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Mechanical Properties of Uncrosslinked and Crosslinked Linear Low-Density Polyethylene/Wax Blends

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ABSTRACT: The mechanical properties of uncrosslinked and crosslinked linear low-density polyethylene (LLDPE)/wax blends were investigated, using differential scanning calorimetry (DSC), tensile testing, and melt flow indexing. A decrease in the degree of crystallinity, as determined from the DSC melting enthalpies, was observed with an increase in the dicumyl peroxide (DCP) concentration. The Young's modulus increased with increased wax portions, and there was a higher increase for crosslinked blends. The yield stress generally decreased with increased peroxide content. Crosslinking caused an increase in elongation at yield, but increased wax content caused a decrease in elongation at yield. The stress at break generally increased with increasing peroxide content, but it decreased with increased wax content. The elongation at break decreased with an increase in the DCP concentration. Melt flow rate measurements indicated a mutual miscibility in LLDPE/wax blends. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 973–980, 2001

Key words: linear low-density polyethylene/wax blends; mechanical properties

INTRODUCTION

It is generally accepted that it is not always necessary to synthesize new polymers to satisfy the need for new materials. Blending of existing commodity or engineering polymers is often a more rapid and less expensive alternative than the realization of new polymer chemistry.[1] Over the years, numerous systems have been developed and commercialized. These systems include mechanical blends of two or more components and a chemical combination of different monomers, grafted copolymers, and so forth.[2] A big part of this family of new materials is based on polyolefins, which are the most widely used polymers in industry.[3]

In this article we discuss the static mechanical properties such as the Young's modulus, yield point, and ultimate properties of uncrosslinked and crosslinked linear low-density polyethylene (LLDPE)/wax blends and their dependence on the concentration of the crosslinking agent dicumyl peroxide (DCP) and wax portion. The flow rates of uncrosslinked blends are also discussed. LLDPE has good mechanical properties and is often used in industry. Grocery bags, heavy duty shipping sacks, agricultural films, pipes, and liners for consumers, landfills, and waste ponds are only a few examples.[4–6]

Low-density PEs (LDPEs) are frequently blended with LLDPEs. The superior mechanical properties of LLDPE's are retained in combination with the easier processability of LDPE,[7] which results in a decrease of the melt tension.[8]

Paraffins are a class of aliphatic hydrocarbons that are characterized by straight or branched carbon chains with the generic formula C_nH_{2n+2}. Their physical properties vary with increasing molecular weight from gases to waxy solids. 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. Their density is approximately 0.880–0.915 g mL^{-1}, their melting point is 47–65°C, and their flash point is 198°C. Common properties are water repellency, smooth texture, low toxicity, and freedom from objectionable odor and color. They are combustible and have good dielectric properties. Paraffins are used for the preparation of candles, paper coatings, protective sealants for food products and beverages, glass-cleaning preparations, hot-melt carpet backing, biodegradable mulch, lubricants, stoppers for acid bottles, electrical insulation, and so forth.[9]

There are few polymer/wax blends reported in the literature. One example is paraffin wax that is flexibilized and strengthened by blending it with an ethylene vinyl acetate copolymer.[10]

Crosslinking is a broadly used method for the modification of polymer properties. This process involves the formation of tridimensional structures (gels) that cause substantial changes in material properties.[11] Different procedures may be used for the initiation of polyolefin crosslinking. One of them is based on macroradical formation via thermal decomposition of organic peroxides.[12–14] A detailed description of the various initiation procedures is given in a comprehensive review by Lazar et al.[15]

The molecular weight of polymers increases during crosslinking, and this is directly interrelated with the change of properties of the polymer connected with the sample deformability. The crosslinking leads to an increase in the viscosity of the polymer melt, increased tensile strength,[16] improvement of creep properties,[17,18] and an increase in the resistance to environmental stress cracking.[19] Crosslinking stabilizes the natural molecular network (entanglements, crystallites), and every system is potentially elastically operative and can contribute to the stress in tensile experiments.[20]

The influence of crosslinking on the physical properties of waxes was also investigated.[21,22] DCP and potassium persulfate were used in those studies. It was found that crosslinking increased the elasticity of waxes and when the amount of DCP was increased beyond 1.1 mol/mol hard wax, insoluble and infusible hard brittle gels were obtained.

