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RESEARCH ARTICLE

Cross-linking of LDPE/wax Blends in the Presence of Dicumyl peroxide

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Abstract

Thermal properties of cross-linked and uncross-linked LDPE/wax blends were investigated. The blends were prepared by thoroughly mixing the powdery ingredients, followed by pressing at 180 °C for ten minutes. The extent of cross-linking was determined by means of gravimetric analysis of the gel content of the samples. The thermal properties were determined by differential scanning calorimetry (DSC). The analyses of cross-link density of the samples indicated that increased amounts of peroxide gives rise to more efficient cross-linking, but only the PE phase in the blends is cross-linked. The DSC results indicated that LDPE and wax are probably miscible in the crystalline phase at low wax concentrations, but at higher wax concentrations the wax is only partially miscible in the crystalline phase.

Keywords LDPE/wax blends, differential scanning calorimetry.

1. Introduction

Blending of existing common polymers is often used for the preparation of new materials. Over the years, numerous systems have been developed and commercialized.[1] A large part of polymeric blends is based on polyolefins, which are the widest used polymers in industry.[2]

Low-density polyethylenes (LDPEs) are often used in industry. They have high impact strength, low brittleness temperature, flexibility, film transparency and outstanding electro-insulation properties. Major markets are in food packaging products, industrial sheeting and trash bags.[3]

Synthetic waxes (Fischer–Tropsch synthesis) are white, translucent, tasteless and odourless solids consisting of a mixture of solid hydrocarbons of high molecular weight. They are not soluble in many solvents due to their high crystallinity, but they dissolve in boiling xylene, as is the case with LDPE. They are used, *inter alia*, for the preparation of candles, paper coating, protective sealant for food products and beverages, biodegradable mulch, stoppers for acid bottles, electrical insulation and others.[4] They have low melt viscosity and a relatively high straight hydrocarbon chain character.

Cross-linking is a broadly used method for the modification of polymer properties. This process involves the formation of three-dimensional structures, gels, causing substantial changes in material properties.[5] Different procedures may be used for the initiation of polyolefin cross-linking. One of them is based on macroradical formation *via* thermal decomposition of organic peroxides.[6,7,8] A detailed description of the various initiation procedures has been given in a comprehensive review by Lazar *et al*.[9]

In this paper we shall discuss some thermal properties such as melting temperature, crystallization temperature, as well as specific melting and crystallization enthalpies of cross-linked LDPE/wax blends and their dependence on the concentration of cross-linking agent (dicumyl peroxide) and wax content. As far as potential applications of LDPE/wax blends are concerned, lower viscosity of the melt (at temperatures lower than the efficient cross-linking temperature) and imperviousness to water can be expected.

2. Experimental

Low-density polyethylene (MFI = 2 g / 10 min, density = 0.919 g cm^{-3}) from Slovnaft Bratislava, hard, brittle, straight-hydrocarbon chain synthetic wax (carbon distribution C28–C120, average molar mass 785 g mol^{-1}, density = 0.94 g cm^{-3}, melting point 104 °C) from Schümann-Sasol and dicumyl peroxide (DCP) from Sigma Aldrich Co. Ltd. were used. All blends were at first mechanically mixed for a few minutes and then pressed for 10 min at 180 °C.

Differential scanning calorimetry was carried out on a Perkin Elmer DSC7 thermal analyzer in nitrogen atmosphere. Samples were heated from 25 °C to 140 °C at a heating rate of 10 °C min^{-1} and cooled at the same rate, after which the cycle was repeated. Thermal properties such as melting and crystallization temperatures and enthalpies, were determined from the second scan.

Efficiency of cross-linking was determined gravimetrically in terms of the insoluble portion (gel) after 12 h extraction of the samples in boiling xylene. Xylene was replaced every 2 h.

3. Results and Discussion

3.1. Determination of Gel Content

The results of gel content measurements are summarized in Table 1. In this table (as well as in Table 2), samples are marked as follows: the x/y/z number in the sample column indicates the weight concentration ratio LDPE/wax/DCP in the blends. Unfortunately it was not possible to investigate the uncross-linked blends because we did not have a large enough stock of the LDPE used in this investigation. Our experience is, however, that uncross-linked PE and wax and their blends dissolve completely when extracted into boiling xylene.

