

Binary Mixtures of Polyethylene and Oxidized Wax: Dependency of Thermal and Mechanical Properties upon Mixing Procedure

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ABSTRACT: The influence of the preparation procedure on the thermal and mechanical properties of linear low-density polyethylene (LLDPE)- and LDPE-oxidized wax blends was investigated. It was found that mechanically mixed blends show reduced thermal stability as well as ultimate mechanical properties (stress and strain at break) compared to that of extrusion mixed blends. However, the structure of the blend and consequently its thermal and mechanical behavior also depend on the initial morphology of polyethylene. DSC measurements show miscibility up to high wax contents in both blend types, but increasing the amount of wax in LDPE blends induces increasing crystallinity. As a result, the LDPE/wax blends show improved

thermal stability of between 20 and 50°C at low wax concentrations. Although the elasticity modulus of the blends increases, increasing the amount of wax generally degrades the mechanical properties. The main reason for this is the reduced number of tie chains. Changes in the average concentration of tie chains with increasing wax content were calculated and a correlation was made with the ultimate properties of the blends. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2446–2456, 2003

Key words: blends; differential scanning calorimetry (DSC); mechanical properties; polyethylene (PE); thermogravimetric analysis (TGA)

INTRODUCTION

Miscible polymer blends have recently seen a tremendous surge in industrial applications¹ because they offer an economic alternative to the development of new polymeric materials. Miscibility of the polymer components, in fact, enables one to tailor material properties by changing the blend composition. It is therefore important to understand how preparation conditions affect the final properties of the blends.

In previous studies^{2–5} we investigated the blends of polyethylene (PE) and Fischer–Tropsch wax. It was found that they are miscible with each other up to high wax concentrations. Wax also induces an increase in crystallinity, which consequently improves some of the mechanical properties such as elastic modulus or stress at yield. Although the results from the mentioned studies are more or less compatible, it was observed that the type of mixing (mechanical or extrusion) of wax and PE can influence the morphology and the deformation behavior of the blends. However, the fact that we used different types of waxes as well as different types of polyethylenes enabled us to draw a definite conclusion about the effect of blend prepara-

tion on its properties. Therefore, in the present study, this aspect will be more carefully considered.

The other aim of this study was to establish the reason for the detrimental effects of wax on the ultimate mechanical properties of the blends, especially at high wax contents. It is well known that the strength of a semicrystalline polymer depends on the concentration of tie chains.⁶ Because it was observed that the strength of blends decreases with increasing wax content, this implied that tie chain concentration must be somehow affected by blending. To prove this assumption, we estimated the average tie chain concentration in the blends by using a method formerly proposed by Gedde et al.⁷ in the case of blends of high and low molecular weight polyethylene. The results show that this approach offers a possible explanation of the influence of the wax content on the ultimate properties.

EXPERIMENTAL

Materials

An oxidized, hard Fischer–Tropsch wax (average molar mass $M_w = 750 \text{ g mol}^{-1}$, density 0.95 g cm^{-3}), supplied by Schumann-Sasol, was used. Linear low-density polyethylene (LLDPE, $M_w = 192,000 \text{ g mol}^{-1}$, $\rho = 0.938 \text{ g cm}^{-3}$) and low-density polyethylene (LDPE, $M_w = 96,000 \text{ g mol}^{-1}$, $\rho = 0.925 \text{ g cm}^{-3}$) were supplied by Sasol Polymers. The diameter of approx-

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imately 90% of the polymer particles was less than 600 μm .

Preparation of blends

Mechanically mixed samples

LLDPE and LDPE powders were mechanically mixed (using a coffee mill) in different ratios with powdered oxidized wax (5, 10, 20, 30, 40, and 50 wt %). The mixtures were then melt pressed at 160°C for 5 min.

Extrusion mixed samples

LLDPE and LDPE were blended in different ratios with powdered oxidized wax (5, 10, 20, 30, 40, and 50 wt %), in an industrial extruder (Brabender film blower at 1000 rpm) at 180°C. The samples were then hot melt pressed at 160°C for 5 min.

It should be noted that the pure polyethylenes were treated in the same way as the blends.

Methods

Differential scanning calorimetry (DSC) analyses were carried out on a Perkin–Elmer DSC-7 thermal analyzer (Perkin Elmer Cetus Instruments, Norwalk, CT) 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. The samples (5–10 mg) were heated in the first scan from 25 to 160°C at a rate of 20°C min⁻¹, kept at 160°C for 1 min, and cooled at the same rate to 25°C, to remove the thermal history of the material. For the second scan, the same samples were heated from 25 to 160°C at a rate of 10°C min⁻¹, kept for 1 min at 160°C, and then cooled at the same rate. The melting temperatures and the enthalpies of melting were determined from the second scan. Mass crystallinity was calculated according to

$$w_c = \frac{\Delta H_m}{\Delta H_m^0} \quad (1)$$

where ΔH_m is the melting enthalpy obtained from the DSC melting endotherms and $\Delta H_m^0 = 293 \text{ J g}^{-1}$ is the melting enthalpy of 100% crystalline polyethylene. Crystal thickness is obtained from the Thomson–Gibbs equation,⁸ as follows:

$$L_c = \frac{2\sigma T_m^0}{(T_m^0 - T_m)\Delta H_m^0 \rho_c} \quad (2)$$

where $\Delta H_m^0 = 293 \text{ J g}^{-1}$ is the melting enthalpy of 100% crystalline polyethylene at the equilibrium melting point $T_m^0 = 418.5 \text{ K}$, $\sigma = 93 \text{ mJ m}^{-2}$ is the fold surface free energy, and $\rho_c = 1 \text{ g cm}^{-3}$ is the crystal phase density. The long period is given by⁶:

$$L = \frac{L_c \left[w_c + \left(\frac{\rho_c}{\rho_a} \right) (1 - w_c) \right]}{w_c} \quad (3)$$

where $\rho_a = 0.855 \text{ g cm}^{-3}$ is the density of the amorphous phase of PE and w_c is the mass crystallinity.

