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PE/Wax Blends: Interesting Observations

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SUMMARY: The thermal and mechanical properties of different cross-linked and uncross-linked polyethylene/wax blends were investigated over a period of time. This paper summarizes the results and observations. It was found that (i) both LLDPE and LDPE cross-links in the presence of low dicumyl peroxide concentrations, while wax only grafts onto the polyethylene chains, (ii) polyethylene and wax have relatively good miscibility, (iii) both wax content and cross-linking change the mechanical properties of polyethylene in one way or the other, (iv) the route of sample preparation has a marked influence on the thermal and mechanical properties of the blends, and (v) oxygen-containing groups in oxidised wax apparently do not change the way in which the wax interacts with polyethylene.

Introduction

A lot of work has been done on polymer blends and composites [1], but not much is known about the thermal and mechanical properties of polymer/wax blends. There are, however, a few papers describing the morphology of polyethylene blends with paraffins. Lee and Choi [2] investigated the crystalline morphology of HDPE/paraffin blends used for thermal energy storage. They found that an injection-molded sample of an h-HDPE/paraffin had compact spherulites of about 7 μ in radius, while l-HDPE paraffin blends had a coarser morphology leading to poorer sealant properties. Kim and Kim [3] invesigated the effect of the liquid-liquid phase separation on the crystalline behaviour and mechanical properties of poly(ethylene-ran-vinyl acetate) and paraffin wax blends. Sun *et al* [4] investigated HDPE/liquid paraffin blends and found that the homogeneous blends in the molten state became heterogeneous systems to yield microporous HDPE membranes during the course of cooling due to thermally induced phase separation.

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Paraffin waxes are white, translucent, tasteless and odourless solids consisting of a mixture of solid hydrocarbons of high molar mass. Common properties are water repellency, smooth texture, low toxicity, and freedom from objectionable odour and colour. They are combustable and have good dielectric properties [5].

During the past year our group investigated the influence of blending with different types of wax, as well as cross-linking, on the thermal and mechanical properties of linear low-density polyethylene (LLDPE) and low-density polyethylene (LDPE) [6-11].

Experimental

Our different wax and polyethylene samples were obtained from Sasolchem and Sasol Polymers in South Africa. Dicumyl peroxide (DCP) was obtained from Sigma-Aldrich. The LLDPE had an MFI of 3.5 g / 10 min., a density of 0.94 g cm^{-3}, and it was in a powder form with particle size less than 600 μm. Two different LDPE's were used. The first had an MFI of 2 g / 10 min. and a density of 0.92 g cm^{-3}, while the second had an MFI of 20 g / 10 min. and a density of 0.91 g cm^{-3}. The waxes used were a (i) hard, brittle straight hydrocarbon-chain paraffin wax with a melting point of 90 °C, a carbon distribution of C28-C120, an average molar mass of 785 g mol^{-1} and a density of 0.94 g cm^{-3}, and (ii) hard, brittle, oxidised straight hydrocarbon-chain paraffin wax with an average molar mass of 785 g mol^{-1}, a density of 0.94 g cm^{-3}, and a C/O ratio of 18.8/1.

After mixing, all the samples were pressed into 100 x 80 x 0.7 mm shapes for 10 min. at 180 °C. The DSC and TGA analyses were done with a Perkin Elmer DSC7 and TGA7 respectively at a heating rate of 10 °C min^{-1} and in nitrogen atmosphere. Flow rates of molten blends were determined with a Ceast Melt Flow Junior at 190 °C and under a 1 kg mass. The mechanical properties were tested with a Hounsfield W5K tensile tester at a speed of 50 mm min^{-1}. The extent of cross-linking was gravimetrically determined as the gel content after a 12 hour extraction in xylene.

Results and Discussion

LLDPE/wax blends prepared through mechanical mixing of powders

Pure LLDPE, and blends containing 2, 5, 10, 20, 30 and 40 % paraffin wax respectively, were heated under pressure in the presence of respectively 0.5, 2 and 3 % DCP. It was observed that a DCP concentration of 0.5 % has a low cross-linking efficiency. By using 2 and 3 % DCP, high gel contents were observed. Calculation of gel content relative to the LLDPE phase gave values in excess of 100 % for blends containing more than 20 % wax, indicating that part of the wax was probably grafted onto the LLDPE chains at higher wax concentrations.