EXPERIMENTAL

The following materials were used: LLDPE (3.5 $\times$ 10^{-3} kg/10 min melt flow index; 9.38 $\times$ 10^5 kg m^{-3} density; 90% of the particle size less than 600 μm); hard, brittle, straight-hydrocarbon chain paraffin wax from Schümann–Sasol (C28–C120 carbon distribution, 7.85 $\times$ 10^{-1} kg mol^{-1} average molar mass, 9.4 $\times$ 10^5 kg m^{-3} density, 104°C melting point); and DCP from Sigma Aldrich Co. Ltd.

All blends were mechanically mixed for a few minutes and then pressed for 10 min at 180°C.

Differential scanning calorimetry (DSC) was carried out on a Perkin–Elmer DSC7 thermal analyzer in a nitrogen atmosphere. Samples were heated from 25 to 140°C at a heating rate of 10°C min^{-1} and then cooled at the same rate. The specific enthalpy of melting was determined from the second scan by using a sigmoidal baseline to account for any differences between the heat capacities before and after melting.

The mechanical properties were tested on a J. J. Lloyd 5-kN tensile tester at room temperature. The crosshead speed was 50 mm min^{-1}.

The flow rates of the molten blends were determined in a Ceast Melt Flow Junior apparatus at 190°C and under a 1-kg mass.

RESULTS AND DISCUSSION

The measurements of the degree of crystallinity are summarized in Table I. The *x/y/z* numbers in the sample columns in the table indicate the weight concentration ratio of LLDPE/wax/DCP in the blends.

The degree of crystallinity was calculated via the total enthalpy method, according to eq. (1):

$$X_c = \Delta H_m / \Delta H_m^+ \qquad (1)$$

where X_c is the degree of crystallinity, ΔH_m is the specific enthalpy of melting, and ΔH_m^+ is the specific enthalpy of melting for 100% crystalline PE. We used a ΔH_m^+ value of 288 kJ kg^{-1}.[23] A decrease in the degree of crystallinity with an increase in DCP content was observed (Table I). Therefore, it

Table I Degrees of Crystallinity of LLDPE/Wax/DCP Blends

Sample $w_{\text{Px}} = 0\%$	X_c (%)	Sample $w_{\text{Px}} = 0.5\%$	X_c (%)	Sample $w_{\text{Px}} = 2\%$	X_c (%)	Sample $w_{\text{Px}} = 3\%$	X_c (%)
LLDPE	58.8	99.5/0/0.5	52.8	98/0/2	42.1	97/0/3	36.0
98/2/0	58.4	97.5/2/0.5	51.8	96/2/2	42.0	95/2/3	38.1
95/5/0	60.2	94.5/5/0.5	49.9	93/5/2	43.6	92/5/3	39.1
90/10/0	59.8	89.5/10/0.5	50.2	88/10/2	52.1	87/10/3	42.3
80/20/0	66.0	79.5/20/0.5	53.1	78/20/2	48.0	77/20/3	47.4
70/30/0	68.1	69.5/30/0.5	54.9	68/30/2	52.4	67/30/3	48.0
60/40/0	61.1	59.5/40/0.5	61.5	58/40/2	51.7	57/40/3	49.0
Wax	74.0	—	—	—	—	—	—

w_{Px}, weight percentage peroxide in samples.

seemed as if crosslinking reduced the polyolefin crystallinity. Crosslinks play the role of defect centers, which impede the folding of macromolecular chains and thus decrease the sizes of the lamellar crystals.[15]

