

Thermal and Mechanical Properties of Linear Low-Density Polyethylene/Low-Density Polyethylene/Wax Ternary Blends

A. S. Luyt, M. J. Hato

Department of Chemistry, University of the Free State (Qwaqwa Campus), Private Bag X13, Phuthdithaba, 9866, South Africa

Received 26 April 2004; accepted 4 August 2004

Published online in Wiley InterScience (www.interscience.wiley.com).

DOI 10.1002/app.21642

ABSTRACT: The thermal and mechanical properties of uncrosslinked three-component blends of linear low-density polyethylene (LLDPE), low-density polyethylene (LDPE), and a hard, paraffinic Fischer–Tropsch wax were investigated. A decrease in the total crystallinity with an increase in both LDPE and wax contents was observed. It was also observed that experimental enthalpy values of LLDPE in the blends were generally higher than the theoretically expected values, whereas in the case of LDPE the theoretically expected values were higher than the experimental values. In the presence of higher wax content there was a good correlation between experimental and theoretically expected enthalpy values. The DSC results showed changes in peak temperature of melting, as well as peak width, with chang-

ing blend composition. Most of these changes are explained in terms of the preferred cocrystallization of wax with LLDPE. Young's modulus, yield stress, and stress at break decreased with increasing LDPE content, whereas elongation at yield increased. This is in line with the decreasing crystallinity and increasing amorphous content expected with increasing LDPE content. Deviations from this behavior for samples containing 10% wax and relatively low LDPE contents are explained in terms of lower tie chain fractions. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1748–1755, 2005

Key words: polyethylene (PE); wax; blends; thermal properties; mechanical properties

INTRODUCTION

A substantial amount of research has been done on polyethylene (PE)/PE blends. Most of the research concentrated on the morphology of the blends and the possible cocrystallization of the blend components. A variety of reports indicate that miscibility of PE blend components is strongly dependent on molecular weight and branch content. It was found¹ that binary blends of the lowest and highest branch content fractions appeared to be immiscible. Stephens et al.² found that homogeneous ethylene–octene copolymers (EO) with low comonomer content were completely miscible with high-density polyethylene (HDPE), whereas copolymers with higher comonomer contents provided a composition window of partial miscibility that revealed the effects of temperature and constituent molecular weight. They also found that low molecular weight tails of HDPE readily dissolve in EO when EO was the minor constituent, but that there was a persistence of the HDPE-rich phase to higher temperatures when HDPE was the minor constituent. It was also found that low molecular weight material crys-

tallizes at low temperatures in subsidiary lamellae located between the dominant lamellae and in the spherulite boundaries, and that the segregation of low molecular weight material has a major effect on the weakest-link properties of linear polyethylene.^{3–6}

Rego Lopez et al.⁷ found, for blends containing high and low molecular weight components, that at high temperatures crystallization is confined to the high molecular weight component, and that the low molecular weight component is almost completely prohibited from entering the crystal phase. At intermediate temperatures both components crystallize separately into dominant lamellae and subsidiary lamellae sandwiched between the dominant lamellae. At low temperatures there was partial cocrystallization of the components. This is supported by Norton and Keller,⁸ who reported that the linear PE fraction crystallizes into regular shaped sheets, whereas the branched PE crystallizes during the subsequent cooling phase to form finer, S-shaped lamellae. Edwards⁹ and Hu et al.¹⁰ presented data indicating cocrystallization between linear and ethyl-branched PE. Conde Brana et al.¹¹ found direct evidence for cocrystallization of binary mixtures of low molecular weight linear PE and branched PE, whereas pure branched PE samples showed lower crystallinity compared with that of the binary mixtures.

Correspondence to: A. S. Luyt (luytas@qwa.uovs.ac.za).

Lee et al.¹² showed that LLDPE is miscible with LDPE in the amorphous region. However, they showed that the two polymers exclude one another during crystallization. Yamaguchi and Abe¹³ found that LLDPE is miscible with LDPE in the molten state, and that LDPE acts as a nucleating agent for the crystallization of LLDPE. Blending a small amount of LDPE into LLDPE therefore enhances the degree of crystallinity, melting temperature, and hardness. The yield stress increases and the ultimate stress decreases with an increase in LDPE content. The same authors¹⁴ investigated the viscoelastic properties of these blends. Their results indicated a well-organized crystalline structure and a depression of the mobility of crystalline fragments.

Huang and Brown¹⁵ extensively studied the influence of branch density in LLDPE on lamellar thickness and tie molecule fraction. They assumed that, if the end-to-end distance of a molecule in the melt is equal to or greater than the distance between adjoining lamellar crystals, then a tie molecule will probably form. If not, a tie molecule will never form. They concluded that the primary morphological effect of the branches is to reduce the thickness of the lamellar crystal, and that the reduction in lamellar thickness produces more tie molecules. These conclusions are important for our system, given that the presence of wax will decrease the fraction of tie molecules and this will lead to changes in the tensile properties.