Both 0.5% and 2% DCP induce cross-linking of the LDPE/wax blends. As expected, the efficiency of cross-linking in the presence of 2% DCP is much higher. If the wax content increases, the gel content decreases. Wax needs a much higher concentration of peroxide for cross-linking,[10,11] because of its much lower molar mass, and since the DCP concentration is too small for cross-linking of the wax, only the PE phase is cross-linked.

The evidence of this statement is clear from the following. If we calculate gel content values, related to PE phase (g_0), using equation 1, we can see that in the

case of 0.5% DCP the g_0 values are similar in the concentration region 0–20% wax, and in the case of 2% DCP the g_0 values are similar in all the wax concentration regions. This supports the opinion that only the PE phase is cross-linked. In the case of 0.5% DCP and 30 or 40% wax, there is a sharp decrease in gel content related to the PE phase, since the portion of DCP in the PE phase is too small.

$$g_0 = g/w_{PE} \quad (1)$$

where g is the gel content and w_{PE} is the weight portion of PE in the blends.

Table 1 Gel content of LDPE /wax/DCP blends.

Sample W_{Px} = 0.5%	g [%]	$g_o = g/w_{PE}$ [%]	Sample w_{Px} = 2%	g [%]	$g_o = g/w_{PE}$ [%]
99.5/0/0.5	70	70	98/0/2	85	85
94.5/5/0.5	66	70	93/5/2	80	86
89.5/10/0.5	57	64	88/10/2	76	86
79.5/20/0.5	50	63	78/20/2	65	83
69.5/30/0.5	35	50	68/30/2	55	81
59.5/40/0.5	11	19	58/40/2	46	79

3.2. Differential Scanning Calorimetry

DSC curves for both 0.5% DCP (Fig. 1) and 2% DCP (Fig. 2) show only one endothermic peak for the blends consisting of 5 and 10% of wax, despite the fact that pure wax has three peaks (two of them significant). This peak is at about 100 °C and the presence of wax does not influence its position (see $T_{o,m}$ and T_m values in Table 2). A probable explanation is that LDPE and wax are miscible in the crystalline phase[12] in this concentration region. From 20% wax, but especially for 30 and 40% wax a second, broad peak is observed at about 80 °C (Figures 1 and 2). This peak falls in the same temperature region as that of the melting of unblended wax. This means that LDPE and wax are only partially miscible in this concentration region. In our previous paper[13] we investigated linear low-density polyethylene/wax blends, and we observed only one endothermic peak in the concentration region from 0 to 40% of wax both for uncross-linked and cross-linked blends.

