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Thermal properties of polypropylene/wax blends

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Abstract

Some thermal properties of isotactic polypropylene/hard Fischer–Topsch wax blends were investigated in this paper. Mutual miscibility of components in the solid and melt states is discussed. It was found that, at low wax concentrations, polypropylene and hard paraffin wax are homogeneous on a macroscopic level. TGA results confirmed the lower thermal stability of blends containing larger concentrations of wax. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

One possible route of preparation of new materials is blending of two or more polymeric components with each other. The final properties generally depend on the physical and chemical properties, as well as the morphology of the pure components, their portion in the blends, interactions among components and also processing routes [1,2]. These factors generally influence all physical properties.

In our previous studies, we devoted attention to the preparation and characterization of crosslinked and uncrosslinked LLDPE/wax and LDPE/wax blends [3–6]. The blends were prepared in different ways. They were either mechanically mixed in a powder form, or kneaded in the melt in a screw extruder. Very different behavior was observed for all physical properties. It is, therefore, clear that the morphology of blends strongly influences the final properties [2]. This also depends on processing conditions.

In this paper, we investigate some thermal properties of polypropylene (PP)/wax blends. PP is synthesized entirely by a low pressure process using Ziegler–Natta catalysts. Usually 90% or more of the polymer is in the isotactic form. Major markets for homopolymers are filaments and fibers, automotive and appliance components, packaging materials, furniture, high tenacity yarns, tufted carpets and so on [7].

Paraffin waxes (Fischer–Tropsch synthesis) are white, translucent, tasteless and odorless solids consisting of a mixture of solid hydrocarbons of high molecular weight. They are soluble in benzene, ligroin, warm alcohol, chloroform and carbon disulfide, but insoluble in water and acids. They are used for preparation of candles, paper coating, protective sealant for food products and beverages, biodegradable mulch, stoppers for acid bottles, electrical insulation and others [8].

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2. Experimental

In this work, isotactic PP (MFI = 12 g per 10 min at 230°C and 2.16 kg, density $= 9 \times 10^2$ kg m^{-3}) and hard, brittle, straight-hydrocarbon chain paraffin wax carbon distribution C28–C120, average molar mass 7.85×10^{-1} kg mol^{-1}, density $= 9.4 \times 10^2$ kg m^{-3}) from Schümann–Sasol were used. All blends were blended in an industrial extruder (Bandera film blower) at 100 rpm and 180°C. Samples for testing were taken after about 15 min of blending, after which they were pressed for 3 min at 180°C.

Differential scanning calorimetry (DSC) was carried out on a Perkin-Elmer DSC7 thermal analyzer in nitrogen atmosphere. Samples were heated from 25 to 180°C at a heating rate of 10°C min^{-1} and then cooled at the same rate. Thermal properties, like melting and crystallization temperatures and enthalpies, were determined from the second scan.

Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer TGA7 thermal analyzer from 25 to 560°C at a heating rate of 10°C min^{-1} in nitrogen atmosphere.

3. Results and discussion

3.1. Differential scanning calorimetry

The results obtained from DSC analyses are summarized in Table 1. In the Fig. 1, DSC heating curves for both pure components and blends are shown. For 5% of wax, only one endothermic peak is observable, despite the fact that the DSC curve of wax shows three endothermic peaks. Since PP and wax can in principle not be miscible, because isotactic PP crystallizes in a helical form in which there are three monomer units per turn of the helix [7], and wax probably crystallizes in a planar zigzag form, a probable explanation is that PP and wax shows a *macroscopic* homogeneity at this concentration.

For 10% of wax, another small peak is observable (in the original figure). For increased amounts of wax, two other significant peaks are observable (Fig. 1). These peaks correspond to the endothermic peaks of wax. This means that, if the concentration of wax is higher than 5%, no macroscopic homogeneity is observed in the solid state.

Similar trends are observed during the crystallization of blends. For 5% of wax, only one exothermic peak is observable (Fig. 2). This may mean that PP and wax are immiscible in the molten state, but display macroscopic homogeneity. It can, however, also mean that PP and wax are really miscible in the molten state. Certain crystallizable polymers are thermodynamically miscible in the melt, but upon cooling each polymer separates and forms its own unique crystal structure. Only occasionally two polymers have such similar isomorphous crystal structures that both can enter the same crystal lattice and co-crystallize, thus forming a single homogenous solid product [2]. For example, PE/PP blends were reported to be miscible in the melt [9], but crystallized separately upon cooling, nucleating each other [10]. On the other hand,

