LDPE/20%	110	59	56	16.4	97	-64
LDPE/30%	101/110	-/57	49	13.9	97	-/ -58
LDPE/40%	99/112	0.3/55	42	11.5	-/97	-/ -50

**Figure 3** Difference of ΔH compared to the virgin matrix.

in the wax content may be due to the reduction in the size or lamella thickness (AlMaadeed et al., 2012).

The decrease in the enthalpy content with the addition of wax is due to the impurity effect of the wax which leads to smaller crystalline structure and less ordered crystals (As'habi et al., 2013). But the addition of 40% wax increases the enthalpy which may be due to the wax acting as nucleation sites for the polymer inducing more crystallinity, which is in accordance with that reported in literature (AlMaadeed et al., 2012; Moly et al., 2005).

Crystallinity percentage (and the related enthalpy content) depends on many factors including the lamellar thickness, such as distribution, length and type of curvature (AlMaadeed et al., 2012; Woodhams et al., 1984).

However, the melting point of the matrix is not affected by the addition of wax, as it remains fixed at approximately 122

or 123 °C. Nevertheless, the enthalpy decreases with increasing wax content. Then, the enthalpy slightly increases again at 40% wax content (Table 2).

In the case of the LDPE/Q wax composites, one endothermic peak can be observed at wax contents of up to 20%, indicating that LDPE and Q wax are miscible up to this wax content. At 30% and 40% wax, two peaks can be observed. The first is a peak shoulder at approximately 100 °C, which indicates that LDPE and Q wax are partially miscible at this wax content (Table 2). At wax contents of up to 20%, the wax may co-crystallise with the chains of the polymer matrix (Peacock, 2000), melting at the same temperature as the polyethylene matrix and being unable to contribute to the plasticising effect of the wax. The melting point is not affected by the addition of the wax. The enthalpy decreases from 70 to 55 J/g, and the percent crystallinity of the blend decreases as well.

The difference between the theoretical enthalpy and the experimental one at 30% and 40% wax, especially for the LDPE matrix, may be due to a leakage phenomenon during the transformation steps.

The difference in delta H between each blend and the virgin matrix is presented in Fig. 3. The LDPE matrix seems to be less affected by the addition of the wax compared to HDPE and LLDPE. This is due to the long side chains of LDPE and to the fact that there is more similarity in molecular structure between the wax and LDPE than between the wax and the other 2 polymers. Nevertheless, the short branched chains presented in HDPE and especially LLDPE support the interaction with the short chains of wax.

The stability of the melting peak and crystallisation peak of the polymers indicate that there is no pronounced plasticising effect of the wax on the polymer. This is clearly observed in LDPE, as the melting temperature remains unchanged. The LLDPE and the HDPE are slightly affected by high concentrations of wax (30% and 40%). This may be due to the broad distribution of branching densities of LLDPE and to a lesser extent HDPE, which can interact with the wax structure