Thermogravimetric (TGA) analyses were carried out on a Perkin–Elmer TGA7 thermal analyzer. Samples of 5–10 mg were heated under nitrogen atmosphere from 25 to 600°C at a heating rate of 10°C min⁻¹.

A basic tensile tester (Hounsfield W5K) was used for the mechanical measurements. The dumbbell samples with a 40 mm gauge length were stretched at a speed of 50 mm min⁻¹. The final mechanical properties were evaluated from at least five different measurements.

RESULTS AND DISCUSSION

Thermal properties

Figures 1 and 2 show the DSC melting endotherms of mechanically mixed LLDPE–wax and LDPE–wax blends, respectively. It can be seen that the melting curves of the blends show behavior similar to that of pure polyethylenes (PEs). Wax, however, melts over quite a broad temperature interval. Similarity between the melting curves of polyethylene and the blends suggests miscibility of the components. However, the appearance of a small, low-temperature peak in the case of higher wax contents shows the presence of partial segregation. It should be noted that the melting endotherms of the extrusion mixed LLDPE–wax blends are similar to those of the mechanically mixed samples. Figures 3 and 4 respectively, show the melting temperatures and the melting enthalpies as a function of wax content in the blend. The dependency of melting temperatures on wax content for both PEs is almost the same, and is obviously not affected by the type of mixing. Although changes are not significant, melting temperatures gradually decrease with increasing wax content.

Melting enthalpies, on the other hand, do depend on the preparation conditions as well as on the type of polyethylene, that is, molecular weight and the degree of branching. Although the melting enthalpies of the mechanically mixed LLDPE–wax samples remain unchanged, the melting enthalpies of the extruded samples decrease with increasing amount of wax in the blend. To compare the effect of the mixing procedure for LDPE samples, we also include in Figure 4 data from our previous investigations⁵ on extruded LDPE–oxidized wax blends. Those blends were prepared according to the same procedure as that for extruded LLDPE–wax blends. In the case of LDPE, blending with wax increases the melting enthalpies (i.e., crystallinity) for both mechanically and extrusion mixed

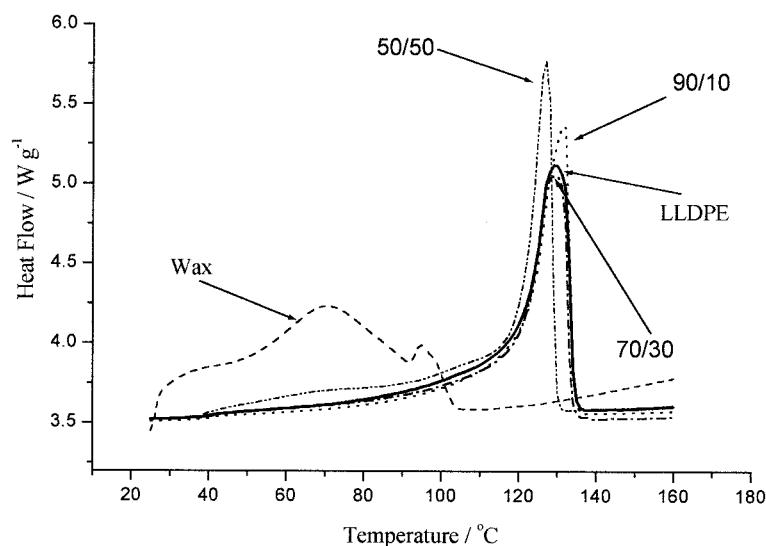


Figure 1 DSC heating curves for mechanically mixed LLDPE-wax blends.

samples. The extruded blends also have higher crystallinities than those of the mechanically mixed samples. In a recent study Puig⁹ showed enhanced crystallization in branched polyethylenes when blended with linear polyethylene. It was found that most of the linear methylene sequences of the branched polyethylene are incorporated in the linear polyethylene lamellae. In our case the linear chains of wax probably cocrystallize with the linear sequences of polyethylene, which favors the crystallization process. As a result the crystallinity of the LDPE-wax blends increases with increasing wax content. However, this effect will be more pronounced in the extruded blends because of the higher mobility of the chains during the mixing in the molten state (Fig. 4). It seems that, because of the molecular structure of LLDPE whose chains have much shorter branches, cocrystallization

will be less pronounced for LLDPE-wax blends. These results are in agreement with previous results of Gedde et al.,^{7,10} who observed true cocrystallization of linear low molecular weight polyethylene ($M_w = 2500 \text{ g mol}^{-1}$) with branched polyethylene.

The TGA curves of mechanically and extruded mixed LLDPE-wax blends are shown in Figures 5 and 6, respectively. A significant difference in the thermal stability of the blends, induced by mixing, is noticed. The decomposition curves of the extruded blends are slightly shifted to higher temperatures compared to pure PE. Mechanically mixed LLDPE-wax blends, on the other hand, show the opposite behavior. In Figure 7 the decomposition temperatures at 10% decomposition are plotted as a function of wax content. Thermal stability is slightly changed for small wax concentrations (up to 20%), but further increases in the amount

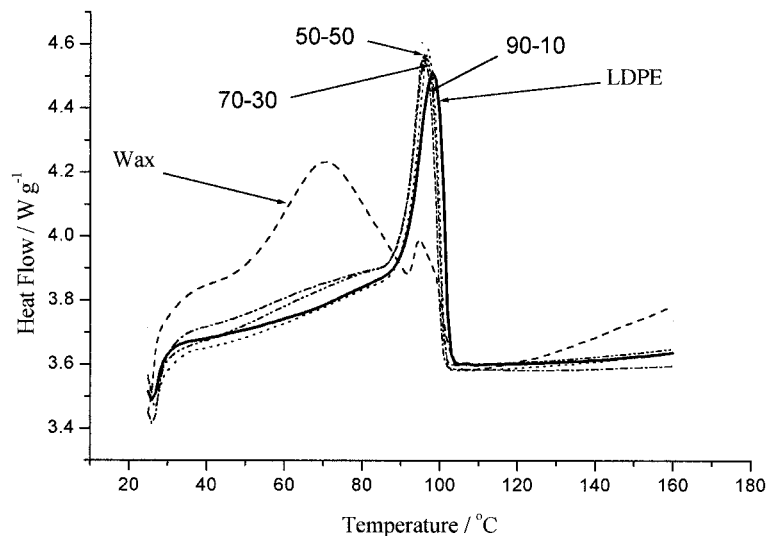


Figure 2 DSC heating curves for mechanically mixed LDPE-wax blends.