The use of wax-based processing agents is a well-known practice in the polyolefin industry. There is, however, very little published on the influence of wax on the thermal and mechanical properties of polyolefin/wax blends, except for a number of studies published by one group.^{16–22} For mechanically mixed, uncrosslinked LLDPE/wax blends, where a hard paraffinic Fischer–Tropsch wax was used, it was found that wax was completely miscible with LLDPE, and that the presence of up to 40 wt % wax had no influence on the DSC onset and peak temperatures of melting of the blends compared to that of neat LLDPE.¹⁶ It was further found that the presence of wax increased Young's modulus, but decreased stress and strain at yield, as well as stress and strain at break.¹⁷ Extruded, uncrosslinked LLDPE/wax blends, on the other hand, showed miscibility only up to 20% wax content.¹⁸ This was reflected in the mechanical properties where samples containing higher wax contents showed brittle rupture. Change in material strength with increasing wax content is explained in terms of a reduced number of tie molecules in the presence of wax.¹⁹

In this article we describe the influence of the presence of small amounts of wax in LLDPE/LDPE blends on their thermal and mechanical properties.

TABLE I
List of Samples Used in the Present Study

LLDPE/LDPE/wax (w/w/w)	LLDPE/LDPE/wax (w/w/w)
100/0/0	20/70/10
0/100/0	85/10/5
0/0/100	75/20/5
90/10/0	65/30/5
80/10/10	55/40/5
70/20/10	40/55/5

EXPERIMENTAL

Materials

A hard Fischer–Tropsch wax, supplied by Sasol Wax GmbH (Hamburg, Germany), was used. It has an average molecular weight (MW) of 800 g mol⁻¹, a melting point of 90°C, a density of 0.94 g cm⁻³ at 25°C, solidification points of 96 to 100°C, and a drop point of 105–108°C. It decomposes at 250°C and is chemically inert. LLDPE, supplied in powder form by Sasol Polymers, (division of Sasol Chemical Industries, Johannesburg, South Africa), was used. It has a melt flow index (MFI) of about 3.5 g/10 min, a MW of 191,600 g mol⁻¹, a melting point of 126°C, a density of 0.94 g cm⁻³, and a particle size of 90% less than 600 μm. LDPE, also supplied by Sasol Polymers, had an MFI of 20 g/10 min, melting point of 103°C, a MW of 96,000 g mol⁻¹, a density of 0.93 g cm⁻³, and a particle size of 90% less than 850 μm.

Preparation of blends

Powdered samples of LLDPE, LDPE, and wax were mixed in a coffee mill to form a homogeneous mixture. The compositions of the blends are summarized in Table I. Samples (20 g) were melt-pressed into 10.3 × 0.3 × 0.08-cm plates at 180°C for 5 min in a hot-melt press, after which they were left at room temperature to solidify.

Analyses

DSC analyses were conducted in a Perkin-Elmer (Norwalk, CT) DSC7 thermal analyzer under flowing nitrogen atmosphere. The instrument was calibrated using the onset temperatures of melting of indium and zinc standards, as well as the melting enthalpy of indium. Samples of 5–10 mg were put in aluminium pans and heated from 25 to 160°C at a rate of 10°C min⁻¹, kept at this temperature for 1 min, and cooled at the same rate to 25°C. This was done to remove the thermal history of the materials. For the second scan, the samples were heated and cooled under the same conditions. Onset and peak temperatures of melting,

TABLE II
Melting Enthalpies and Crystallinities of Investigated Samples^a

LLDPE/LDPE/wax (w/w/w)	$\Delta H_{m,LDPE}$ (exp.) (J g ⁻¹)	$\Delta H_{m,LDPE}$ (theor.) (J g ⁻¹)	$\Delta H_{m,LLDPE}$ (exp.) (J g ⁻¹)	$\Delta H_{m,LLDPE}$ (theor.) (J g ⁻¹)	$\Delta H_{m,tot}$ (exp.) (J g ⁻¹)	$X_{c,tot}$ (exp.) (%)
100/0/0	—	—	105.2	105.2	105.2	36.5
0/100/0	50.7	50.7	—	—	50.7	17.7
90/10/0	—	5.1	87.9	94.7	87.9	30.7
85/10/5	—	5.1	98.4	89.4	98.4	34.2
75/20/5	2.6	10.1	94.4	78.9	97.0	33.8
65/30/5	9.1	15.2	81.7	68.4	90.8	31.7
55/40/5	18.9	20.3	65.8	57.9	84.7	29.1
40/55/5	11.8	27.9	79.6	42.1	91.4	31.7
30/65/5	32.8	33.0	21.5	31.6	54.3	18.8
20/75/5	33.8	38.0	23.9	21.0	57.7	20.7
80/10/10	—	5.1	96.0	84.2	96.0	33.7
70/20/10	5.1	10.1	83.2	73.6	88.3	30.8
60/30/10	13.7	15.2	61.1	63.1	74.8	25.8
50/40/10	12.8	20.3	47.7	52.6	60.5	21.7
40/50/10	22.1	25.4	40.5	42.1	62.6	21.7
30/60/10	35.4	30.5	27.9	31.6	75.9	26.8
20/70/10	38.4	35.5	18.8	21.0	57.2	19.8

^a Parameters: $\Delta H_{m,LLDPE}$ (exp.), experimentally measured melting enthalpy of LLDPE in the blend; $\Delta H_{m,LDPE}$ (theor.), theoretically calculated melting enthalpy of LDPE in the blend, based on the measured enthalpy of neat LDPE and the fraction of LDPE in the blend; $\Delta H_{m,LLDPE}$ (exp.), experimentally measured melting enthalpy of LLDPE in the blend; $\Delta H_{m,LLDPE}$ (theor.), theoretically calculated melting enthalpy of LLDPE in the blend, based on the measured enthalpy of neat LLDPE and the fraction of LLDPE in the blend.

as well as melting enthalpies, were determined from the second scan.