The influences of the wax portion and crosslinking on the Young's modulus of the blends are shown in Figure 1. The modulus of the wax was somewhat higher than the modulus of the LLDPE, because the modulus of the blends was slightly increased with an increase in the wax portion. This increase was higher for crosslinked blends than for uncrosslinked blends. There were differences between the modulus of pure LLDPE and the moduli of the blends that contained 40% wax (maximum concentration used) for uncrosslinked and crosslinked blends. This difference can be calculated from eq. (2):

$$\Delta E = \{[E_b(40\%) - E_{\text{PE}}]/E_{\text{PE}}\} \times 100\% \quad (2)$$

where E_{PE} is the modulus of LLDPE and $E_b(40\%)$ is the modulus of blends that contained 40% wax. We obtained the following values: 10.1% for blends that were crosslinked with 0.5% DCP, 35.5% for blends that were crosslinked with 2% DCP, and 76.0% for blends that were crosslinked with 3% DCP. This behavior further supported the conclusion that the crosslinking caused a decrease in the crystallinity of the LLDPE, because the modulus of the crystalline phase was higher than the modulus of the amorphous phase and the wax did not crosslink at such low peroxide concentrations. Because there was a decrease in the crystallinity of the unblended LLDPE with an accompanying decrease in modulus, and because the wax in the blends did not crosslink, it was expected that the difference in modulus between the unblended LLDPE and the samples blended

with 40% wax would increase with increasing peroxide concentration. The proportionality between the crystallinity and modulus is also illustrated in Figure 2, where a (nonlinear) decrease in modulus is shown for a decrease in crystallinity for all (crosslinked and uncrosslinked) LLDPE/wax blends.

The influence of the wax portion and crosslinking on the yield stress of the blends is shown in Figure 3. Previous studies showed that there were several PEs for which the tensile yield strength of chemically crosslinked PE decreased with increasing crosslinking agent concentration.[24,25] This decline in yield stress stemmed from the decreasing degree of crystallinity.[26] In our case only a small decrease in the yield stress was observed for crosslinked LLDPE at DCP concentrations of 0.5 and 2%. If 3% DCP was used, the decrease in yield stress was larger (19.0 MPa for uncrosslinked LLDPE vs. 14.4 MPa for crosslinked LLDPE). The influence of the wax on the yield stress was strange. It seemed as if there was very little change in the yield stress for uncrosslinked blends. An increase in yield stress with an increase in wax content was observed for crosslinked blends. The higher the peroxide content, the more the yield stress increased with increasing wax content.

The influence of the wax portion and crosslinking on the elongation at yield of the blends is shown in Figure 4. The elongation at yield increased with crosslinking at all the wax concentrations investigated. An increase in the wax portion caused a decrease in the elongation at yield. This was expected, because the wax was harder than the LLDPE.