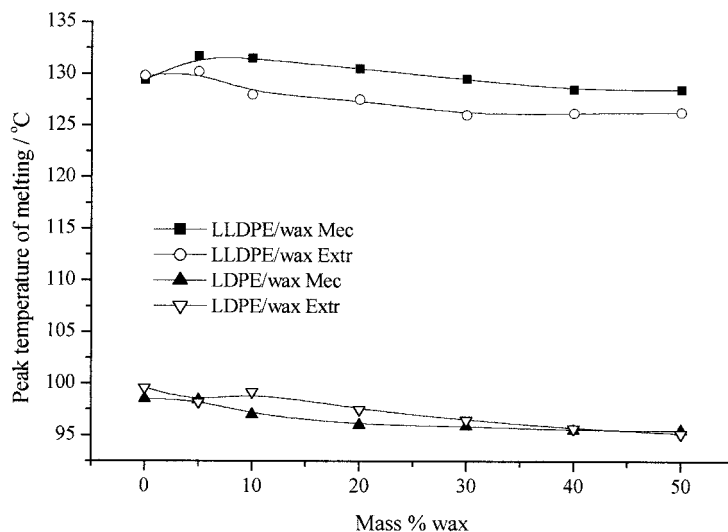


Figure 3 Peak temperatures of melting versus mass % wax for mechanically and extrusion mixed LLDPE-wax and LDPE-wax blends as a function of wax content.

of wax reduce stability to a large extent. However, the thermal stability is less affected by extrusion blending. A probable reason for the poor resistance of LLDPE-wax blends to thermal degradation is the low molecular weight of the wax. Short-chain fractions of wax, as well as fragments formed by chain scission, will have sufficient energy to leave the matrix at lower temperatures. Thus, introducing more of the low molecular weight material induces a gradual decrease in temperatures at which decomposition starts. If we assume that, during extrusion mixing, more wax chains are incorporated into the crystals because of their higher mobility, the difference in behavior of extruded blends compared to that of mechanically mixed blends can be explained. It seems as if wax chains in PE lamellae are protected from degradation. At higher wax concentrations, however, partial segre-

gation of the components takes place and the dependency of thermal stability on the type of mixing becomes less obvious. This conclusion can be confirmed by the improved thermal stability of mechanically mixed LDPE-wax blends (at low wax contents) compared to that of pure PE (Fig. 8). In this case the previously observed increase in crystallinity, attributed to cocrystallization of wax chains with linear sequences of PE, leads to an improvement in thermal stability up to about 20°C. To compare the effect of mixing in the case of LDPE-wax blends, we included the data on the thermal stability of extrusion mixed LDPE-wax blends in Figure 9, where 10% decomposition temperatures are plotted as a function of wax content. Again, the extrusion mixed blends show better thermal stability. The mixing in the molten state obviously allows better cocrystallization of the com-

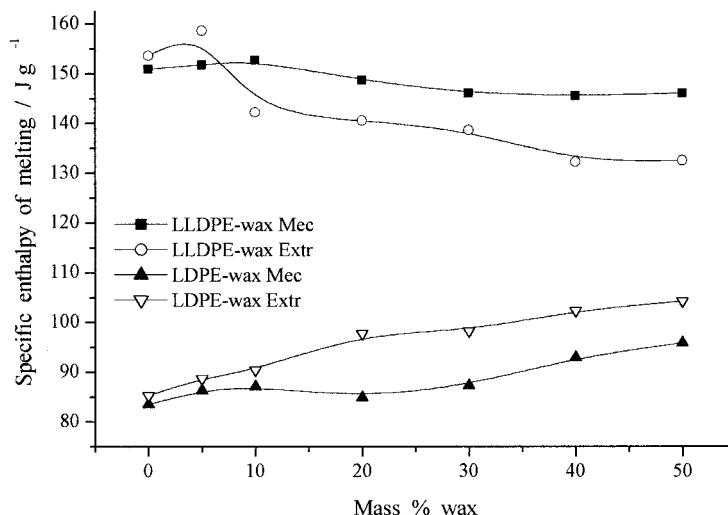


Figure 4 Specific melting enthalpies versus mass % wax for mechanically and extrusion mixed LLDPE-wax and LDPE-wax blends as a function of wax content.

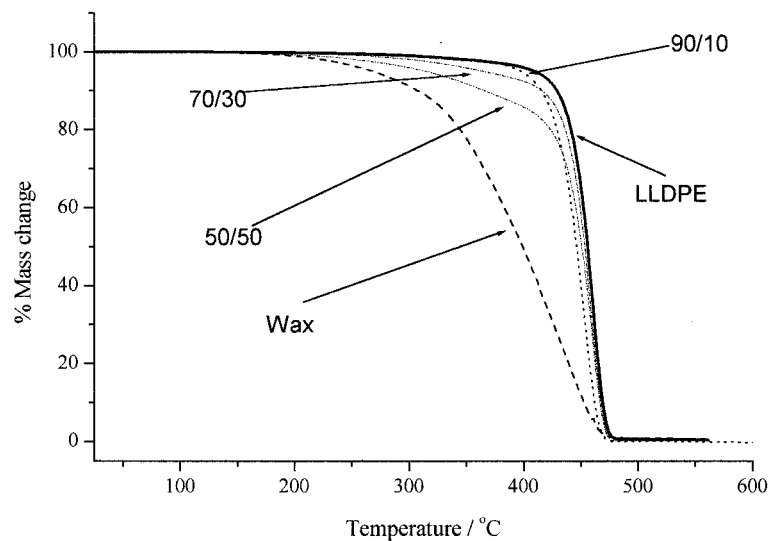


Figure 5 TGA curves for pure wax, LLDPE, and mechanically mixed LLDPE-wax blends.

ponents. Nevertheless, as the results on mechanically mixed LDPE-wax blends show, the final properties of the blends depend not just on mixing, but also on the initial molecular structure of the components.