A Hounsfield H5KS tensile tester (Tinius Olsen Ltd., Survey, UK) was used for tensile analysis of the samples. The dumbbell samples were stretched at a speed of 50 mm min⁻¹. The thickness of each sample was about 1.00 mm, width 4.7 mm, and length 75 mm. The final mechanical properties were evaluated from at least five different measurements.

RESULTS AND DISCUSSION

Degree of crystallinity

The degree of crystallinity of LLDPE/LDPE/wax blends was estimated using the following equation:

$$X_c = \Delta H_m / \Delta H_m^* \times 100 \quad (1)$$

where ΔH_m is the melting enthalpy, X_c is the degree of crystallinity, and $\Delta H_m^* = 288 \text{ J g}^{-1}$ was used as the melting enthalpy of 100% crystalline PE. It was assumed that the wax has a structure similar to that of PE, and therefore no distinction was made between wax and PE in the calculation of crystallinities. The estimated values are shown in Table II.

It can be seen that the total crystallinity decreases with an increase in LDPE content (Fig. 1). LDPE is more branched than LLDPE and, because branching acts as a system of defects that reduce crystallinity, preventing the lamellae from packing together regu-

larly and closely, the presence of branches interferes with the ability of the polymer to crystallize. Therefore the presence of a higher number of branched PE will prevent crystal growth, which has an influence on the total degree of crystallinity. It can also be seen that the experimental enthalpy values of LLDPE in the blends are generally higher than the theoretically expected values. This behavior is probably a consequence of cocrystallization of LLDPE with both LDPE branches and short wax chains. In the presence of higher wax contents, however, there is a good correlation between

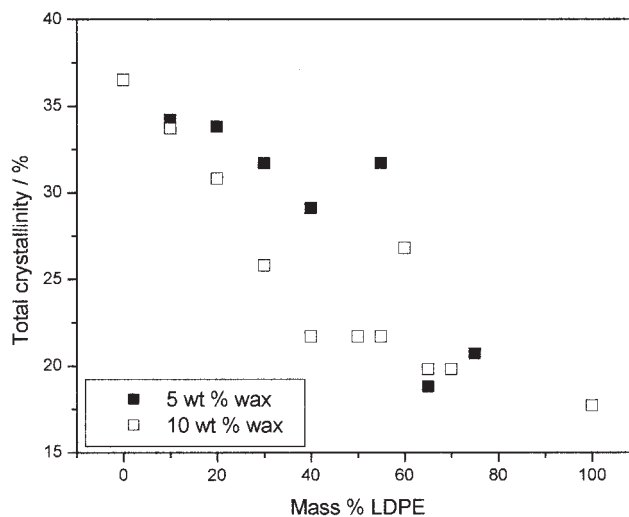


Figure 1 Total crystallinity as a function of LDPE content.

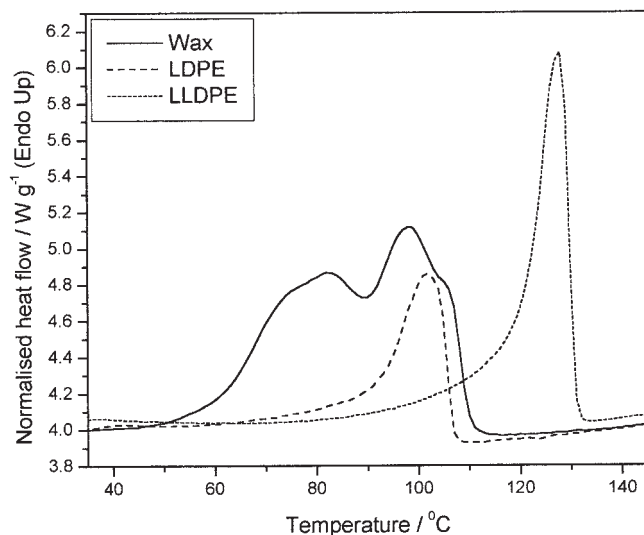


Figure 2 DSC reheating curves for pure wax, LDPE, and LLDPE.

experimental and theoretically expected enthalpy values.

The experimental enthalpies of LDPE in the blends are generally lower than the theoretically expected values, as can be seen in Table II. This may also be explained by the cocrystallization of LLDPE chains and LDPE branches, which leaves fewer LDPE chains to crystallize. The higher LDPE melting enthalpy values for blends with higher LDPE and wax contents also indicate that wax may preferably cocrystallize with LLDPE, replacing LDPE chains in LLDPE lamellae. The preferential cocrystallization of wax with LLDPE has been confirmed in CRYSTAF crystallization experiments.²³ It is not yet clear why wax would preferentially cocrystallize with LLDPE. One possible explanation is that LLDPE has a higher crystallinity than that of LDPE and, because the wax is highly crystalline, it is thermodynamically easier for the wax to preferentially cocrystallize with LLDPE.

Total crystallinity also decreases with an increase in wax content, although it is still higher than that in the absence of wax. Krupa and Luyt^{17,18,20} found that wax seems to be more miscible with LLDPE than with LDPE. This supports the above conclusion that wax may preferably cocrystallize with LLDPE. We are, however, not certain why a higher wax content would give rise to lower crystallinity.