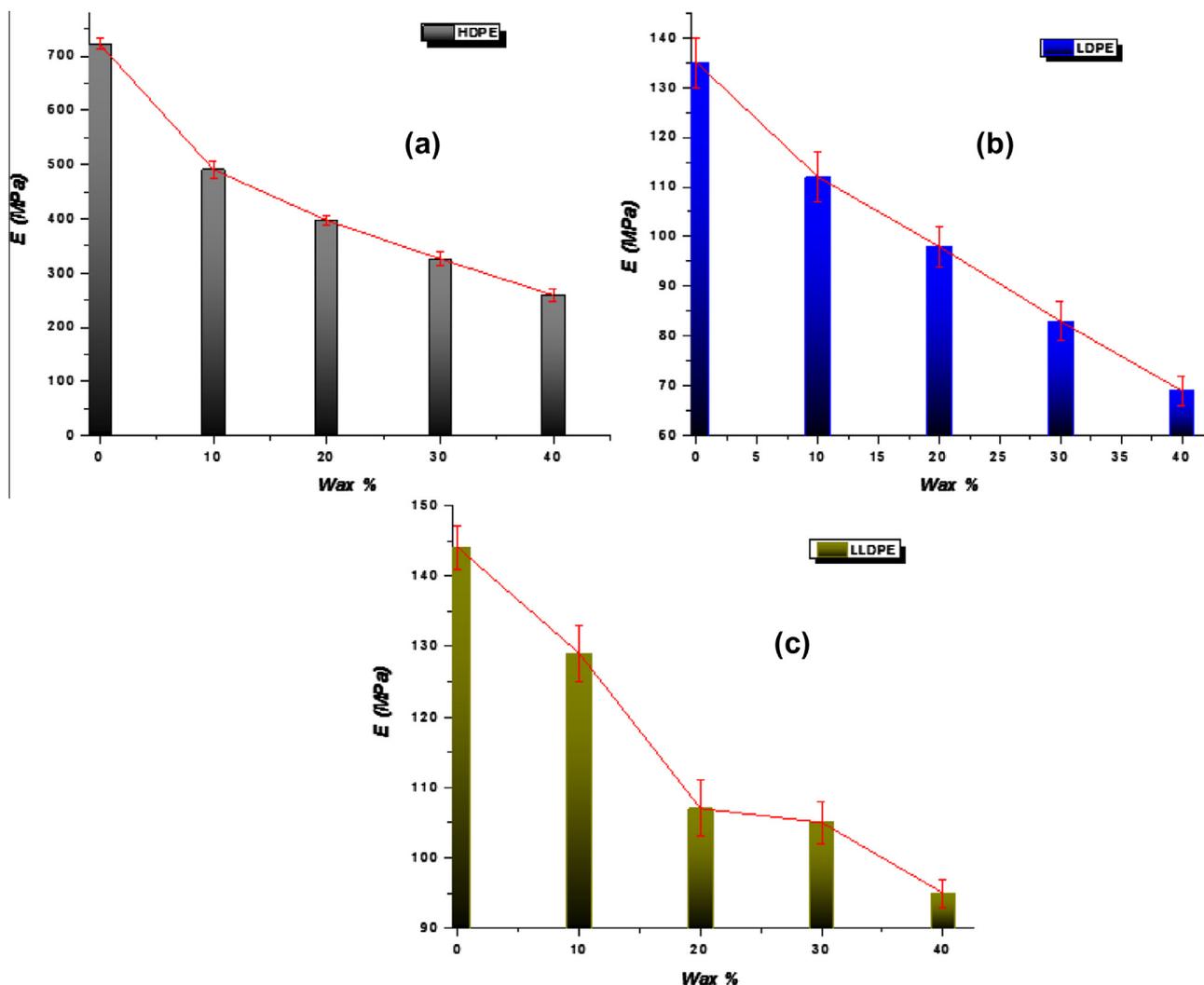


Figure 4 Young's modulus vs. wax content.

(Plaza et al., 1997). These are not the same results obtained by Peacock (2000); however, Molefi et al. used Fischer–Tropsch wax, which has pronounced effects on all types of PE and has a melting point of 58 °C.

As discussed above, a decrease in the percent crystallinity of the blends was observed due to the addition of wax. The results regarding the mechanical properties of the samples, presented in Figs. 4 and 5, show that the addition of wax significantly reduced the Young's modulus and tensile strength of the polyethylene blends.

For the HDPE and LDPE matrices, starting from 10% wax content, the decrease in the Young's modulus was approximately linear.

The addition of 40% wax to the polyethylene matrix reduced the rigidity of the HDPE blend by 64%, that of the LDPE blend by 50% and that of the LLDPE blend by 34%. This may be due to the low molecular weight of the wax compared to that of the polyethylene matrix (Moly et al., 2005). Thus, the wax acts as a plasticiser or a defect point for the initiation and propagation of stress cracking and a weak point in stress transfer during deformation. Moreover, the decrease in the Young's modulus of the blend may be due to the low

modulus of the wax compared to that of PE. This result was expected with decreasing % crystallinity (see DSC results) because Young's modulus depends on the energy transformation between the amorphous and crystalline regions.

The long chains in LDPE are more flexible and can fold around the wax, while rigid chains cannot (Shanks and Amarasinghe, 2000).

This decrease in % crystallinity is also responsible for the decrease in the tensile strength of the blends with the addition of wax (Table 2). The wax domains (together with the PE/wax interface) also represent defects that lead to the decrease in the tensile strength.