It should be noted that the mixing treatment changes the properties not only of the blends, but also of pure polyethylenes. Figures 7 and 9 show that mechanically "mixed" LDPE and LLDPE have reduced thermal stability compared to that of extrusion "mixed" blends. The reason could be the enhanced degradation of the material during mechanical treatment. It will be seen that the degradation induced by mixing will also influence the mechanical properties.

Mechanical properties

The data presented in Tables I and II show that an increase in the amount of wax significantly affects the

mechanical properties of the blends. Strain at yield decreases with increasing amount of wax independent of the type of mixing or type of PE used. At small wax concentrations the changes are within experimental uncertainty, but as the amount of wax increases, the onset of plastic deformation is shifted to lower strains. If we adopt a former assumption that, at higher wax concentrations partial segregation of the components occurs, this can offer a possible explanation for this behavior. Because of the presence of short wax chains, structural rearrangements of the amorphous fraction before the macroscopic yield point will be much easier, which consequently induces the beginning of plastic deformation at lower strains.

On the other hand, as can be seen in Tables I and II, yield stress depends on the type of PE and slightly on mixing. Yield stress values actually follow changes in crystallinity with increasing wax content. In the case

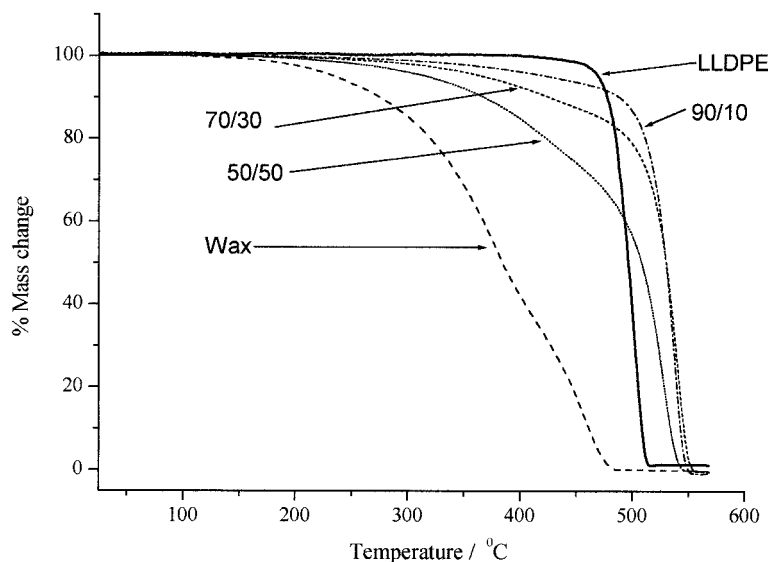


Figure 6 TGA curves for pure wax, LLDPE, and extrusion mixed LLDPE-wax blends.

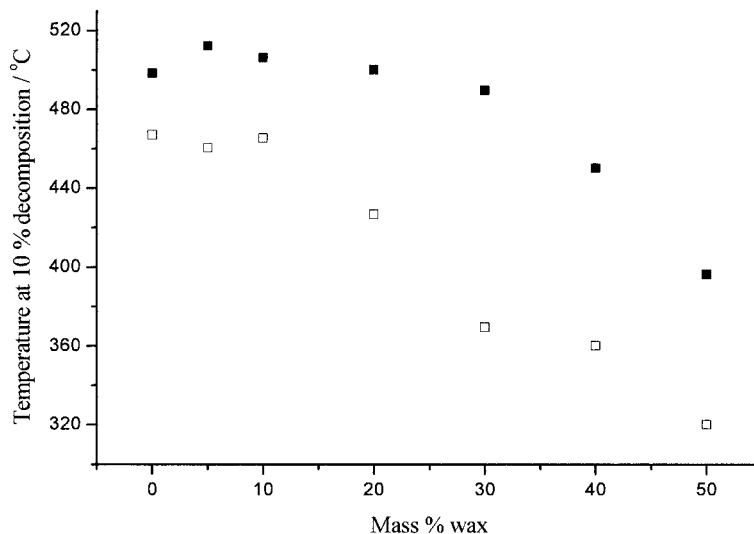


Figure 7 Temperatures of 10% decomposition versus mass % wax for mechanically (open symbols) and extrusion (filled symbols) mixed LLDPE-wax blends.

of LLDPE blends (Table I), changes in yield stress with increasing wax content are within experimental uncertainty, in agreement with the small changes in melting enthalpies, as shown in Figure 4. It can further be seen in Figure 4 that, at higher wax contents, the melting enthalpies slightly decrease (especially for extruded LLDPE-wax samples), and this is manifested by a decrease in yield stress for the 50–50% mechanically mixed samples, as well as for the 60–40 and 50–50% extrusion mixed samples. Because the melting enthalpies (i.e., crystallinities) of the LDPE blends increase with an increase in the amount of wax, it will also induce an increase in yield stress (Table II and Fig. 4). It should be noted that extruded LDPE-wax blends⁵ show behavior similar to that of mechanically mixed blends. The strain at yield decreases, whereas stress at

yield increases with increasing wax content. However, the extruded blends do not show a brittle point at higher wax contents.⁵ Their yield stress values are also higher than those of mechanically mixed blends (for one specific blend composition) because of higher crystallinity (Fig. 4). We discuss the reasons for the brittle fracture later in the text.