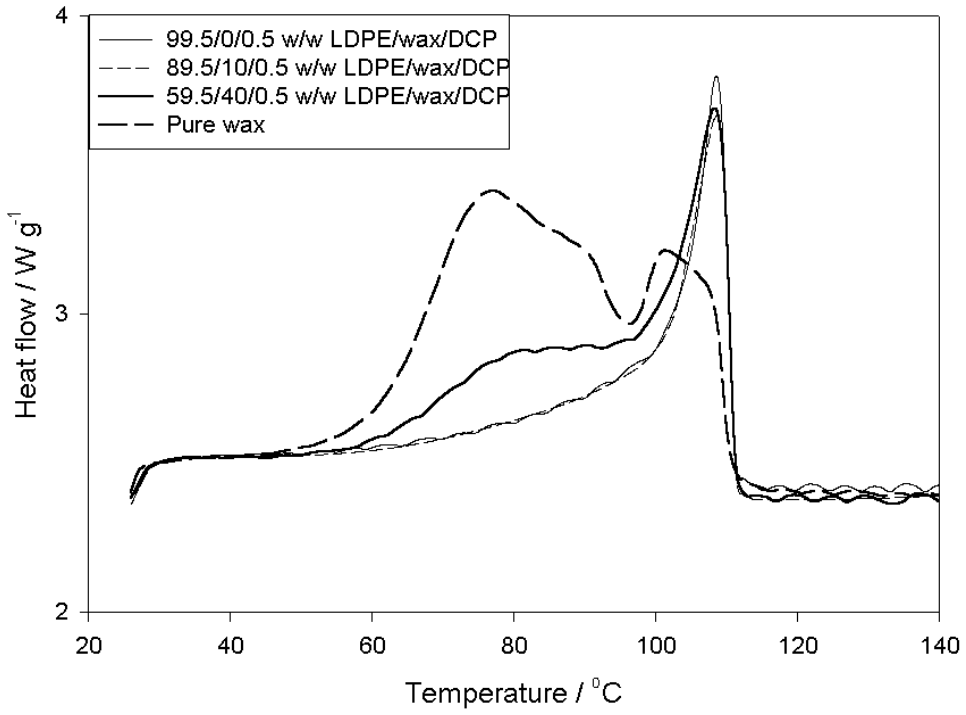

Figure 1 DSC heating curves of different LDPE/wax blends in the presence of 0.5 weight percent DCP.

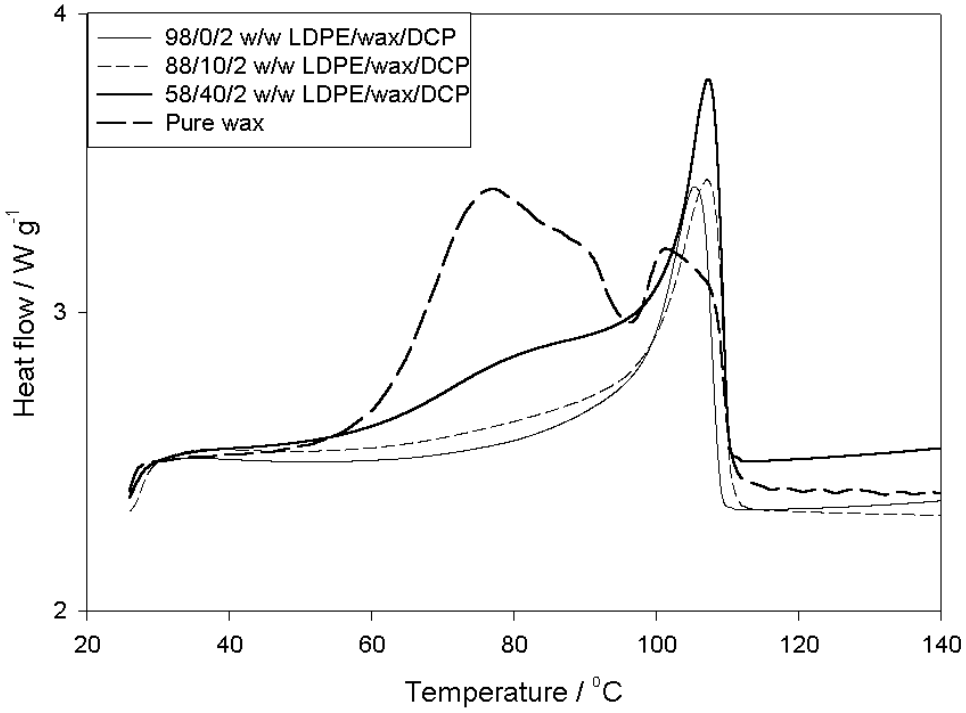

Figure 2 DSC heating curves of different LDPE/wax blends in the presence of 2.0 weight percent DCP.

A decrease in $T_{o,m}$, T_m and enthalpy (ΔH_m being a measure of the degree of crystallinity) with an increase in DCP is observed (Table 2). For 0.5% DCP the influence of cross-linking on both T_m and ΔH_m is very small, but for 2% DCP it is significant. In this case the ΔH_m values have deviations from the additive rule in equation 2.

$$\Delta H_m^{add} = \Delta H_{m,PE}\, w_{PE} + \Delta H_{m,w}\, w_w \qquad (2)$$

where $\Delta H_{m,PE}$ and $\Delta H_{m,w}$ are the specific melting enthalpies of LDPE and wax, and w_{PE} and w_w are the weight portions of LDPE and wax.