The DSC curves of uncross-linked LLDPE/wax blends showed that wax content has no influence on the melting points (T_m) and onset temperatures of melting ($T_{o,m}$) of LLDPE. Moreover, the curves of the blends showed only one endothermic peak, despite the fact that pure wax has 3 peaks (two of them significant). This may indicate miscibility in the crystalline phase, but it is not without doubt. Firstly, the main melting peak of the blends does not lie between those of LLDPE and wax as would be expected for miscible blends and, secondly, mechanical mixing followed by melt pressing may not ensure sufficient miscibility of the components. Further analyses using DMTA and micro-thermal analysis will be used to establish whether LLDPE and wax really are mutually miscible in the solid state. The viscosities of blends, that consist of components that are miscible, often behave according to the log-additive rule. Since flow rate is associated with melt viscosity, this rule can also be applied to flow rate. Our measurements of the flow rate of the melt of uncross-linked blends confirmed linear behaviour. This also points to LLDPE/wax blends being mutually miscible in the observed concentration region. A decrease in $T_{o,m}$, T_m and enthalpy (ΔH_m) with an increase in DCP was observed. The ΔH_m values have strong deviations from the additive rule, $\Delta H_m^{add} = \Delta H_{m,PE}\, w_{PE} + \Delta H_{m,w}\, w_w$. It is therefore clear that cross-linking reduces the polyethylene and wax crystallinity.

The thermal stability of blends (as determined with TGA) in synthetic air atmosphere is much lower than in nitrogen atmosphere, and it decreases with an increase in wax content. This is a logical consequence of the lower thermal stability of the wax.

Correlation between thermal stability and cross-link density (characterized in terms of the gel content) was not observed.

Young's modulus slowly increased with an increase in wax content. This increase was higher for cross-linked blends than for uncross-linked blends. A small decrease in yield stress of cross-linked LLDPE was observed when the concentrations of DCP were 0.5 and 2 %. If 3 % DCP was used, the decrease in yield stress was bigger. Cross-linking caused an increase in elongation at yield at all concentrations. The increase in wax content caused a decrease in elongation at yield. There was only a small influence of cross-linking on stress at break, both for pure LLDPE and blends, if the concentrations of DCP were 0.5 and 2 %. In the presence of 3 % DCP the stress at break increased more. Increasing wax content caused a decrease in stress at break at all DCP concentrations. An increase in wax content resulted in a decrease in elongation at break, both for uncross-linked and cross-linked blends. This decrease was higher for cross-linked blends, especially for DCP concentrations of 2 and 3 %. Generally, a decrease in elongation at break with an increase in DCP concentration, for cross-linked LLDPE and blends was observed, since cross-linking reduces PE drawability.

LLDPE/wax blends prepared through extrusion

For LLDPE/wax blends prepared through extrusion, the DSC measurements indicated that the blends consisting of 10 and 20 % of wax may be miscible in the crystalline phase, but further analyses are needed to confirm this (see discussion above). Only one peak was observed in the DSC curve. For 30 % and more wax two other peaks were observed. This indicates phase separation of the components. It also had an influence on the mechanical properties. T_0 and T_m decreased with an increase in wax content. For these blends we also observed that an increase in wax content slightly decreased the temperature of crystallization.

An increase in Young's modulus with an increase in wax content was observed, indicating that the modulus of the wax is higher than the modulus of LLDPE. It is probably associated with its higher degree of crystallinity. An increase in wax content caused a decrease in elongation at yield. This is to be expected, since the wax is harder than the LLDPE. A small increase in yield stress was observed for blends consisting of

10 and 20 % of wax. For blends consisting of 30 % and more wax, no yield point, but brittle rupture, was observed. The influence of wax content on stress at break depended on its concentration. Since pure LLDPE underwent significant strain hardening, its value of stress at break was the highest - even higher than the yield stress. Samples containing 10 and 20 % wax underwent strain softening after their yield points. Stress at break was therefore much smaller than yield stress. Samples, which consisted of 30 % and more wax, did not have yield points, and exhibited brittle rupture giving rise to an increase in stress at break. An increase in wax content resulted in a decrease in elongation at break in the whole concentration region. This decrease was the sharpest for 30 % and more wax in the blends. In this case, the material lost its drawability and was very brittle.

LLDPE/ox-wax blends prepared through mechanical mixing of powders

DSC analyses of LLDPE/ox-wax blends (ox-wax: oxidised paraffin wax), containing up to 50 % of wax, showed only one endothermic peak, despite the fact that pure wax showed two significant peaks. This may be the result of the LLDPE and the wax being miscible in the crystalline phase, despite the method used in the preparation of the blends (see discussion above). An increase in wax content of the blends did not appreciably influence either the onset and peak temperatures of melting, or the specific enthalpies of melting of the blends. The same was true for the crystallization temperatures and specific enthalpies of crystallization. Only one exothermic peak was observed. This indicates that the components were miscible with each other at all LLDPE/ox-wax ratios investigated. An increase in flow rate with an increase in wax content of the blends was observed. When these data were tested against the log-additive rule, it gave a straight line indicating miscibility of the components in the molten state.