The TGA for HDPE composites showed that all blends are less stable compared to the virgin matrix (Fig. 6). At high temperatures, the stability decreases significantly with increasing wax content up to 30%. Above this content, the thermal stability of the blends is approximately the same. Indeed, the more crystalline a polymer sample is, the higher is its thermal stability. From the DSC results, it is clear that the crystallinity of HDPE decreases with addition of wax (Table 2) and therefore negatively affects the thermal stability of the material. In addition, the wax (very low molecular weight) may disrupt the

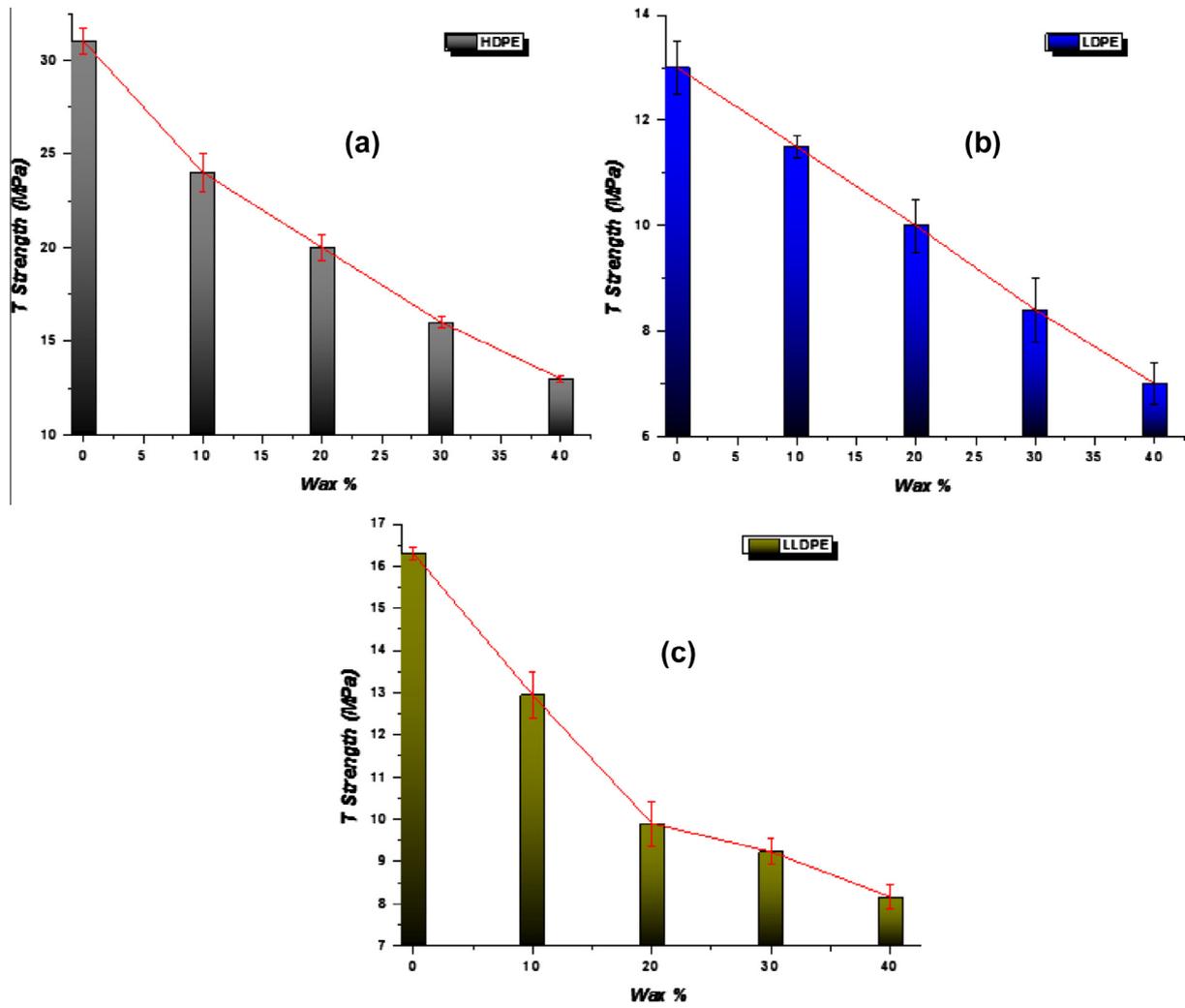


Figure 5 Tensile strength of PE matrices vs. wax content.

