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Influence of low-density polye[thylene](http://www.elsevier.com/locate/tca) [on](http://www.elsevier.com/locate/tca) [the](http://www.elsevier.com/locate/tca) [therma](http://www.elsevier.com/locate/tca)l characteristics and crystallinity of high melting point macro- and micro-crystalline waxes

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ABSTRACT

The influence of low-density polyethylene on the thermal characteristics and the crystallinity of high melting point macro- and micro-crystalline waxes were investigated. The samples were prepared through melt blending using mechanical stirrer. The thermal characteristics of the blended samples were determined using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The crystallinity of the samples was obtained using X-ray diffraction analyzer (XRD). The observations are discussed in terms of possible changes when the polymer is mixed with two types of waxes. The wax–polymer miscibility differed with the type of the wax and the amount of polymer mixed into the wax. Also, the crystallinity and congealing point of the waxes differed with the amount of polymer mixed into the wax. Moreover, the resulting data indicate that, blending of polymer with high melting point micro-crystalline wax elevates its melting point to reach the limits of high melting point ceresin waxes which can be used in different industrial applications.

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1. Introduction

Macro-crystalline waxes (paraffin waxes) are solid and crystalline mixtures of hydrocarbons; they are usually produced in the form of relatively large crystals and consist mainly of n-paraffins ranging from C_{16} to C_{30} and possibly higher. Varying proportions of slightly branched-chain paraffins (C_{18} to C_{36}) and naphthenes are present [1–5].

Micro-crystalline waxes are extremely small crystals or microscopic in size and sometimes called amorphous. They are petroleum waxes containing substantial proportion of hydrocarbons other than normal paraffins. They consistmainly of highly branched chain [paraffin](#page-5-0)s, cycloparaffins and small amounts of n-paraffins and alkylated aromatics [1,2,5].

Much more work had been done on the thermal and mechanical properties of polymer/wax. Whereas, blending of polymers represents a cost-effective way to improve material properties. An important class of blends is miscible blends, consisting of component[s](#page-5-0) [that](#page-5-0) [ar](#page-5-0)e not phase separated. Therefore, miscibility of the components offers the opportunity for optimization of physical properties by controlling blend morphology [6,7].

Krupa and Luyt [8] studied some thermal properties of isotactic polypropylene/hard Fischer–Tropsch wax blends. The DSC results indicated that polypropylene (PP) and hard paraffin wax are homogeneous on a macro-scale when the wax content is less than 10%, whereas, at higher wax concentrations, there is a clear separation between wax and PP melting endotherms. TG analyses of these blends confirmed that an increase in wax content causes a decrease in the thermal stability of blends, since wax is thermally less stable than PP.

Djokovic et al. [6] investigate the thermal, mechanical and viscoelastic properties of the blends of low-density polyethylene (LDPE) and oxidized wax. The results show that blending of LDPE with small concentrations of wax (up to 10 wt%) can improve its physical properties. Co-crystallization of PE and wax chains leads to an inc[rease](#page-5-0) in the blend crystallinity. As a result, thermal stability is improved by more than 50 ◦C, and the elastic modulus and stress at yield increase. However, in blends with higher wax concentrations, crystal phase separation occurs. This effect, as well as, the presence of short wax chains in the amorphous fraction, induces deterioration of the thermal and mechanical properties. It should be noted that small amounts low molecular weight oligomers, such as wax, are sometimes added to polyethylene in order to improve its processing.