The DSC curves of pure LLDPE, LDPE, and wax are shown in Figure 2. Both LLDPE and LDPE show only one thermal event, whereas wax melts over a broad temperature range and shows a triple endothermic peak. The DSC curves of the ternary blends are shown in Figures 3 and 4, the results are summarized in Table III, and the trends are illustrated in Figures 5–7. It can be seen that all the DSC curves show two endothermic

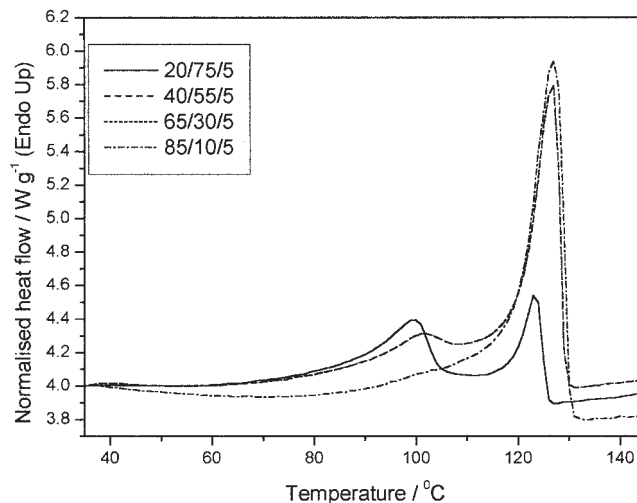


Figure 3 DSC reheating curves for LLDPE/LDPE/wax blends ($x/y/z$ depicts w/w/w LLDPE/LDPE/wax).

peaks, with no indication of the wax melting peak attributed to incorporation of wax into the crystal lamellae of LLDPE and/or LDPE. The peak width ($T_{p,m} - T_{o,m}$) increases for both LLDPE and LDPE peaks as a function of an increase in their respective contents. This behavior indicates the formation of less-perfect crystals. Wax content does not seem to have much influence on the observed peak broadening. The peak temperature of melting values for the LLDPE peak generally increases in the presence of 5 and 10% wax with an increase in LLDPE content (Fig. 6). This indicates the formation of thicker LLDPE lamellae in the blend, whereas the wax content does not seem to have any influence on the lamellar thickness. In the case of the LDPE peak, the $T_{p,m}$ values show a slight

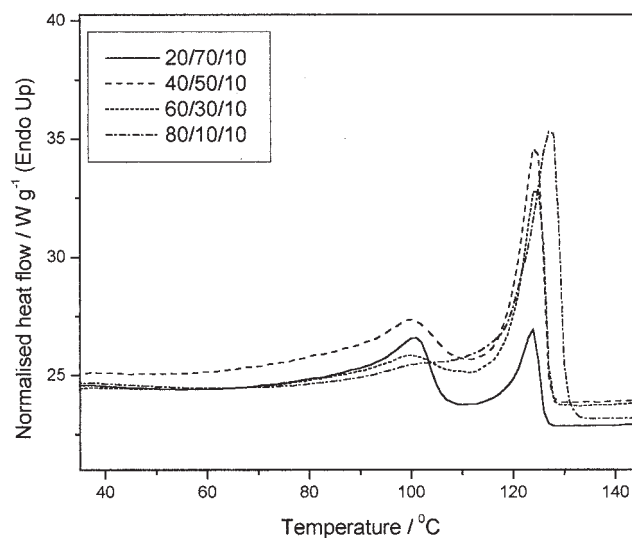


Figure 4 DSC reheating curves for LLDPE/LDPE/wax blends ($x/y/z$ depicts w/w/w LLDPE/LDPE/wax).

TABLE III
Summary of DSC Data for Uncrosslinked LLDPE/LDPE/Wax Blends^a

LLDPE/LDPE/wax (w/w/w)	$T_{o,m}$ (°C)	$T_{p,m} = T_m$ (°C)	ΔH_m (J g ⁻¹)	$T_{p,c}$ (°C)	$T_{o,c} = T_c$ (°C)	ΔH_c (J g ⁻¹)
100/0/0	120.5	126.4	105.2	108.5	111.0	-113.9
0/100/0	104.7	111.5	50.7	95.0	99.7	-75.6
0/0/100	60.8	77.2	195.3	92.6	96.1	-186.0
90/10/0	119.5	129.5	87.9	107.1	110.7	-101.0
80/10/10	119.8	127.7	96.0	106.5	109.8	-93.5
70/20/10	120.1	126.4	83.2	106.8	109.9	-72.9
	92.6	100.7	5.1	85.8	93.2	-1.5
60/30/10	119.1	124.5	61.1	106.5	109.8	-80.1
	90.4	99.5	13.7			
50/40/10	119.3	126.2	47.7	106.6	109.4	-73.7
	89.5	101.4	12.8			
40/50/10	118.9	124.2	40.5	107.3	109.6	-45.2
	88.1	100.0	22.1	87.6	96.4	-14.4
30/60/10	119.7	126.7	27.9	104.9	109.5	-32.4
	94.7	100.3	35.4	87.9	92.7	-35.0
20/70/10	118.5	123.8	18.8	106.8	108.9	-17.5
	86.5	100.8	38.4	86.5	93.1	-30.4
85/10/5	120.5	127.7	98.4	109.3	111.9	-105.4
75/20/5	121.5	127.4	94.4	109.1	111.7	-82.7
65/30/5	120.9	126.5	81.7	109.1	111.8	-101.5
	92.4	101.0	9.1			
55/40/5	120.9	127.2	65.8	109.1	111.5	-57.8
	91.0	101.5	18.9	88.1	95.4	-11.4
40/55/5	121.1	127.0	79.6	109.5	111.7	-71.5
	94.7	100.5	11.8	88.0	94.8	-4.0
30/65/5	119.1	123.9	21.5	107.8	109.7	-19.3
	87.3	100.2	32.8	87.0	94.3	-30.8
20/75/5	118.4	123.5	23.9	108.0	109.9	-18.6
	87.8	99.7	33.8	86.9	94.6	-29.8