Table 2 Parameters obtained from DSC measurements for LDPE/wax/DCP blends [T = temperature, ΔH = specific enthalpy, m = melting, c = cooling, o = onset, p = peak, ad = additive rule, given by equation (2)]

Sample	$T_{o,m}$ [°C]	$T_{p,m}=T_m$ [°C]	ΔH_m [J g^{-1}]	$T_{o,c}=T_c$ [°C]	$T_{p,c}$ [°C]	ΔH_c [J g^{-1}]	ΔH_m^{add} [J g^{-1}]
Wax	60.1	77.2[a]	213.06	95.2	91.8[b]	211.21	213.06
LDPE	102.5	108.5	96.95	96.5	92.0	107.26	96.95
99.5/0/0.5	102.5	108.5	101.65	94.2	91.1	100.56	97.44
94.5/5/0.5	100.4	108.5	103.17	94.6	91.7	106.97	102.27
89.5/10/0.5	99.0	108.5	107.65	94.9	91.5	112.32	108.07
79.5/20/0.5	100.2	109.0	106.85	95.3	92.1	114.18	119.68
69.5/30/0.5	100.3	108.5	130.41	95.9	92.0	138.61	131.30
59.5/40/0.5	99.9	108.4	148.77	95.8	93.5	151.46	152.60
98/0/2	95.9	105.4	86.42	91.4	87.0	99.92	98.93
93/5/2	97.1	106.2	96.53	92.4	87.5	101.07	100.81
88/10/2	95.4	107.0	104.92	92.4	88.3	105.38	106.62
78/20/2	96.5	106.4	114.07	93.2	89.5	114.32	118.23
68/30/2	96.3	107.2	128.95	93.7	91.5	132.11	129.84
58/40/2	95.3	107.4	140.48	93.2	91.1	141.05	151.15

[a] The DSC heating curve of pure wax shows three endothermic peaks. The tabulated peak is the main peak; the others are at about 90 °C and 101 °C (see Fig.1).

[b] The DSC cooling curve of a pure wax shows two exothermic peaks. The tabulated peak is the main peak; the other is at 70 °C (see Fig. 3).

It therefore seems as if cross-linking reduces the polyolefin crystallinity. Cross-links play the role of defect centres, which impede the folding of macromolecular chains, and thus decrease the size of the lamellar crystals.[9] The reduction of lamellar thickness of crystallites leads to a decrease in T_m.

The effect of cross-linking on the heat capacity, as well as specific enthalpy, of PE is mediated through the change of crystallinity and reduced mobility of macromolecules. The higher extent of the amorphous parts of a polymer increases the heat capacity or specific enthalpy, while the reduced mobility leads to its decrease.

Wax does not influence the crystallization temperatures (T_c) of the blends. Cross-linking, on the other hand, influences T_c, since it reduces crystallinity and therefore T_c decreases with an increase in DCP concentration (Table 2), as noted above for T_m.

DSC curves of the crystallization of blends show, beside the main exothermic peak, another small peak (Figures 3 and 4). For wax concentrations of 5 to 20%, this peak is at about 55 °C, and for wax concentrations of 30 and 40% this peak starts at above 55 °C and is at about 70 °C (Figures 3 and 4). It therefore seems that wax and LDPE are only partially miscible in the molten state.