Mpanza and Luyt[9] study the influence of three different waxes (EnHance wax, H_1 wax and M_3 wax) on the thermal and mechanical properties of low-density polyethylene (LDPE). 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](#page-5-0) 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

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wax content. At all contents of EnHance wax (1, 3, 5 and 10 wt%) in LDPE/EnHance blends, which was developed to improve processing, had a small influence on the melt flow properties. The DSC curves for LDPE and H_1 wax showed that they were miscible up to 3% wax content. For 5 and 10% wax, LDPE and H_1 wax were only partially miscible. The presence of H_1 wax slightly increased the enthalpy of its blends with LDPE, and the peak tempera[ture](#page-5-0) [o](#page-5-0)f melting slightly increased up to 5% wax content. The TGA results showed that H_1 wax is clearly less thermally stable than LDPE, but that the blends were more stable, except for the sample containing 1% wax. H_1 wax generally improved the flow rate of LDPE. The $LDPE/M₃$ 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 M_3 wax content increased. The TGA results showed an increase in onset temperature of degradation for low M_3 wax contents, despite the lower thermal stability of the wax, but the stability decreased with increasing wax content. Stress and elongation at break decreased with increasing wax content.

On the other hand, wax/polymer blends are manufactured for a range of uses (e.g. hot melt adhesives, laminates, coatings, casting waxes and rubber additives). They vary in composition, depending on their use, from a simple blend of paraffin and micro-crystalline wax to complex blends of waxes, polyethylene, polypropylene, resins and other additives. The thermal properties of wax/polymer blends are very important to their industrial applications, and therefore DSC analysis is an essential tool in controlling quality, matching competitor blends, product development and raw materials characterization [10]. As, the previous studies still not clear to investigate the effect of polymer on the wax characteristics. Thus, our present work aims with the influence of low-density polyethylene on the thermal characteristics and the crystallinity of high melting point macro- and micro-crystalline waxes by using different t[ools](#page-5-0) [of](#page-5-0) analysis such as DSC, TGA and XRD.

2. Experimental

2.1. Materials

Two different prepared waxes (high melting point macro- and micro-crystalline waxes) were produced from heavy slack wax and crude petrolatum obtained from El-Ameria Refining Company and Alexandria Petroleum Company, respectively. Low-density polyethylene (LDPE) was supplied by Aldrich Company. It has a melting point of 111 °C, a density of 0.921 g/cm³, hardness of 45 and an average molecular weight of 25,000 g/mol.

2.2. Methods

Two types of high melting point waxes (macro- and microcrystalline waxes) were blended with LDPE. The blends were mechanically mixed through melt blending using mechanical stirrer at a temperature of 160 ℃ and a rotation speed of 100 rpm for half an hour. Two blend groups were formed as represented in Table 2.

High melting point macro- and micro-crystalline waxes and their blends with LDPE were physically and mechanically characterized according to American Society for Testing and Materials (ASTM) standard methods [11]. The standard methods for analy[s](#page-3-0)is are congealing point (ASTM D-938), kinematic viscosity (ASTM D-445), refractive index (ASTM D-1747), mean molecular weight (ASTM D-2502) and needle penetration (ASTM D-1321).

The aromatic content of high melting point macro- and microcrystalline wax[es](#page-5-0) [wa](#page-5-0)s determined using liquid–solid column chromatography technique. A 1.3 cm diameter and height of 130 cm column packed with activated (60–200 mesh) silica gel was used [12]. The column was then moistened with 100 ml of n-heptane to dissipate the heat of adsorption. 10 g of wax sample were dissolved in few milliliters of n-heptane and transferred to the column. The column was then eluated with 300 ml of n-heptane followed by 200 ml benzene and finally 100 ml of a 1:1 mixture of absolute methanol and benzene. Fractions of 25 ml were taken from the column, the solvent distilled off and the refractive index of each fraction was determined. According to the refractive index data at 20 °C, eluates were combined into saturates, mono-, di- and polyaromatics. The saturate hydrocarbons have refractive indices not more than 1.48. The mono-cyclic, bi-cyclic and poly-cyclic aromatics have refractive indices from 1.48 to 1.53, 1.53 to 1.59 and higher than 1.59, respectively [13].