Tables I and II show that strain at break of all blends decreases with increasing amount of wax. The same is true for the stress at break, except for the mechanically mixed LDPE samples, which show brittle transitions. Introduction of the low molecular weight material obviously affects the blends' structure in such a way as to favor fracture propagation. It was shown¹¹ that fracture in pure PE depends on the stress distribution in the material. The stress distribution is actually non-

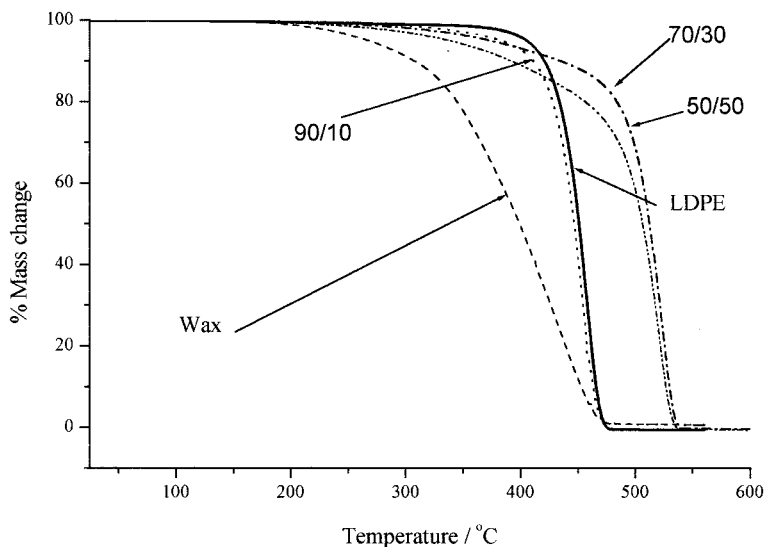


Figure 8 TGA curves for pure wax, LDPE, and mechanically mixed LDPE-wax blends.

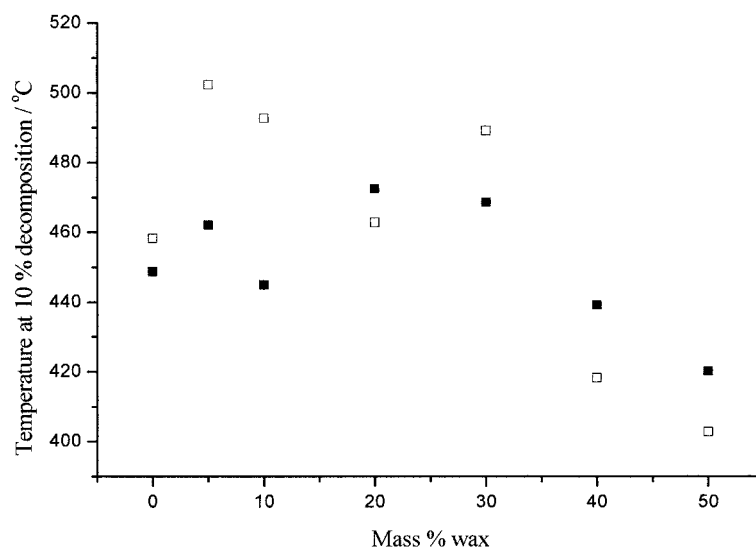


Figure 9 Temperatures of 10% decomposition versus mass % wax for mechanically (open symbols) and extrusion (filled symbols) mixed LDPE–wax blends.

uniform because the strength of the crystalline regions is experimentally proven to be higher than that of the amorphous region.¹² However, there is a variation in the strength in different amorphous regions. The amorphous portion, which contains a higher number of tie molecules, will be stronger because tie chains can store considerably more strain energy than other types of amorphous chains (chain folds and cilia).¹¹ The tie chains will also transfer the strain energy to the lamellae, which will take a greater portion of the energy on themselves because of their higher elasticity moduli. On the other hand, the concentration of tie molecules depends on the molecular weight, given that the probability of forming tie chains decreases

with a decrease in the length of the chains. This is why the introduction of low molecular weight material, such as wax, will have detrimental effects on the ultimate properties of the blends.

It was further shown that, when the molecular weight of PE is sufficiently small, fracture will be macroscopically brittle regardless of stress.¹³ This could be a reason for the brittle fracture observed in mechanically mixed LDPE–wax blends at higher wax contents (Table II). The other effect of the introduction of wax into the blend, which could also explain the occurrence of brittle fracture, is the change in the isotropy of the material. During the stretching of the semicrystalline material, deformation of the crystal-

TABLE I
Mechanical Properties of Extrusion and Mechanically Mixed LLDPE–Wax Blends^a

LLDPE/wax	$\epsilon_y \pm s\epsilon_y$ (%)	$\sigma_y \pm s\sigma_y$ (MPa)	$\epsilon_b \pm s\epsilon_b$ (%)	$\sigma_b \pm s\sigma_b$ (MPa)	$E \pm sE$ (MPa)
Mechanically mixed					
100/0	21.2 ± 1.5	7.6 ± 3.5	978.9 ± 111.2	10.2 ± 0.4	67.5 ± 12.1
95/5	20.9 ± 0.6	9.1 ± 4.8	950.5 ± 85.8	9.9 ± 0.2	70.9 ± 13.8
90/10	19.0 ± 0.6	8.2 ± 1.2	493.3 ± 46.7	6.8 ± 0.1	82.8 ± 10.7
80/20	18.5 ± 0.7	6.4 ± 5.4	388.9 ± 34.2	5.7 ± 0.3	107.4 ± 9.5
70/30	18.3 ± 0.3	9.3 ± 3.6	332.0 ± 23.9	6.4 ± 1.5	86.5 ± 4.9
60/40	17.7 ± 0.01	9.4 ± 3.3	358.0 ± 10.2	5.9 ± 1.2	91.5 ± 3.5
50/50	16.6 ± 2.8	4.3 ± 2.4	224.7 ± 9.4	4.2 ± 0.1	115.3 ± 5.2
Extrusion mixed					
100/0	21.8 ± 2.5	9.5 ± 1.3	1017.3 ± 92.5	13.7 ± 1.2	124.8 ± 3.4
95/5	20.7 ± 2.6	9.8 ± 1.5	989.3 ± 67.4	11.2 ± 2.7	136.6 ± 3.7
90/10	18.3 ± 1.3	9.7 ± 0.9	616.1 ± 62.3	7.8 ± 0.1	144.3 ± 1.2
80/20	18.8 ± 1.2	9.2 ± 2.4	289.2 ± 53.6	6.0 ± 1.5	129.7 ± 2.2
70/30	16.7 ± 1.7	8.2 ± 1.9	444.0 ± 35.4	7.3 ± 1.4	139.9 ± 1.9
60/40	14.2 ± 1.5	4.4 ± 3.2	274.5 ± 10.3	4.2 ± -1	146.5 ± 3.2
50/50	16.1 ± 0.3	4.2 ± 3.4	184.5 ± 16.4	3.6 ± 0.5	148.1 ± 1.5

^a Young's modulus (E), elongation at yield (ϵ_y), stress at yield (σ_y), elongation at break (ϵ_b), stress at break (σ_b), s – is the standard deviation of each parameter.