^a Numbers in italics are for the LDPE peak in the DSC curve. Parameters: $T_{o,m}$, onset temperature of melting; $T_{p,m}$, peak temperature of melting; $T_{o,c}$, onset temperature of crystallization; $T_{p,c}$, peak temperature of crystallization; ΔH_m , melting enthalpy; ΔH_c , crystallization enthalpy.

increase for 5% wax, whereas in the case of 10% wax these values do not change within experimental error. This means that LDPE in the blends does not crystal-

lize into thicker lamellae, probably because the majority of LDPE chains do not cocrystallize with either LLDPE or wax.^{18,20-22}

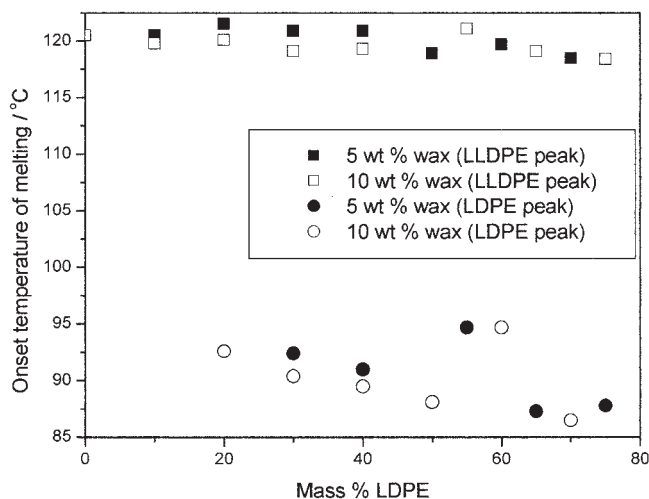


Figure 5 Onset temperature of melting as a function of LDPE content.

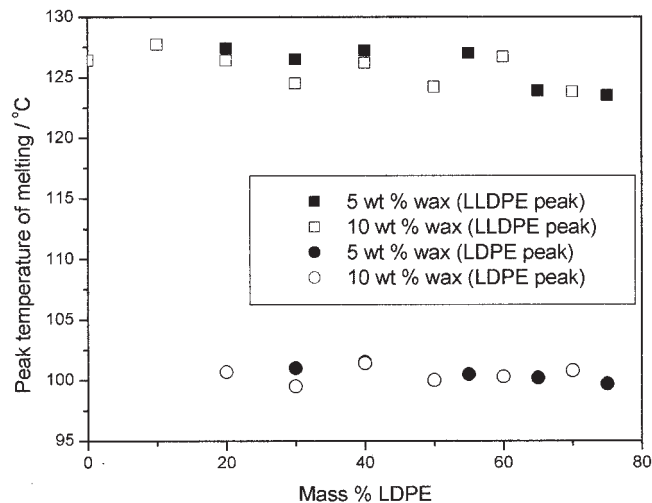


Figure 6 Peak temperature of melting as a function of LDPE content.

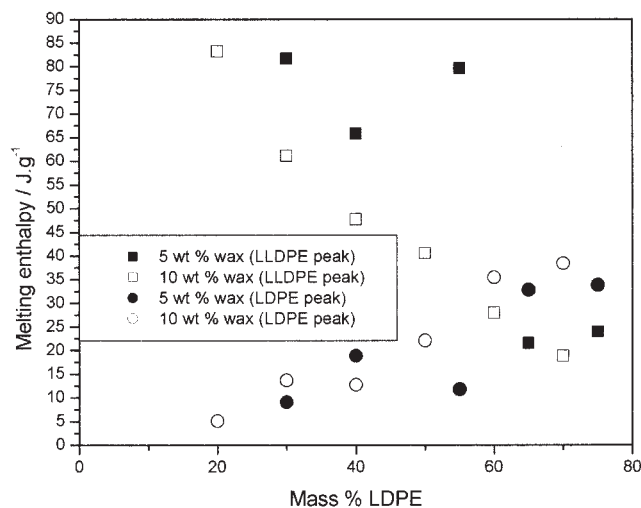


Figure 7 Melting enthalpy as a function of LDPE content.

Mechanical properties

The values of elongation and stress at yield and break, as well as Young's modulus, for all the blends are summarized in Table IV. A typical stress-strain curve of LLDPE/LDPE/wax ternary blends is shown in Figure 8. It can be seen that before break the stress significantly decreases. The stress at break was therefore taken as the maximum stress after yield, as indicated by the arrow.