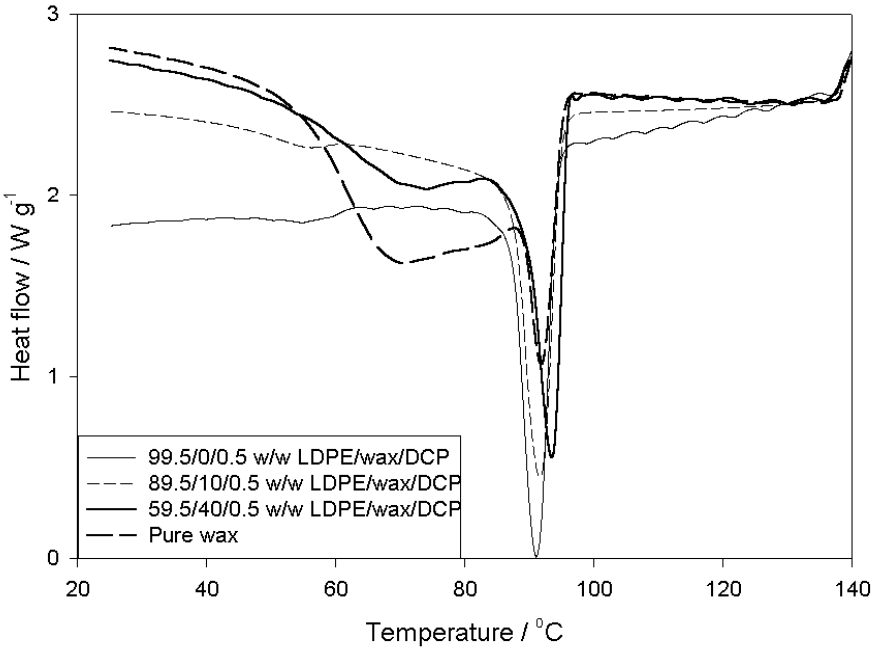

Figure 3 DSC cooling curves of different LDPE/wax blends in the presence of 0.5 weight percent DCP.

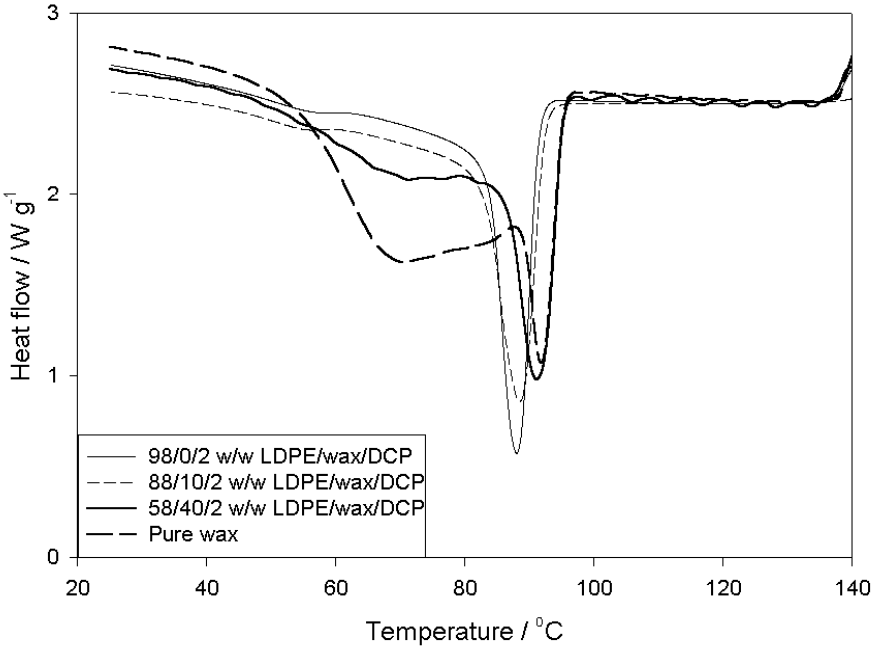

Figure 4 DSC cooling curves of different LDPE/wax blends in the presence of 2.0 weight percent DCP.

4. Conclusions

We observed that, if the wax content increases, the gel content after cross-linking decreases, since wax needs a much higher concentration of peroxide for cross-linking and therefore only the PE phase is cross-linked. Cross-linking with 2% of DCP is much more efficient, but still only the PE phase is cross-linked.

DSC curves for both 0.5% DCP and 2% DCP show only one endothermic peak for the blends consisting of 5 and 10% wax, despite the fact that pure wax has three peaks. A probable explanation is that LDPE and wax are miscible in the crystalline phase[12] in this concentration region. The main endothermic peak is at about 100 °C and the presence of wax does not influence its position. From 20% wax we observe a second, broad peak at about 80 °C. This peak probably forms part of the wax melting endotherm. This means that LDPE and wax are only partially miscible in this concentration region.

A decrease in $T_{o,m}$, T_m and enthalpy (ΔH_m being a measure of the degree of crystallinity) with an increase in DCP was observed. The ΔH_m values have also deviations from the additive rule, especially for 2% of DCP, since cross-linking reduces polyolefin crystallinity.

We also observed that wax does not influence the crystallization temperatures (T_c) of the blends, and that cross-linking influences T_c, since it reduces crystallinity and therefore T_c decreases with an increase in DCP concentration. DSC curves of crystallization of blends show beside the main exothermic peak another small peak for all blends. For wax contents of 30 and 40% this peak is significant. We conclude that wax and LDPE are only partially miscible in the molten state.

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