TABLE II
Mechanical Properties of Mechanically Mixed LDPE–Wax Blends

LDPE/wax	$\varepsilon_y \pm s\varepsilon_y$ (%)	$\sigma_y \pm s\sigma_y$ (MPa)	$\varepsilon_b \pm s\varepsilon_b$ (%)	$\varepsilon_b \pm s\varepsilon_b$ (%)	$E \pm sE$ (MPa)
100/0	27.1 ± 1.5	7.5 ± 1.3	1148.8 ± 22.3	8.3 ± 2.2	42.1 ± 14.2
95/5	25.7 ± 1.2	7.9 ± 1.5	1134.1 ± 21.4	6.3 ± 1.6	44.3 ± 10.2
90/10	23.4 ± 2.4	7.8 ± 0.9	765.6 ± 18.7	5.1 ± 1.9	48.5 ± 11.0
80/20	22.3 ± 3.8	9.6 ± 3.8	560.6 ± 16.2	5.0 ± 1.5	34.1 ± 13.5
70/30	20.1 ± 1.9	10.4 ± 2.7	436.8 ± 21.3	4.3 ± 1.9	55.5 ± 17.2
60/40	—	—	15.2 ± 1.2	6.3 ± 1.6	66.1 ± 9.8
50/50	—	—	18.8 ± 2.5	6.9 ± 1.4	69.6 ± 5.7

^a Young's modulus (E), elongation at yield (ε_y), stress at yield (σ_y), elongation at break (ε_b), stress at break (σ_b), s — is the standard deviation of each parameter.

line regions is essentially anisotropic because certain crystallographic directions are more favorable. It is, however, accepted that no shear bends develop when the morphology of the material is satisfactorily isotropic.¹⁴ It is believed that the interaction of localized shear bends, resulting in the formation of microcracks, is the precursor for the brittle fracture in semicrystalline polymers.¹⁴ Therefore it is possible that wax, because of its significantly lower molecular weight compared to those of PEs, could change the isotropy of the blend, inducing its brittle fracture. Extruded LDPE blends do not show a brittle ductile transition because more of the wax chains are incorporated in the crystalline lamellae, which will more or less preserve the isotropy of material. The TGA results also show that mechanical mixing induces degradation of the PEs and the blends, which can additionally alter the isotropy attributed to a change in the molecular distribution.

The change in material isotropy can probably explain the observed increase in Young's moduli with increasing wax content in LLDPE–wax blends, despite the small changes in crystallinity (Table I). It is well known that, because of the low shear strength of lamellae, that plastic deformation begins at very low strains.¹⁴ Before that, up to 1% strain, the deformation is confined to the disordered amorphous regions. Because of the altered isotropy of the blends, the activation of the crystalline shear bands will be much easier, leading to the enhanced contribution of crystals to the deformation. As a result the elastic modulus of the blend will increase, although the macroscopic yield point and the fracture will be shifted to lower strains (Table I). It is, however, still ambiguous why extruded LLDPE blends have higher elasticity moduli than those of mechanically mixed blends. A possible reason can be the higher lamellar perfection obtained by extrusion mixing. Even before the macroscopic yield point, in the so-called linear domain, fracture of lamellae under tension occurs, usually at the crystal defect points. Incorporation of short, linear wax chains improves lamellar perfection, which will enhance their resistance to crack formation. This, however, can increase the stress necessary to stretch the material, that

is, increase the material modulus. The fact that stress at break of those samples, which show increased brittle fracture, increases despite the decrease in the concentration of tie chains with increasing amount of wax (Table II), is in line with the discussion about the reasons for the increase in elasticity moduli. The activation of shear bends leads to the brittle–ductile transition but, because of the enhanced contribution of the crystal fraction to the deformation stress at break, the values will be higher. On the other hand, the higher crystallinities of the LDPE blends are clearly manifested by an increase in Young's moduli with increasing wax content (Fig. 4 and Table II). The same is observed in extrusion mixed LDPE–wax blends.⁵

These results show that the mechanical properties are significantly altered after the introduction of wax, attributed to changes in the concentration of tie chains and the isotropy of the material. In the next section we correlate the calculated tie chain concentrations of the blends with their ultimate properties.

Tie chain concentration

The calculation of the tie chain concentration in polyethylene is made according to the method proposed by Huang and Brown.¹⁵ The method is based on the assumption that only those molecules that are longer than $2L_c + L_a$, where L_c is the average lamellar thickness and L_a is the thickness of the amorphous layer, can form tie chains. The other type of tie molecules, formed by strong random entanglement of two chains of adjacent crystals, is not taken into account. To calculate the tie chain concentration P_{tc} , Huang and Brown proposed the following equation:

$$P_{tc} = \frac{1}{3} \frac{\int_{L_a+2L_c}^{\infty} r^2 e^{-(3r^2)/2\langle r^2 \rangle} dr}{\int_0^{\infty} r^2 e^{-(3r^2)/2\langle r^2 \rangle} dr} \quad (4)$$

where $\langle r^2 \rangle$ is the square of the end-to-end distance of the random coil and 1/3 is introduced because the