n-Paraffin content was determined for the high melting point macro- and micro-crystalline waxes using GC technique. The GC apparatus used was PerkinElmer (Clarus 500), equipped with a hydrogen flame ionization detector and fused silica capillary column (60 m [lengt](#page-5-0)h \times 0.32 mm i.d.), packed with poly (dimethyl siloxane) HP-1 (non-polar packing) of 0.5 μ m film thickness. In the chromatograph, the injector was heated at 350° C. The column temperature was programmed from 100 to 300 ◦C at a fixed rate of 3 ℃/min, and nitrogen (oxygen-free) was used as a carrier gas with flow rate of 2 ml/min. The detector was heated at 350 \degree C, and operated with a hydrogen flow rate adjusted to optimize the detector sensitivity. The sample was melted and 0.1 μ l of it was introduced into the injector. A mixture of pure n-paraffins was used as standard. The peak area of each resolved component (consisting of either n- and iso-paraffin) is determined individually. However, the unresolved complex mixtures (humps); composed of non-n-paraffins presumably mainly cycloparaffins and aromatics with long side chains; were determined only as a total.

The degree of branching (%CH₃ content) of the prepared high melting macro- and micro-crystalline waxes was determined using proton nuclear magnetic resonance (Varian Mercury H-NMR spectrometer-Danemark) at 300 MHz in deutrated chloroform. The relative proportions of methyl to methylene groups ($\mathscr{C}CH_3$ content) were calculated from one third of the integrated area under the methyl region (from about 0.5 to 1.0 ppm) and half of the integrated area under the methylene and methine regions (from about 1.0 to 1.7 ppm) [14].

Both DSC and TGA analyses were carried out using SDTQ 600 thermal and thermogravimetric analyzer (TA-USA) to test the thermal properties and thermal stability of high melting point macroand micro-crystalline waxes, LDPE and their blends in the temper[atur](#page-5-0)e range of 25–180 °C and a heating rate of $5 \degree C/m$ in for DSC analysis and in the temperature range of $25-700$ °C and a heating rate of 10° C/min for TGA analysis, under dynamic nitrogen gas.

The X-ray diffraction patterns of high melting point macro- and micro-crystalline waxes and their blends with LDPE were recorded in the range 2 θ =5–70° with a step size of 0.03 (2 θ) every 2s, in a Philips Analytical X-ray diffractometer with K-alpha1 radiation and equipped with a Cu source with K-alpha1 wavelength of 1.54056 Å. The instrument was operated at 40 kV and the incident angle of the parallel beams was 8° (2 θ). The degree of crystallinity of high melting point macro- and micro-crystalline waxes and their blends with LDPE was calculated by dividing the total area under Bragg peaks on the total area under Bragg peaks plus the area under hump.

3. Results and discussion

3.1. Characterization of the prepared waxes

The physical characteristics and the molecular type composition for the two prepared waxes are represented in Table 1. The

Table 1

Physical characteristics and molecular type composition of high melting point macro- and micro-crystalline waxes.

Characteristics	Macro-crystalline wax	Micro-crystalline wax
Congealing point $(°C)$	75.5	86.5
Kinematic viscosity at 98.9 °C (mm ² /s)	7.00	13.00
Refractive index at 98.9 °C	1.4302	1.4360
Mean molecular weight	587	830
Needle penetration at 25° C	19	7
Molecular type composition		
Total saturates (wt%)	97.01	91.33
n-Paraffin content (wt%)	62.01	76.03
Iso- and cyclo-paraffins	35.00	15.30
content (wt%)		
Total aromatics (wt%)	2.99	8.67
Mono-aromatics (wt%)	2.99	8.67
Degree of branching $(\%CH_3)$ content)	14.37	4.96
Degree of crystallinity (%)	83	63