Young's moduli of the LLDPE/LDPE/wax blends as a function of LDPE content for both 5 and 10% wax content are shown in Figure 9. The figure shows that for both wax concentrations Young's modulus decreases with an increase in LDPE content. A much larger decrease is observed in the presence of 10%

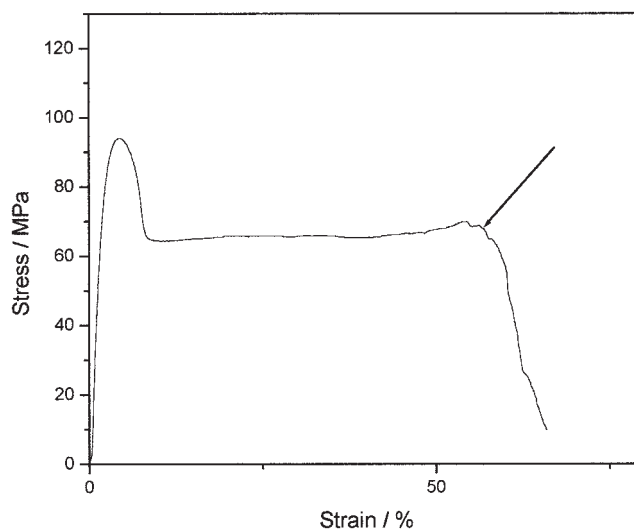


Figure 8 Typical stress-strain curve of LLDPE/LDPE/wax blends.

wax. This is contrary to the decrease in total crystallinity with increasing LDPE content, which shows a similar trend for both wax concentrations (Table II). This substantial influence of wax content on Young's modulus may therefore be related to cocrystallization with LLDPE and the resultant influence on LDPE crystallization.

In Figure 10 the elongation at yield for the LLDPE/LDPE/wax blends is plotted as a function of LDPE content. There is an increase in elongation at yield for both wax concentrations, but the values for 10% wax and low LDPE content are significantly lower than the values for the same samples with 5% wax. A probable reason for the increase in elongation at yield is the

TABLE IV
Mechanical Properties of LLDPE/LDPE/Wax Blends^a

LLDPE/LDPE/wax (w/w/w)	$\varepsilon_y \pm s(\varepsilon_y)$ (%)	$\sigma_y \pm s(\sigma_y)$ (MPa)	$\varepsilon_b \pm s(\varepsilon_b)$ (%)	$\sigma_b \pm s(\sigma_b)$ (MPa)	$E \pm s(E)$ (MPa)
100/0/0	20.2 ± 1.1	15.8 ± 0.5	1104.3 ± 91.3	19.1 ± 0.5	129.1 ± 36.7
0/100/0	81.4 ± 2.5	6.5 ± 0.2	120.5 ± 29.2	5.6 ± 0.9	39.7 ± 6.9
90/10/0	18.5 ± 0.4	14.2 ± 0.3	377.0 ± 226.6	10.8 ± 0.5	126.9 ± 16.0
80/10/10	16.7 ± 0.9	17.1 ± 0.2	73.0 ± 7.2	9.5 ± 1.3	171.4 ± 8.0
70/20/10	17.2 ± 1.0	14.9 ± 0.5	30.7 ± 14.5	8.2 ± 1.0	185.8 ± 2.9
60/30/10	19.9 ± 0.3	12.1 ± 0.4	75.9 ± 6.5	7.8 ± 0.4	151.4 ± 16.2
50/40/10	85.7 ± 2.2	3.6 ± 0.2	656.2 ± 25.2	2.9 ± 0.7	137 ± 1.9
40/50/10	107.9 ± 2.1	2.6 ± 0.2	156.9 ± 43.0	1.2 ± 0.6	102.1 ± 0.9
30/60/10	119.4 ± 5.2	2.4 ± 0.4	263.6 ± 12.4	1.6 ± 0.1	52.8 ± 1.0
85/10/5	63.3 ± 0.6	3.3 ± 0.3	1925.1 ± 74.3	2.6 ± 0.4	177.4 ± 7.4
75/20/5	70.9 ± 1.2	2.8 ± 0.1	610.1 ± 13.6	2.3 ± 0.3	174.5 ± 2.9
65/30/5	86.3 ± 2.1	2.7 ± 0.4	623.7 ± 82.2	2.2 ± 0.2	156.7 ± 3.6
55/40/5	103.1 ± 1.9	2.7 ± 0.3	790.8 ± 151.2	2.0 ± 0.2	145.9 ± 2.3
40/55/5	107.7 ± 1.9	2.4 ± 0.5	1391.0 ± 134.5	2.1 ± 0.1	151.1 ± 5.4
30/65/5	130.2 ± 1.3	1.8 ± 0.1	338.0 ± 92.6	1.6 ± 0.2	134.5 ± 3.9
20/75/5	138.1 ± 2.7	1.7 ± 0.6	285.7 ± 49.9	1.4 ± 0.9	145.2 ± 2.7

^a Parameters: E , modulus; ε_y , elongation at yield; σ_y , stress at yield; ε_b , elongation at break; σ_b , stress at break; s , standard deviation of each parameter.