The influence of the wax portion and crosslinking on the stress at break of the blends is shown in Figure 5. Generally, the tensile strength at
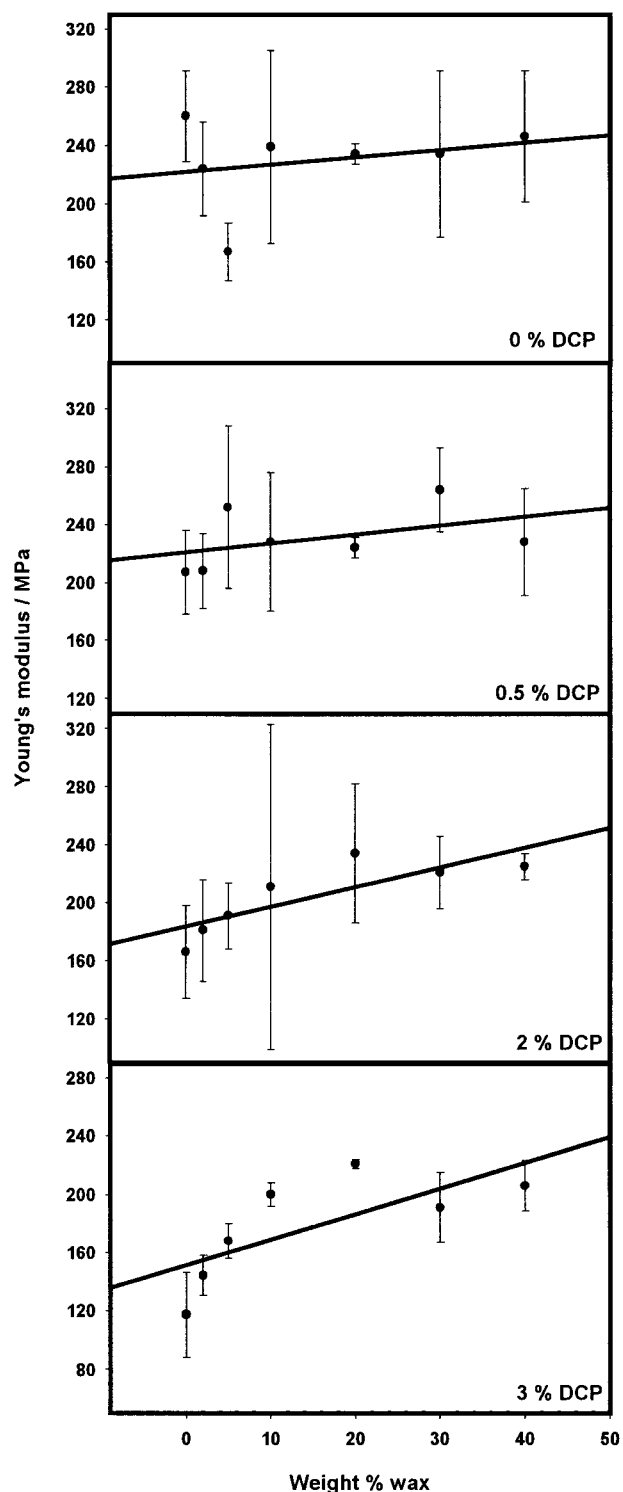
Figure 1 The Young's modulus as a function of the weight percentage of wax in uncrosslinked and crosslinked LLDPE/wax blends.

break depends on the polymer structure in a more complicated way. The tensile strength is strongly affected by the drawability of the polymer prior to

failure. The PEs that undergo strain hardening during stretching have higher strength at break than PEs that do not undergo strain hardening. Narkis et al. observed that crosslinking had much more of an effect on the reduction of the strength at break of polymers that underwent strain hardening, because crosslinking reduced their drawability (elongation at break).[24] We observed that crosslinking had a small influence on the stress at break of pure LLDPE and the blends at DCP concentrations of 0.5 and 2%. However, there was a larger decrease in the stress at break in the presence of 3% DCP (27 MPa for uncrosslinked LLDPE vs. 20 MPa for crosslinked LLDPE). An increase in the wax content caused a decrease in the stress at break at all DCP concentrations.

The influence of the wax portion and crosslinking on the elongation at break of the blends is shown in Figure 6. An increase in the wax portion resulted in a decrease in the elongation at break for the uncrosslinked and crosslinked blends. This decrease was higher for crosslinked blends, especially for DCP concentrations of 2 and 3%. Generally, a decrease of the elongation at break with an increase in DCP concentration for the crosslinked LLDPE and blends was observed because crosslinking reduced the PE drawability.[24]

One of the most important factors influencing the final properties is the mutual miscibility of the components. Most polymeric substances are not miscible with each other.[2,7] A few methods can be used to investigate the miscibility: DSC, dynamic mechanical thermal analysis, transmission electron microscopy, and others.[7] In our previous article[27] we showed that the DSC curves for uncrosslinked and crosslinked LLDPE/wax blends had only one endothermic peak, despite
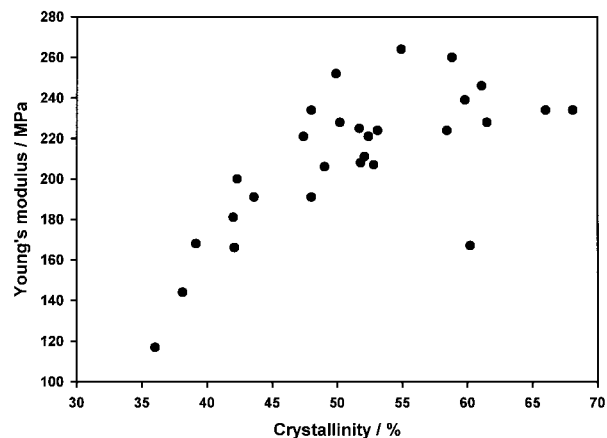