physical characteristics data such as congealing point, kinematic viscosity, refractive index, mean molecular weight and needle penetration are within the limits of high melting point macro- and micro-crystalline waxes' specifications [15]. Also these data indicate that the congealing point, kinematic viscosity and refractive index of micro-crystalline wax are higher than those of macrocrystalline wax. This is due to the high boiling point range and/or mean molecular weight of the micro-crystalline wax. Usually, macro-crystalline waxes con[sist](#page-5-0) [m](#page-5-0)ainly of n-paraffins and varying proportions of slightly branched-chain paraffins and naphthenes while micro-crystalline waxes consist mainly of highly branched chain paraffins, cycloparaffins and small amounts of n-paraffins and alkylated aromatics [1–5]. However, molecular type composition data indicated that the prepared macro-crystalline wax has lower n-paraffin content and consequently higher iso- and cycloparaffin content than those obtained for the micro-crystalline wax. The degree of branching data confirmed the previous findings but the degree of [crystall](#page-5-0)inity of macro-crystalline wax was found to be higher than that obtained for the micro-crystalline wax. This is due to that micro-crystalline wax contains the highest aromatic content (8.67 wt%). These aromatic components impose their amorphous shape on the crystal shape of micro-crystalline wax. SEM photographs confirmed the previous results whereas, the macro-crystalline wax crystals appear in large and loose needle form (Fig. 1a). Meanwhile the micro-crystalline waxes crystallize in needle form which are small crystals or microscopic in size (Fig. 1b).

3.2. Differential scanning calorimetry

The DSC curves of high melting point macro- and microcrystalline waxes, LDPE and their blends are shown in Figs. 2 and 3, respectively. Only one endothermic peak was observed for 100% macro-crystalline wax, 100% micro-crystalline wax and 100% LDPE which relates to the melting temperature of the pure materials (70.73, 80.04 and 120.08 ◦C, respectively). Meanwhile, for the blend groups 1 and 2 two endothermic peaks were shown whereas, the first one represents the melting temperature of the wax and the second one represents the melting temperature of the polymer. The observation of these two endothermic peaks in all blends is an indication that both macro- and micro-crystalline waxes are partially miscible with LDPE; i.e., the two waxes may crystallize separately in the amorphous phase of the LDPE. Also, DSC data show that, blending of 10 wt% LDPE to macro- and micro-crystalline waxes increases their onset and peak temperatures of melting and decreases those for LDPE in the blends (curves a and f in Figs. 2 and 3, respectively).

Fig. 1. SEM photographs of high melting point macro- (a) and micro-crystalline (b) waxes.

This is due to the plasticizing effect of the molten wax on the LDPE. Another increase of LDPE content from 10 to 30 wt% increases the onset and peak temperatures of melting for the two waxes and LDPE (Table 2, curves b–e in Fig. 2 and curves g–k in Fig. 3), possibly indicating a small increase in lamellar thickness of the wax and confirming the partial miscibility of the two waxes with the polymer [9].

Comparing between the two waxes, data observed that blending [up](#page-3-0) [to](#page-3-0) 30 wt% LDPE with macro-crystalline [wax](#page-3-0) [inc](#page-3-0)reases the peak temperatures of melting of the wax to higher values (from 70.73

Fig. 2. DSC curves for 100%macro-crystalline wax, 100% LDPE and their blends (a–e).

Fig. 3. DSC curves for 100% micro-crystalline wax, 100% LDPE and their blends (f–k).

to 78.05 ◦C) than blending with micro-crystalline wax (from 80.04 to 84.48 \degree C). This is due to the higher difference in melting points between macro-crystalline wax and LDPE (70.73 and 120.08 ◦C, respectively) than micro-crystalline wax and LDPE (80.04 and 120.08 \degree C, respectively)