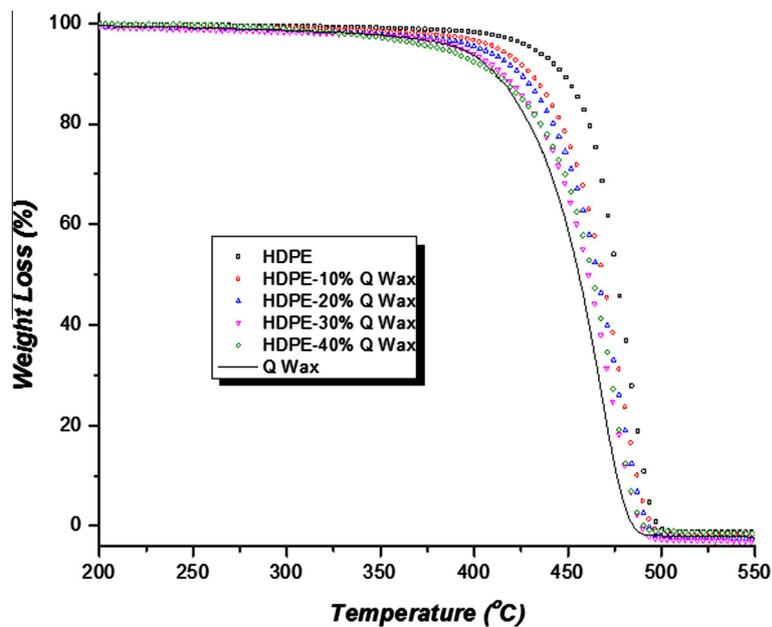


Figure 6 TG curves of HDPE/wax blends.

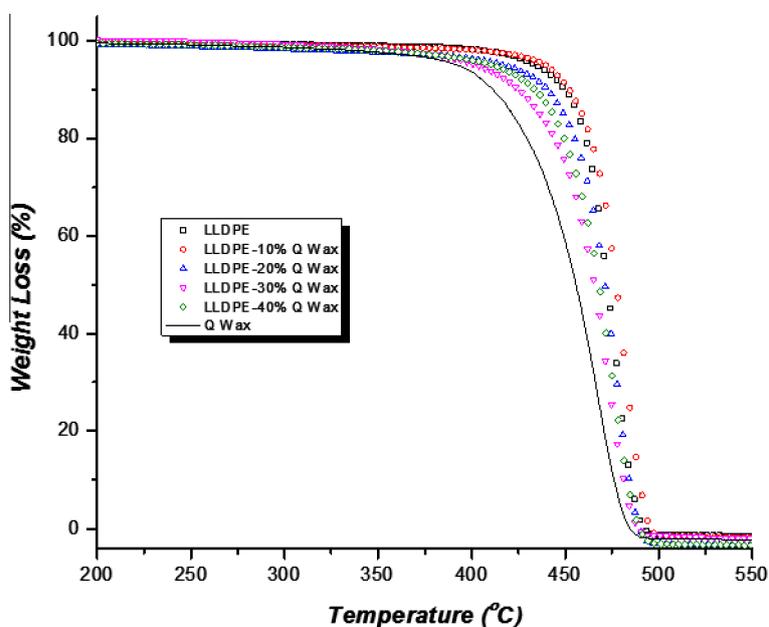


Figure 7 TG curves of LLDPE/wax blends.