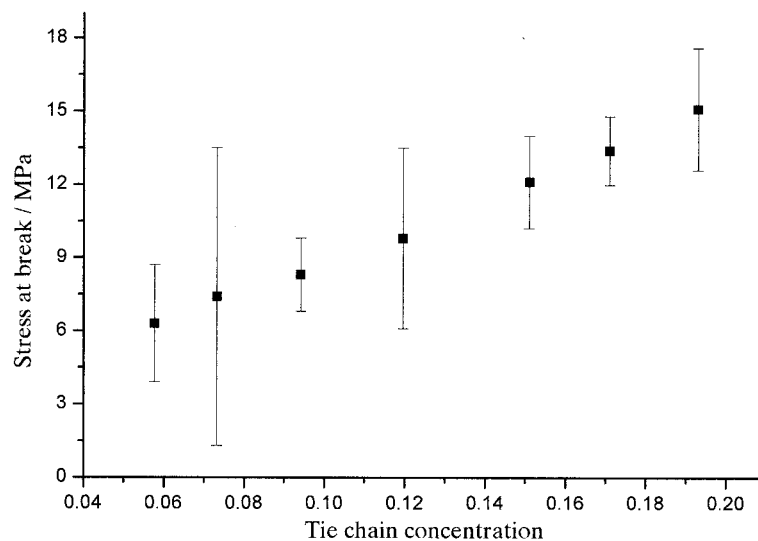


Figure 10 Stress at break as a function of average tie chain concentration calculated according to eqs. (4) and (6) for pure LDPE and extrusion mixed LDPE–wax blends.

other two dimensions of lamellar crystals are longer than the long period $L = L_c + L_a$. By use of the square of the end-to-end distance of the random coil given by

$$\langle r^2 \rangle = 6.85nl^2 \quad (5)$$

where n is the number of C—C bonds and l is the C—C bond length ($l = 0.153 \text{ nm}^{16}$), the effective length of the molecule is actually included in the calculations. Equation (2) is derived for molecules in the liquid state, but Mandelkern et al.¹⁷ showed that $\langle r^2 \rangle$ will not change after crystallization from the melt. To calculate P_{tc} for pure polyethylene, the crystal thickness and long period are calculated by using eqs. (2) and (3). The obtained values for LLDPE, $L_c = 16.7 \text{ nm}$ and $L = 33.2 \text{ nm}$, and LDPE, $L_c = 5.4 \text{ nm}$ and $L = 21.3 \text{ nm}$, are in agreement with the previous data of Gedde et al.⁷ They also found that the long period and crystal thickness values of linear very low molecular weight polyethylene ($M_w = 2500 \text{ g mol}^{-1}$) and normal molecular weight polyethylene blends calculated from DSC and SAXS data are in close agreement. This suggests that DSC data can be used for the investigation of the blends as long as there is no significant crystal phase separation. Assuming that cocrystallization does not change the crystal thickness and the long period of the blends to a great extent (Figs. 1 and 2 show melting behavior for the blends similar to that for pure PE), it can be concluded that wax chains are really too short to form tie molecules. The wax used in this study consists of linear hydrocarbon chains from C_{33} to C_{120} , with the maximum length in the extended state about 18 nm. Because LLDPE and LDPE blends have $2L_c + L_a$ values of about 50 and 27 nm, respectively, this is still much longer than the length of the longest wax chains, even if the long period is affected by blending. To calculate the change in tie chain concentration with

increase in wax content, the following equation proposed by Gedde et al.⁷ is used:

$$P_{tc\text{-blend}} = \frac{P_{tc\text{-PE}}(1 - w_{\text{wax}})w_{c\text{-PE}}}{(1 - w_{\text{wax}})w_{c\text{-PE}} + w_{\text{wax}}w_{c\text{-wax}}} \quad (6)$$

where $P_{tc\text{-PE}}$ is the average tie chain concentration of pure PE, w_{wax} is the wax content in the blend, $w_{c\text{-PE}}$ is the mass crystallinity of PE, and $w_{c\text{-wax}}$ is the mass crystallinity of wax. The mass crystallinity of the wax is also estimated by using eq. (1), as well as the value $\Delta H_m^0 = 293 \text{ J g}^{-1}$, which is debatable. Although this value may be different from the actual melting enthalpy of wax, DSC measurements show cocrystallization of wax and PE chains. We therefore assumed that the value $\Delta H_m^0 = 293 \text{ J g}^{-1}$, which is related to the orthorhombic crystal structure of PE, should be used in the estimation of the wax crystallinity used in eq. (6). We also used data from our previous study⁵ on extrusion mixed LDPE blends in the calculation, instead of that for mechanically mixed samples, because they do not show brittle fracture.

In Figures 10 to 13 stress and strain at break of extrusion mixed LDPE– and LLDPE–wax blends are plotted as a function of the estimated average tie chain concentration. It can be seen that both tensile strength and fracture strain significantly decrease with decreasing tie chain concentration, that is, increasing amount of wax. The functional dependency, however, is not the same. Stress at break of LDPE blends shows a linear dependency on the average concentration of tie chains (Figs. 10 and 12). This suggests that, beside tie chain concentration, the distribution of tie chains also has an influence on the ultimate properties of the material. Nevertheless, even if we put aside the effect of tie chain distribution, a plausible connection be-

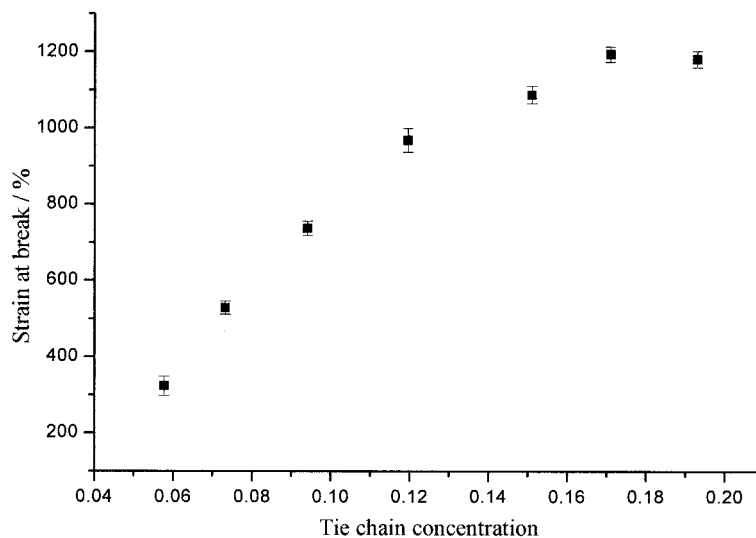


Figure 11 Strain at break as a function of average tie chain concentration calculated according to eqs. (4) and (6) for pure LDPE and extrusion mixed LDPE-wax blends.