Moreover, the increase of LDPE content decreases the total enthalpy (ΔH_{Tm}) of its blends with both macro- and microcrystalline waxes (Table 2). This indicates a decrease in the crystallinity of the wax by increasing LDPE content from 10 to 30 wt%. Blending of 10 wt% of LDPE to the two waxes decreases the enthalpy of both macro- and micro-crystalline waxes to valuable values (from 27.48 to 18.69 cal/g for the former and from 29.41 to 14.39 cal/g for the latter). Increasing the LDPE content from 10 to 15 wt% in both waxes leads to much decrease in the total enthalpy of macro-crystalline wax (from 18.69 to 12.78 cal/g) than that of micro-crystalline wax (from 14.39 to 12.16 cal/g). Another increase of LDPE content from 20 to 30 wt% blended with macro- and microcrystalline waxes leads to a slight decrease in the total enthalpy of macro-crystalline wax/LDPE blends (from 11.93 to 10.40 cal/g) and nearly still unchanged for micro-crystalline wax/LDPE blends (from 10.71 to 10.47 cal/g). This means that blending of LDPE to macrocrystalline wax decreases its crystallinity to a higher degree than micro-crystalline wax, suggesting that LDPE causes much more [dis](#page-5-0)tortion in macro-crystalline wax crystal lattice.

3.3. Thermogravimetric analysis

The TGA curves of pure macro-crystalline wax, pure LDPE and their blends are shown in Fig. 4. It is obvious that the

Fig. 4. TGA analysis for 100% macro-crystalline wax, their blends with 10 (a), 15 (b), 20 (c), 25 (d) and 30 wt% (e) LDPE and 100% LDPE.

macro-crystalline wax is clearly less thermally stable and starts decomposing at a much lower temperature than LDPE. Also, it can be noticed that the thermal stabilities of macro-crystalline wax/LDPE blends are between those of wax and LDPE except the blend contains 10 wt% of LDPE which shows a lower onset temperature of decomposition than the pure wax. This means that the addition of 10 wt% of LDPE deteriorates the thermal stability of macro-crystalline wax due to the difference in the crystallinity and crystal shape of each one. The TGA curves of all micro-crystalline wax/LDPE blends show a shift of onset of decomposition to higher temperatures with increasing LDPE content as compared to those of the pure materials (Fig. 5). 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 LDPE lamellae [9]. This means that the thermal stability of micro-crystalline wax/LDPE blends are increased with increasing LDPE content due to the [higher](#page-4-0) [t](#page-4-0)hermal stability of the polymer. Also, TGA curves observed that micro-crystalline wax is clearly higher in thermal stability than macro-crystalline wax due to its higher mean molecular weight (830) and/or boiling point range (Table 1). The effect of blend composition on the thermal stability of the macro- and micro-crystalline waxes/LDPE blends can be seen in Fig. 6a and b, where the temperatures of 10, 20 and 40 wt% decomposition (Fig. 6a) and 60, 80 and 90 wt% decomposition (Fig. 6b) are plotted versus LDPE content. For macr[o-crystall](#page-2-0)ine wax/LDPE blends

Table 2

DSC onset and peak temperatures, as well as enthalpies of melting of the in[vestigate](#page-4-0)d samples.

Sample	$T_{10,m}$ (°C)	$T_{1p,m}$ (°C)	ΔH_{1m} (cal/g)	$T_{20,m}$ (°C)	$T_{2p,m}$ (°C)	ΔH_{2m} (cal/g)	ΔH_{Tm} (cal/g)	Degree of crystallinity (XRD)
100% LDPE				106.96	120.08	9.46	9.46	
Macro-crystalline wax/LDPE (Blend group 1)								
100/0	57.29	70.73	27.48				27.48	83
$90/10$ (Blend a)	57.53	72.67	17.99	93.04	101.08	0.70	18.69	70
85/15 (Blend b)	59.07	75.71	11.89	97.72	104.20	0.89	12.78	68
80/20 (Blend c)	59.72	76.41	10.62	98.23	105.50	1.31	11.93	67
75/25 (Blend d)	60.55	77.90	10.13	99.98	107.24	1.39	11.52	$\qquad \qquad -$
70/30 (Blend e)	62.02	78.05	8.34	101.57	109.60	2.06	10.40	65
Micro-crystalline wax/LDPE (Blend group 2)								
100/0	62.67	80.04	29.41				29.41	63
90/10 (Blend f)	63.21	81.71	14.00	98.30	101.78	0.39	14.39	62
$85/15$ (Blend g)	65.81	83.54	11.33	99.18	103.35	0.83	12.16	62
80/20 (Blend h)	66.46	83.88	9.51	100.76	104.30	1.20	10.71	62
75/25 (Blend i)	66.96	84.22	9.15	100.90	108.14	1.32	10.47	
70/30 (Blend k)	67.76	84.48	8.63	101.16	110.34	1.84	10.47	62