Table 1
Parameters obtained from DSC measurements for PP/wax blends[a]

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})
PP	150.8	164.9	84.56	111.6	103.8	97.75	84.56
95/5 (PP/wax)	153.4	162.8	85.56	112.3	109.1	98.23	90.00
90/10 (PP/wax)	150.3	154.4	97.94	112.4	107.0	109.19	97.41
85/15 (PP/wax)	148.0	161.0	108.34	112.4	105.6	120.8	103.84
80/20 (PP/wax)	145.3	163.0	109.56	108.3	101.8	109.16	110.26
75/25 (PP/wax)	142.8	161.2	111.5	107.8	109.0	120.09	116.69
70/30 (PP/wax)	140.4	161.5	118.18	106.9	100.3	117.18	123.11
Wax	60.1	77.2[b]	213.06	95.2	91.8[c]	211.21	213.06

[a] T is the temperature, ΔH the specific enthalpy, m: melting, c: cooling, o: onset, p: peak. Notation *x*/*y* means weight portion of PP/weight portion of wax.

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

[c] The DSC cooling curve of pure wax shows two exothermic peaks. This one is the main peak. The other one is at 70°C (see Fig. 2).

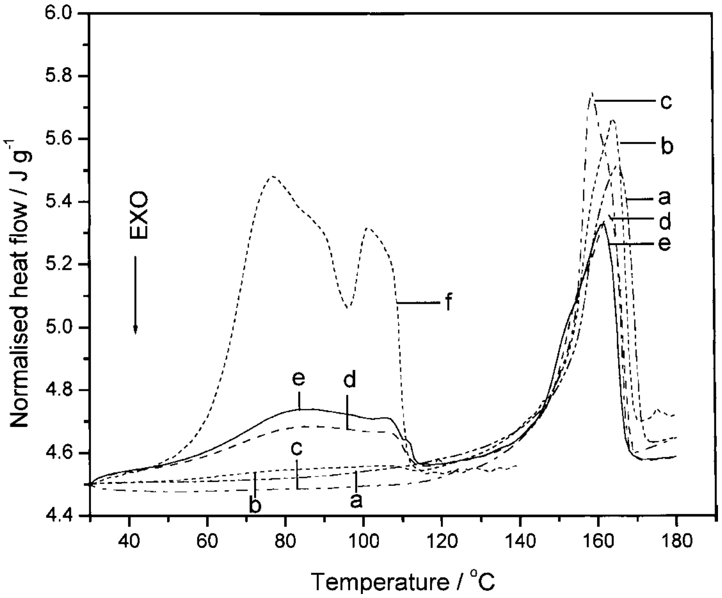

Fig. 1. DSC heating curves for (a) 100% PP; (b) 95/5 w/w PP/wax blend; (c) 90/10 w/w PP/wax blend; (d) 80/20 w/w PP/wax blend; (e) 70/30 w/w PP/wax blend and (f) 100% wax.

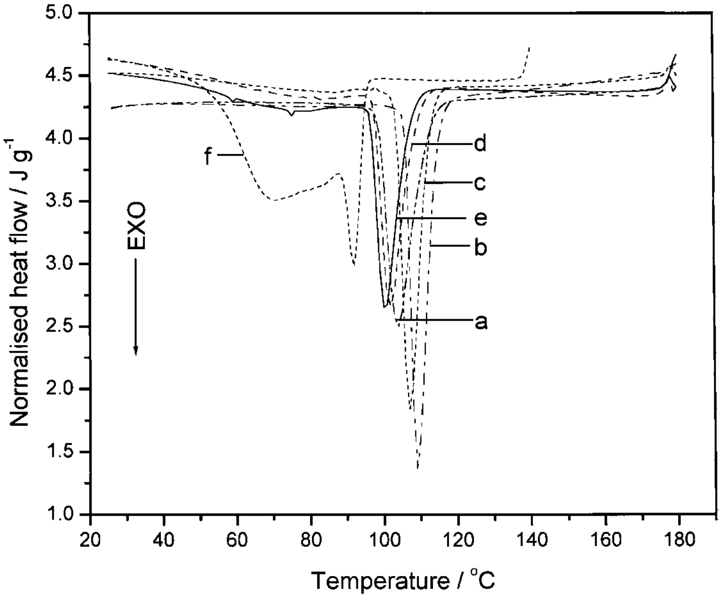

Fig. 2. DSC cooling curves for (a) 100% PP; (b) 95/5 w/w PP/wax blend; (c) 90/10 w/w PP/wax blend; (d) 80/20 w/w PP/wax blend; (e) 70/30 w/w PP/wax blend and (f) 100% wax.