tween the experimental data and the calculated average tie chain concentration can be made. LDPE and its blends have higher values of stress and strain at break than LLDPE blends for one specific blend composition. The reason is the higher average tie chain concentration, as can be seen in Figures 10 to 13. This confirms the assumptions about the influence of tie chains on the ultimate properties, as mentioned above. These results are also in agreement with the study by Gedde et al.⁷ on the blends of linear very low molecular weight polyethylene ($M_w = 2500 \text{ g mol}^{-1}$) and normal molecular weight linear- as well as branched polyethylene.

It should be emphasized that the average tie chain concentrations, calculated according to the above procedure, would be the same for extruded and mechan-

ically mixed samples of one specific polyethylene. Mechanically mixed polyethylene, however, shows lower values of stress and strain at break attributed to enhanced degradation of the material induced by mechanical treatment. As a result of degradation the molecular weight of the polymer decreases, which consequently reduces the number of molecules able to form tie chains. This means that, because it does not include possible changes in the distribution of tie chains and/or isotropy of the material, this method should be used with some restriction. However, we are still convinced that the calculation of the average concentration of tie chains offers a clear physical picture of the nature of changes in the ultimate properties of the blends with increasing wax content.

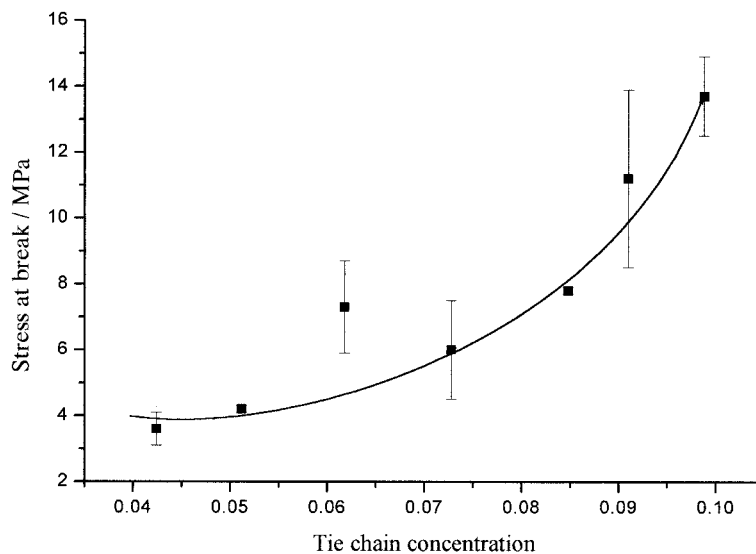


Figure 12 Stress at break as a function of average tie chain concentration calculated according to eqs. (4) and (6) for pure LLDPE and extrusion mixed LLDPE-wax blends.

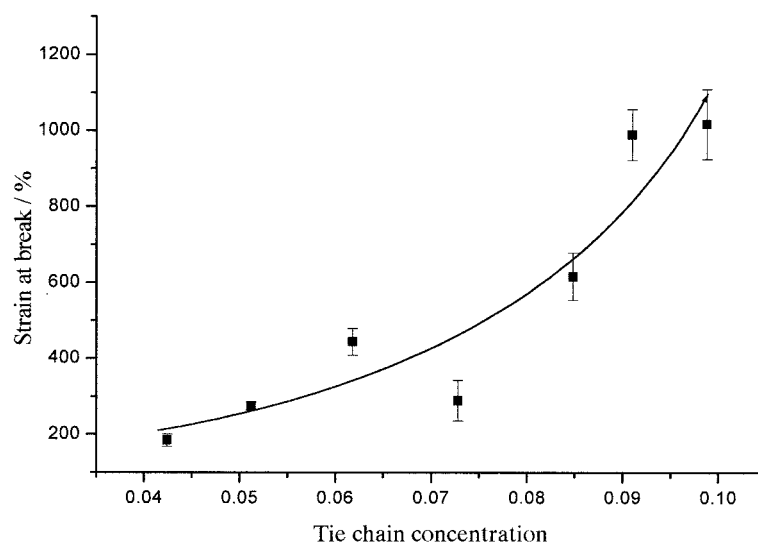


Figure 13 Strain at break as a function of average tie chain concentration calculated according to eqs. (4) and (6) for pure LLDPE and extrusion mixed LLDPE–wax blends.

CONCLUSIONS

The results show that the type of mixing, mechanical or extrusion, can change the mechanical and thermal properties of the polyethylene/wax blends. Mechanically mixed blends as well as pure polyethylenes, treated in a similar way, show reduced thermal stability, lower elastic modulus, and lower strength and fracture strain, compared to extrusion mixed samples. This is a consequence of enhanced degradation of the material induced by mechanical treatment.

We further found that the blend properties also depend on the type of polyethylene. Increasing the wax content induces an increase in crystallinity and improves the thermal stability of LDPE blends up to 50°C. The crystallinity and temperature of decomposition of LLDPE blends are only slightly affected by wax content, except at high concentrations when they drop below the values for pure polyethylene.

In general an increase in the amount of low molecular weight component deteriorates the mechanical properties. Elastic modulus increases, but stress and strain at break decrease with increasing wax content. The main reason for the poor ultimate properties of the blends is the reduced number of tie chains. The change in average tie chain concentration with wax content is calculated by using a method previously proposed by Gedde et al.⁷ Significant correlation was found between the calculated concentration of tie

chains and fracture stress and strain. A different functional dependency of stress at break on the concentration of tie chains for LDPE and LLDPE blends, however, suggests that the distribution of tie chains in the material is also important.

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