 $T_{10,m}$ and $T_{20,m}$ are the onset temperatures of melting, $T_{10,m}$, $T_{20,m}$ are the peak temperatures of melting, ΔH_{1m} , ΔH_{2m} are the melting enthalpies of waxes and LDPE in the blends, respectively and ΔH_{Tm} is the total melting enthalpy of the blends.

Fig. 5. TGA analysis for 100% micro-crystalline wax, their blends with 10 (f), 15 (g), 20 (h), 25 (i) and 30 wt% (k) LDPE and 100% LDPE.

(group 1), by increasing LDPE content from 15 to 30 wt% the temperatures of decomposition at 10, 20 and 40 wt% decomposition are slightly increased, while there is a moderately increase in the temperature of decomposition at 60 wt% decomposition. Moreover, the increase in the temperatures of decomposition is more pronounced at 80 and 90 wt% decomposition with increasing LDPE content and the thermal stability improved by more than 55 ◦C (Fig. 6b). This means that LDPE elevates the thermal stability of

Fig. 7. X-ray diffraction patterns of macro-crystalline wax and its blends with LDPE.

macro-crystalline wax/LDPE blends due to its high thermal stability. Whereas, introducing more of the high molecular weight material induces a gradual increase in the temperature at which decomposition starts [16]. For micro-crystalline wax/LDPE blends (group 2), the temperatures of decomposition at 10 and 20 wt% decomposition are slightly increased (about 10 ◦C) with increasing LDPE content from 10 to 30 wt%. Meanwhile at 40, 60, 80 and 90 wt% decomposition, the temperatures of decomposition are moderately increased [\(from](#page-5-0) [1](#page-5-0)9 to 28 ◦C) with increasing LDPE content. Another interesting observation is the presence of a two-stage decomposition process for macro-crystalline wax/LDPE blends (Fig. 4), while its absence for micro-crystalline wax/LDPE blends (Fig. 5), as a result of the worse wax/polymer partial miscibility for the former blends and the better partial miscibility for the latter blends. It can be explained that in the case of macro-crystalline wax/LDPE blends, the crystal phase separation and the possi[ble](#page-3-0) [pres](#page-3-0)ence of free wax chains in the amorphous phase may induce deterioration of the thermal stability of the blends, while some co-crystallization may have been present in the case of micro-crystalline wax/LDPE blends which results in the suppression of the wax vapor pressure [7,16].

3.4. X-ray diffraction

The X-ray diffraction patterns (Figs. 7 and 8) r[epresen](#page-5-0)t the crystalline lattice behavior of both macro- and micro-crystalline waxes and their blends with LDPE, respectively. It can be observed that macro-crystalline wax is more crystalline than micro-crystalline

Fig. 6. Temperatures of 10, 20 and 40 wt% (a) and 60, 80 and 90 wt% decomposition (b) of blend groups 1 and 2, respectively as a function of LDPE content in the blends.

Fig. 8. X-ray diffraction patterns of micro-crystalline wax and its blends with LDPE.

Table 3 Properties of macro- and micro-crystalline waxes and their blends with LDPE.