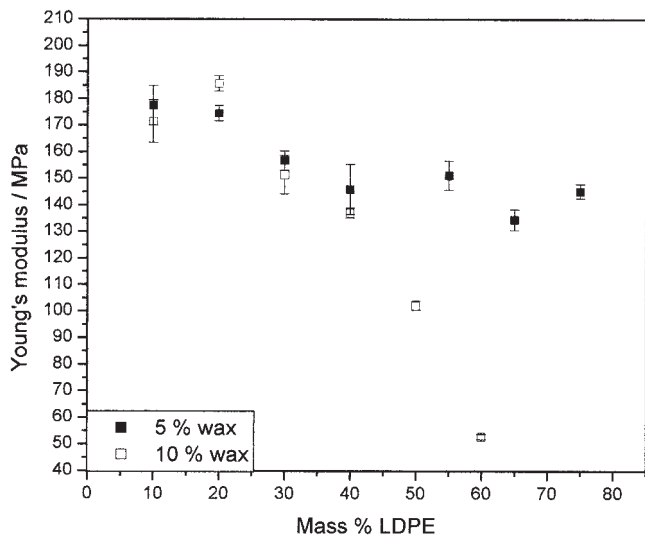


Figure 9 Young's modulus as a function of LDPE content.

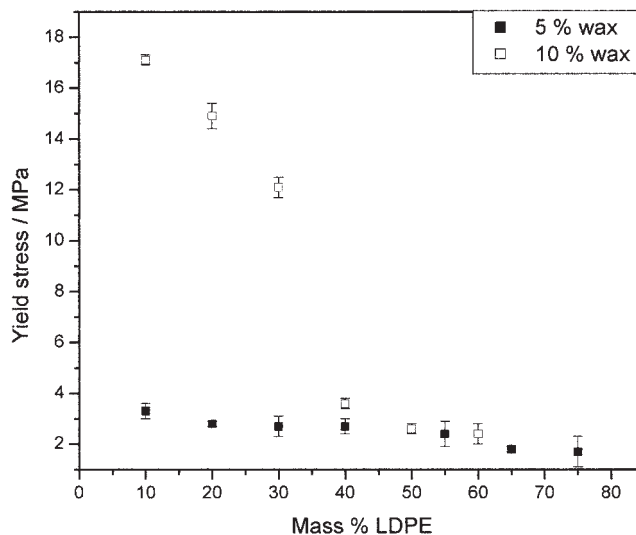


Figure 11 Yield stress as a function of LDPE content.

increasing amorphous content in the samples with increasing LDPE content. Elongation at yield is the onset of strain value at which plastic deformation of the material takes place (i.e., the material starts to flow). Given that, before the macroscopic yield point, there are structural rearrangements of the amorphous fraction induced by the applied stress, it is obvious that increasing the amorphous fraction will increase the strain at which plastic deformation starts. The reason that high wax content gives a much lower elongation at yield value for low LDPE contents is probably related to the decrease in tie-chain fraction in the samples because of the higher number of short wax chains that do not contribute to tie-chain formation in LLDPE.¹⁵ This gives a more brittle polymer with lower elongation at yield.

Yield stress as a function of LDPE content in the blends is shown in Figure 11. It can be seen that these values decrease with an increase in LDPE content for both wax concentrations, but the values are appreciably higher in the case of 10% wax and low LDPE content. Because yield stress is a function of crystallinity, a decrease with an increase in LDPE content is expected. The appreciably higher yield stress values in the samples with high wax content and relatively low LDPE content are also related to the lower tie-chain fraction that gives rise to more brittle samples.

Stress at break as a function of LDPE content of the blends is shown in Figure 12. The stress at break values decrease with an increase in LDPE content. The same trends are observed as those in the case of yield stress, and they can be explained in a similar way.

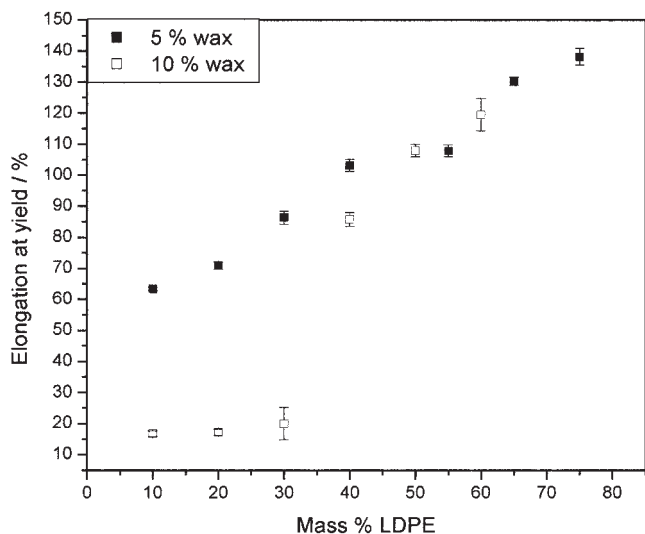


Figure 10 Elongation at yield as a function of LDPE content.

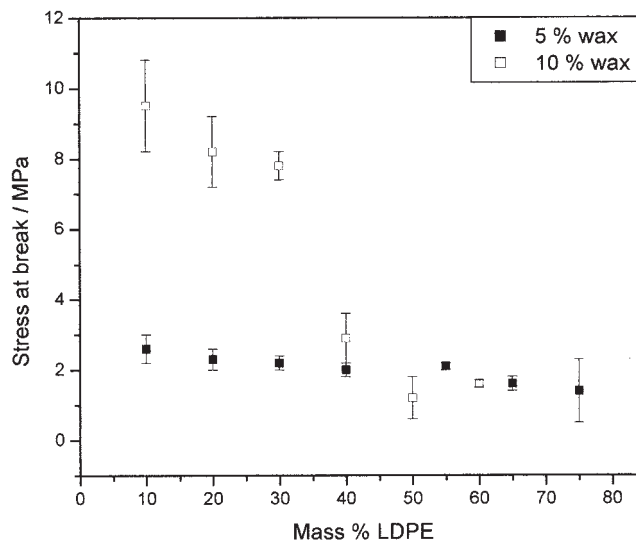


Figure 12 Stress at break as a function of LDPE content.