The TGA analyses of the blends showed that the thermal stability of the blends decreased with an increase in wax content, since the thermal stability of the wax is much lower than the thermal stability of LLDPE. The blends were, however, appreciably more stable than pure wax, even at wax concentrations as high as 50 %.

A small increase in Young's modulus of the blends with an increase in wax content was observed. The wax content was found to have no influence on the yield point (elongation at yield and yield stress) of the blends. An increase in wax content decreased both stress and elongation at break.

LDPE/wax blends prepared through mechanical mixing of powders

In this case (LDPE was of low MFI) it was found that, if the wax content increased, the gel content after cross-linking decreased, since wax needs a much higher concentration of peroxide for cross-linking and therefore only the PE phase was cross-linked. Cross-linking with 2 % of DCP was much more efficient, but still only the PE phase was cross-linked.

DSC curves for both 0.5 % DCP and 2 % DCP showed only one endothermic peak for the blends consisting of 5 and 10 % wax, despite the fact that pure wax had three peaks. As in the above cases, a possible explanation is that LDPE and wax were miscible in the crystalline phase in this concentration region, but further analyses are needed to confirm this. The main endothermic peak was at about 100 °C and the presence of wax did not influence its position. From 20 % wax we observed a second, broad peak at about 80 °C. This peak probably formed part of the wax melting endotherm. This means that LDPE and wax were 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 also had deviations from the additive rule, especially for 2 % of DCP, since cross-linking reduced the polyethylene crystallinity. We also observed that the wax did not influence the crystallization temperatures (T_c) of the blends, but that cross-linking influenced T_c, since it reduces crystallinity and therefore T_c decreased with an increase in DCP concentration. The DSC curves of crystallization of the blends showed, beside the main exothermic peak, another small peak for all the blends. For wax contents of 30 and 40 % this peak was significant. Therefore the wax and LDPE were only partially miscible in the molten state.

LDPE/wax blends prepared through mechanical mixing of powders

In this case (LDPE was of high MFI) there was also an increase in gel content with an increase in DCP content, and a decrease with an increase in wax content. Since the

DCP concentration was too low for the cross-linking of the wax, probably only the LDPE phase was cross-linked. In the presence of 2 % DCP, gel content relative to the LDPE phase gave values in excess of 100 % for blends containing more than 20 % wax, indicating that part of the wax was probably grafted onto the LDPE chains at higher wax concentrations.

Specific melting enthalpies, calculated from the DSC data, were in good agreement with the additive rule for uncross-linked blends, but deviated strongly for cross-linked blends. Again this indicates the reduction of LDPE crystallinity by cross-linking. A small decrease in $T_{o,m}$ and T_m with an increase in DCP concentration was observed. In the absence of DCP, the DSC melting curves for LDPE and the blend containing 10 % wax showed only one endotherm, while the blends containing higher concentrations of wax gave rise to more than one endotherm. This may indicate LDPE/wax miscibility only up to 10 % wax. The same observations were made for cross-linked blends.

TGA results indicated (i) a decrease in thermal stability with an increase in wax content, (ii) little influence of cross-linking on the thermal stability of LDPE or its blends, and (iii) no direct correlation between the thermal stability and the cross-link density (characterized in terms of the gel content).

Conclusions

1. Both LLDPE and LDPE cross-link in the presence of DCP, but all indications are that the wax in the blends does not cross-link, but grafts onto the polyethylene chains at higher DCP and wax concentrations.
2. For most of the blends it was found that polyethylene and wax may have been completely or partially miscible in the crystalline phase, but DMTA and other analyses are needed to confirm this observation. Our present observations indicate better miscibility in the case of LLDPE.
3. As expected, the polyethylene crystallinity was found to decrease with increasing DCP content for all the samples investigated.
4. Both wax content and cross-linking changed the mechanical properties of polyethylene in one way or another. Since polyethylene and wax are completely

miscible up to certain concentrations, it may be possible to control the mechanical properties through blending with wax and/or cross-linking.

5. In the case of LLDPE/wax blends it was found that the route of sample preparation - mechanical mixing *versus* blending in the melt - has a marked (yet unexplained) influence on the thermal and mechanical properties of the blends.
6. It does not seem as if the oxygen-containing groups in oxidised wax cause the wax to interact any differently with the LLDPE than unoxidised wax, except in the case of thermal stabilty, where there is a larger difference between the thermal stability of LLDPE/ox-wax blends and the unblended oxidised wax, than is the case for LLDPE/wax blends.

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