Sample	Congealing point $(°C)$	Needle penetration at 25° C				
Macro-crystalline wax/LDPE (Blend group 1)						
100/0	75.5	18				
90/10 (Blend a)	79	17				
85/15 (Blend b)	80.5	15				
80/20 (Blend c)	82.5	14				
75/25 (Blend d)	84	12				
70/30 (Blend e)	86	9				
Micro-crystalline wax/LDPE (Blend group 2)						
100/0	86.5	7				
90/10 (Blend f)	89	7				
$85/15$ (Blend g)	90	6				
80/20 (Blend h)	91.5	4				
75/25 (Blend i)	92.5	3				
70/30 (Blend k)	93.5	3				

wax as a result of the presence of excess sharp peak at 2 θ \sim 36.07 $^{\circ}$ besides the two well crystalline defined peaks of high intensity observed at 2 θ ~21.58° and 23.96°. This is due to the high amount of crystalline material in macro-crystalline wax which is confirmed with its high degree of crystallinity (above 80%). While micro-crystalline wax have a considerable quantity of amorphous material which probably consists of the non-normal hydrocarbons together with an amount of lower melting point n-paraffin [17,18]. Blending of macro-crystalline wax with 10 wt% LDPE decreases its crystallinity from 83 to 70% which is in line with the disappearance of the sharp peak which was seen in the pure wax at 2θ \sim 36.07°. Another increase of LDPE content leads to somewhat decrease in the crystallinity of macro-crystalline wax/LDPE blends (from 70 to 65%) and this is revealed from the decrease in the intensity of the two peaks of the blends which seen at 2 θ \sim 21.58 $^{\circ}$ and 23.96° (Table 2 and Fig. 7). While blending of micro-crystalline wax with 10 wt% LDPE decreases its crystallinity only from 63 to 62% and the crystallinity nearly unchanged when the LDPE content increases from 10 to 30 wt% (Table 2 and Fig. 8). This means that the crystallinity of macro-crystalline wax is highly affected [by](#page-3-0) [ble](#page-3-0)ndi[ng](#page-4-0) [with](#page-4-0) LDPE than micro-crystalline wax. Data of degree of crystallinity calculated from X-ray diffraction analysis are parallel with the total enthalpy data determined from DSC analysis, whereas they behave [nearly](#page-3-0) [the](#page-3-0) sa[me](#page-4-0) [tre](#page-4-0)nd on increasing LDPE content (Table 2).

3.5. Effect of crystallinity on the properties of wax/polymer blends

The congealing point and needle penetration of both macro[and](#page-3-0) [mi](#page-3-0)cro-crystalline waxes and their blends with LDPE are represented in Table 3. Data indicate that as LDPE content increases, the congealing point of the blends increases and consequently the needle penetration decreases, i.e., the hardness increases. Really, as the hardness (which measured by needle penetration) is increased, the crystallinity of the blends is decreased with increasing LDPE content. Comparing between macro- and micro-crystalline waxes/LDPE blends, data observed that macrocrystalline wax/LDPE blends have lower congealing points and higher needle penetration than micro-crystalline wax/LDPE blends. This is due to that, macro-crystalline wax of low molecular weight are more crystalline and have higher needle penetration values than micro-crystalline wax which have high molecular weight (Tables 1 and 3). Moreover, according to ceresin specifications, the produced wax/polymer blends of micro-crystalline wax with LDPE are considered as high melting point ceresin waxes which can be used in different industrial applications.

[4.](#page-2-0) [Co](#page-2-0)nclusions

The DSC results indicate that both macro- and micro-crystalline waxes are partially miscible with LDPE and the increase of LDPE content to the two waxes decreases the total enthalpy of the blends and consequently decreases their crystallinities.

TGA analysis of these blends confirmed that an increase in LDPE content elevates the thermal stability of the blends. Also, the presence of a two-stage decomposition process for macro-crystalline wax/LDPE blends, while its absence for micro-crystalline wax/LDPE blends.

X-ray diffraction analysis revealed that blending of LDPE to the two waxes leads to somewhat decrease in the crystallinity of macro-crystalline wax/LDPE blends and negligible change in that of micro-crystalline wax/LDPE blends.

Moreover, the resulting data indicate that, blending of polymer with high melting point micro-crystalline wax elevates its melting point to reach the limits of high melting point ceresin waxes which can be used in different industrial applications.

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