HDPE/PP blends were also reported as immiscible in either the amorphous or the crystalline phase [11]. For a detailed understanding of the different behaviors, the exact morphology of the polymers under investigation must be known. In our case, the blends are probably homogenous only on the macro-scale.

For 10% and more wax, another exothermic peak (related to one of exothermic peaks of wax) was observed. It confirms that our PP and wax are not miscible in the molten state.

As far as $T_{\mathrm{o,m}}$ and T_{m} are concerned, an increase in wax content slowly decreases these temperatures (Table 1, Fig. 1). The specific enthalpy of melting increases with an increase in wax content, since this value is bigger for wax than for PP. These values were compared with the values calculated according to the additive rule (Eq. (1)):

$$\Delta H_{\mathrm{m}}^{\mathrm{add}} = \Delta H_{\mathrm{m,PP}} w_{\mathrm{PP}} + \Delta H_{\mathrm{m,w}} w_{\mathrm{w}} \qquad (1)$$

$\Delta H_{\mathrm{w,PP}}$, $\Delta H_{\mathrm{m,w}}$, $\Delta H_{\mathrm{m}}^{\mathrm{add}}$ are the specific enthalpies of melting for PP, wax and blends, and w_{PP} and w_{w} the weight portions of PP and wax in the blends. The agreement is not excellent, but it is acceptable. Differences between experimental results and values according to additive rules can be caused by: (i) degradation of components during kneading (temperature, shear forces), and/or (ii) stearic hindrances between the components in the crystallization process. The crystallization temperature decreases slightly with an increase in wax content.

Table 2
Temperatures of 5 and 10% degradation of PP/wax blends in nitrogen atmosphere

Sample	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)
PP	440.2	453.4
95/5 (PP/wax)	400.2	428.3
90/10 (PP/wax)	400.6	431.0
85/15 (PP/wax)	370.1	414.4
80/20 (PP/wax)	351.1	390.7
75/25 PP/wax	350.3	387.8
70/30 (PP/wax)	341.9	383.1
Wax	336.0	364.1

3.2. Thermogravimetric analysis

Thermal stability of blends was characterized in terms of the temperatures of 5 and 10% degradation. The results are summarized in Table 2 and Fig. 3. The results show that the thermal stability of blends decreases with an increase in wax content. This is a logical consequence of the lower thermal stability of the wax.

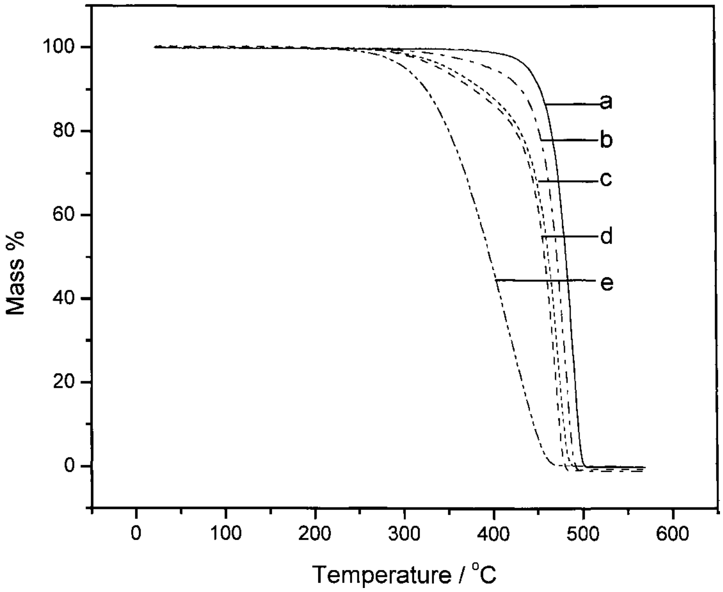

Fig. 3. TGA curves for (a) 100% PP; (b) 90/10 w/w PP/wax blend; (c) 80/20 w/w PP/wax blend; (d) 70/30 w/w PP/wax blend and (e) 100% wax.

4. Conclusion

The DSC results seem to indicate that PP and hard paraffin wax are homogeneous on a macro-scale when the wax content is less than 10%, contrary to the expectation that PP and wax cannot be miscible in the crystalline phase. At higher wax concentrations, there is a clear separation between wax and PP melting endotherms.

TG analyses of these blends confirm that an increase in wax content causes a decrease in the thermal stability of blends, since wax is thermally less stable than PP.

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