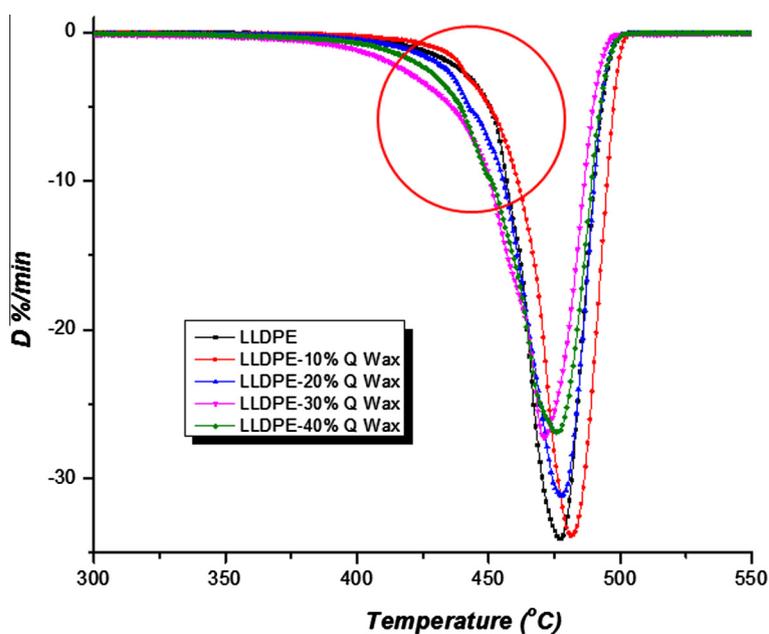


Figure 8 DTG curves of LLDPE/wax blends.

crystallisation of the higher molecular weight chains and therefore reduce the crystallinity of the polymer, making the matrix less stable at higher temperature. Furthermore, the derivative curves show only one weight loss event, which proves that the HDPE backbone protects the small molecules of Q wax at high temperature and most likely that the wax co-crystallises with the HDPE matrix.

Nevertheless, at 40% wax content, a lower temperature step of 460 °C was noticed. This may be due to the decomposition of a small part of the wax that is immiscible with the HDPE matrix, as confirmed before by the DSC results (Table 2). The co-crystallisation of a part of the wax in the amorphous

zone of the HDPE matrix, was consequently not protected by the HDPE crystals and degraded at approximately the same onset temperature of the wax alone.

The same conclusions are noticed for the LDPE composites. However, the thermal stability of LDPE seems to be unaffected by the addition of 10% wax and slightly increases.

For the LLDPE/ Q wax composites, at 10% wax content, the thermal stability is slightly enhanced (Fig. 7). Then, it is reduced by the addition of wax upto 30% wax content. However, at 40%, the thermal stability increased slightly relative to that at 30%. Indeed, as confirmed by the DSC results, the melting enthalpy increased again at 40% wax content

(Table 2), indicating an increase in the crystallinity of the blend, which improved the thermal stability.

The DTG curves show two weight loss events: a rapid one at approximately 460 °C and a second one at approximately 480 °C (Fig. 8). The first one is related to the main decomposition of the wax (represented by the circle in Fig. 8). Furthermore, this is proof that the wax crystallises in the amorphous phase of LLDPE and that consequently the matrix does not protect it at high temperature.

4. Conclusion

The effects of the chain structure of polyethylene and the content of waste wax on the morphological, thermal and mechanical properties of LDPE, LLDPE and HDPE composites were investigated.

The addition of wax to the polymer matrices reduces the mechanical performance and thermal stability of all the blends. The tensile strength of the different blends generally decreases with increasing wax content.

Because LDPE has a random distribution of branching density and a highly long chain branching structure, the polymer undergoes less phase separation when mixed with the waste wax. LLDPE and HDPE exhibit more pronounced plasticisation when mixed with the wax (at contents of 30% and 40%); this is due to their non-uniform distribution of branching densities, which allow for a localised interaction with the wax structure. These findings are very important in understanding the parameters that control the thermal stability, mechanical integrity and overall performance of polyethylene-wax blends for various applications.