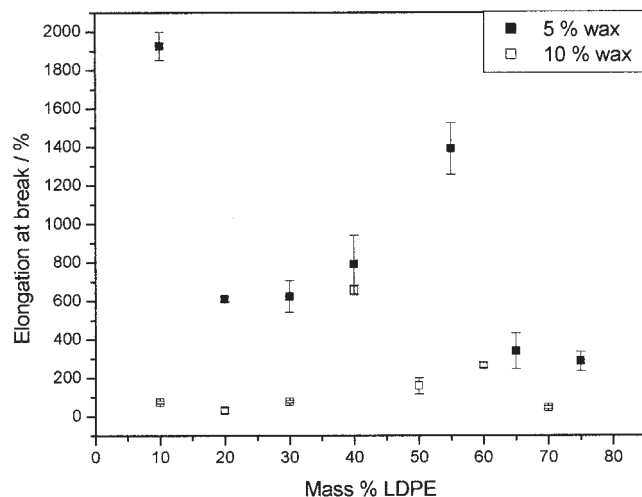


Figure 13 Elongation at break as a function of LDPE content.

Strain-softening before break is, however, observed for the samples with higher wax and relatively low LDPE contents. This is because blending wax depresses strain-hardening before break, in that wax inhibits a high degree of orientation, leading to recrystallization. Figure 13 depicts the elongation at break as a function of LDPE content. It can be seen that the values are too scattered to draw any conclusions.

CONCLUSIONS

1. The presence of wax in LLDPE/LDPE blends causes some very interesting changes in the thermal properties of the blends. Most of these observations can be explained only by accepting that wax preferably cocrystallizes with LLDPE. This preferred cocrystallization was observed and discussed in previous work.

2. At lower wax content the tensile properties change with increasing LDPE content, as one would expect, and the changes are related to the decreasing crystallinity with increasing LDPE content. However, the values for 10% wax and relatively low LDPE contents are out of line with the rest of the results. These deviations from the expected trends were explained in terms of lower tie-chain fractions, giving rise to more brittle samples.

References

1. Defoor, F.; Groeninckx, G.; Reynaers, H.; Schouterden, P. Van der Heijden, B. *J Appl Polym Sci* 1993, 47, 1839.
2. Stephens, C. H.; Hiltner, A.; Baer, E. *Macromolecules* 2003, 36, 2733.
3. Gedde, U. W.; Jansson, J.-F. *Polymer* 1984, 25, 1263.
4. Phillips, P. J.; Patel, J. *Polym Eng Sci* 1979, 18, 943.
5. Gedde, U. W.; Jansson, J.-F. *Polymer* 1985, 26, 1469.
6. Gedde, U. W.; Eklund, S.; Jansson, J.-F. *Polym Bull* 1982, 9, 90.
7. Rego Lopez, J. M.; Conde Brana, M. T.; Terselius, B.; Gedde, U. W. *Polymer* 1988, 29, 1045.
8. Norton, D. R.; Keller, A. *J Mater Sci* 1984, 19, 447.
9. Edwards, G. H. *Br Polym J* 1986, 18, 88.
10. Hu, S.-R.; Kyu, T.; Stein, R. S. *J Polym Sci Polym Phys Ed* 1987, 25, 71.
11. Conde Brana, M. T.; Iragorri Sainz, J. I.; Terselius, B.; Gedde, U. W. *Polymer* 1989, 30, 410.
12. Lee, H.; Cho, K.; Ahn, T.; Choe, S.; Kim, I.; Park, I.; Lee, B. H. *J Polym Sci Polym Phys Ed* 1997, 35, 1633.
13. Yamaguchi, M.; Abe, S. *J Appl Polym Sci* 1999, 74, 3153.
14. Yamaguchi, M.; Abe, S. *J Appl Polym Sci* 1999, 74, 3160.
15. Huang, Y.-L.; Brown, N. *J Polym Sci Part B: Polym Phys* 1991, 29, 129.
16. Krupa, I.; Luyt, A. S. *Polym Degrad Stab* 2000, 70, 111.
17. Krupa, I.; Luyt, A. S. *J Appl Polym Sci* 2001, 81, 973.
18. Krupa, I.; Luyt, A. S. *Polym Degrad Stab* 2001, 73, 157.
19. Hlangothi, S. P.; Krupa, I.; Djokovic, V.; Luyt, A. S. *Polym Degrad Stab* 2003, 79, 53.
20. Krupa, I.; Luyt, A. S. *Polymer* 2001, 42, 7285.
21. Mtshali, T. N.; Luyt, A. S.; Krupa, I. *Thermochim Acta* 2001, 380, 47.
22. Djokovic, V.; Mtshali, T. N.; Luyt, A. S. *Polym Int* 2003, 52, 999.
23. Luyt, A. S.; Brüll, R. *Polym Bull*, to appear.