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References

- AlMaadeed, M.A., Ouederni, M., Noorunnisa, K.P., 2012. Effect of chain structure on the properties of glass fibre/polyethylene composites. *Mater. Des.* 47, 725–730.
- As'habi, L., Jafari, S.H., Khonakdar, H.A., Häussler, L., Wagenknecht, U., Heinrich, G., 2013. Non-isothermal crystallization behavior of PLA/LLDPE/nanoclay hybrid: synergistic role of LLDPE and clay. *Thermochim. Acta* 565, 102–113.
- Brandrup, J., Immergut, E.H., 1988. In: *Polymer Handbook*. Wiley-Interscience, New York (Chapter 8).
- Da Costa, H.M., Ramos, V.D., 2008. Analysis of thermal properties and rheological behavior of LLDPE/EPDM and LLDPE/EPDM/SRT mixtures. *Polym. Testing* 27, 27–34.
- Inaba, H., Tu, P., 1997. Evaluation of thermophysical characteristics on shape-stabilized paraffin as a solid-liquid phase change material. *Heat Mass Transf.* 32, 307–312.
- Salyer, I.O., 1996 Thermoplastic, moldable, non-exuding phase change materials, US Patent No. 5,565,132.
- Kaur, J., Leea, J.H., Shofner, M.L., 2011. Influence of polymer matrix crystallinity on nanocomposite morphology and properties. *Polymer* 52, 4337–4344.
- Krupa, I., Miková, G., Luyt, A.S., 2007a. Polypropylene as a potential matrix for the creation of shape stabilized phase change materials. *Eur. Polym. J.* 43, 895–907.
- Krupa, I., Miková, G., Luyt, A.S., 2007b. Phase change materials based on low-density polyethylene/paraffin wax blends. *Eur. Polym. J.* 43, 4695–4705.
- Luyt, A.S., Krupa, I., 2009. Phase change materials formed by UV curable epoxy matrix and Fischer-Tropsch paraffin wax. *Energy Convers. Manage.* 50, 57–61.
- Molefi, J.A., Luyt, A.S., Krupa, I., 2010. Comparison of LDPE, LLDPE and HDPE as matrices for phase change materials based on a soft Fischer-Tropsch paraffin wax. *Thermochim. Acta* 500, 88–92.
- Moly, K.A., Radusch, H.J., Androsh, R., Bhagawan, S.S., Thomas, S., 2005. Nonisothermal crystallisation, melting behavior and wide angle X-ray scattering investigations on linear low density polyethylene (LLDPE)/ethylene vinyl acetate (EVA) blends: effects of compatibilisation and dynamic crosslinking. *Eur. Polym. J.* 41, 1410–1419.
- Moly, K.A., Radusch, H.J., Androsh, R., Bhagawan, S.S., Thomas, S., 2005. Nonisothermal crystallisation, melting behavior and wide angle X-ray scattering investigations on linear low density polyethylene (LLDPE)/ethylene vinyl acetate (EVA) blends: effects of compatibilisation and dynamic crosslinking. *Eur. Polym. J.* 41, 1410–1419.
- Mpanza, H.S., Luyt, A.S., 2006. Comparison of different waxes as processing agents for low-density polyethylene. *Polym. Testing* 25, 436–442.
- Peacock, A.J., 2000. *Handbook of Polyethylene: Structures, Properties and Applications*, first ed. Marcel Dekker, New York.
- Peng, S., Fuchs, A., Wirtz, R.A., 2004. Polymeric phase change composites for thermal energy storage. *Appl. Polym. Sci.* 93, 1240–1251.
- Pladis, P., Baltas, A., Kiparissides, C., 2006. A comprehensive investigation on high-pressure LDPE manufacturing: dynamic modelling of compressor, reactor and separation units. In: Marquardt, W., Pantelides, C. (Eds.), *Computer Aided Chemical Engineering*. Elsevier, pp. 595–600.
- Plaza, A.R., Ramos, E., Manzur, A., Olayo, R., Escobar, A., 1997. Double yield points in triblend of LDPE, LLDPE and EPDM. *Mater. Sci.* 32, 549–554.
- Sari, A., 2004. Form-stable paraffin/high density polyethylene composites as solid-liquid phase change material for thermal energy storage: preparation and thermal properties. *Energy Convers. Manage.* 45, 2033–2042.
- Shanks, R.A., Amarasinghe, G., 2000. Crystallisation of blends of LLDPE with branched VLDPE. *Polymer* 41, 4579–4587.
- Woodhams, R.T., Thomas, G., Rodgers, D.K., 1984. Wood fibers as reinforcing fillers for polyolefins. *Polym. Eng. Sci.* 24, 1166–1171.
- Xiao, M., Feng, B., Gong, K., 2001. Thermal performance of a high conductive shape-stabilized thermal storage material. *Sol. Energy Mater. Sol. Cells* 69, 293–296.
- Zarandi, M.B., Bioki, H.A., Mirbagheri, Z.A., Tabbakh, F., Mirjalili, G., 2012. Effect of crystallinity and irradiation on thermal properties and specific heat capacity of LDPE & LDPE/EVA. *Appl. Radiat. Isot.* 70, 1–5.