Figure 2 The Young's modulus as a function of the crystallinity of the LLDPE and LLDPE/wax samples.

The term compatibility is often used instead of miscibility in the literature. This term generally means that immiscible or partially miscible poly-
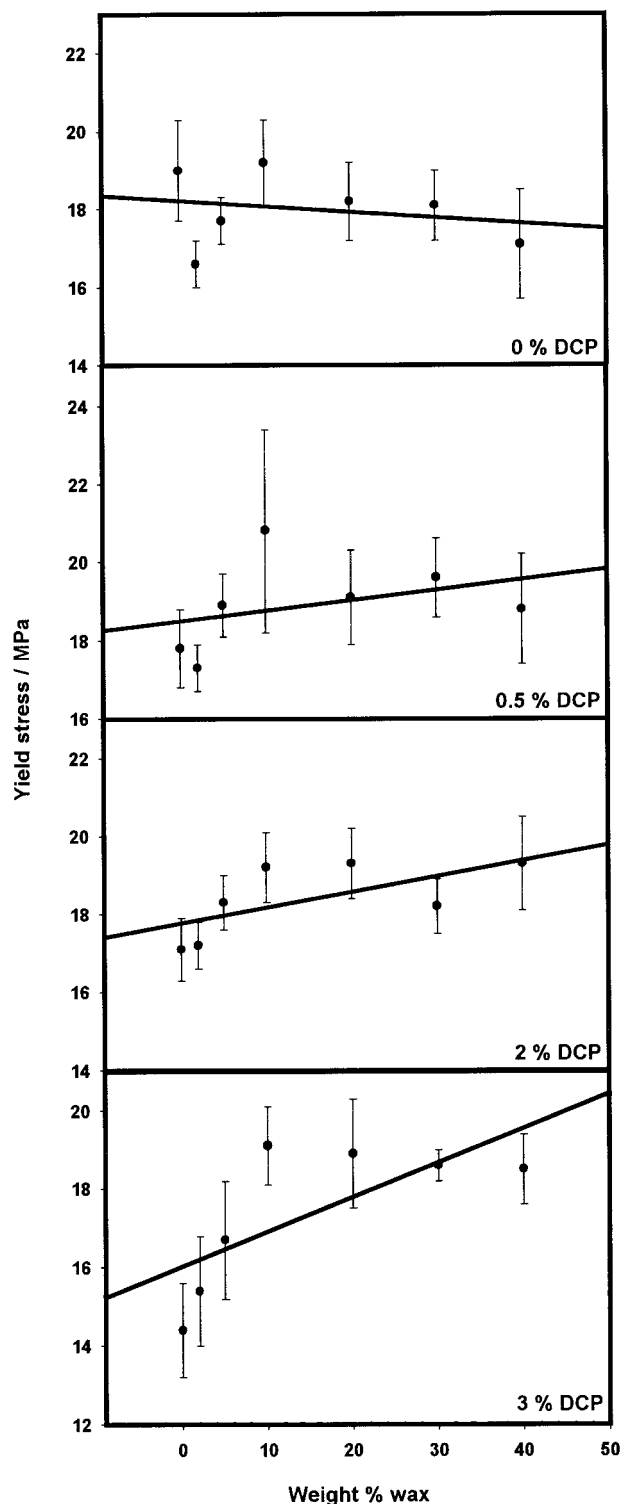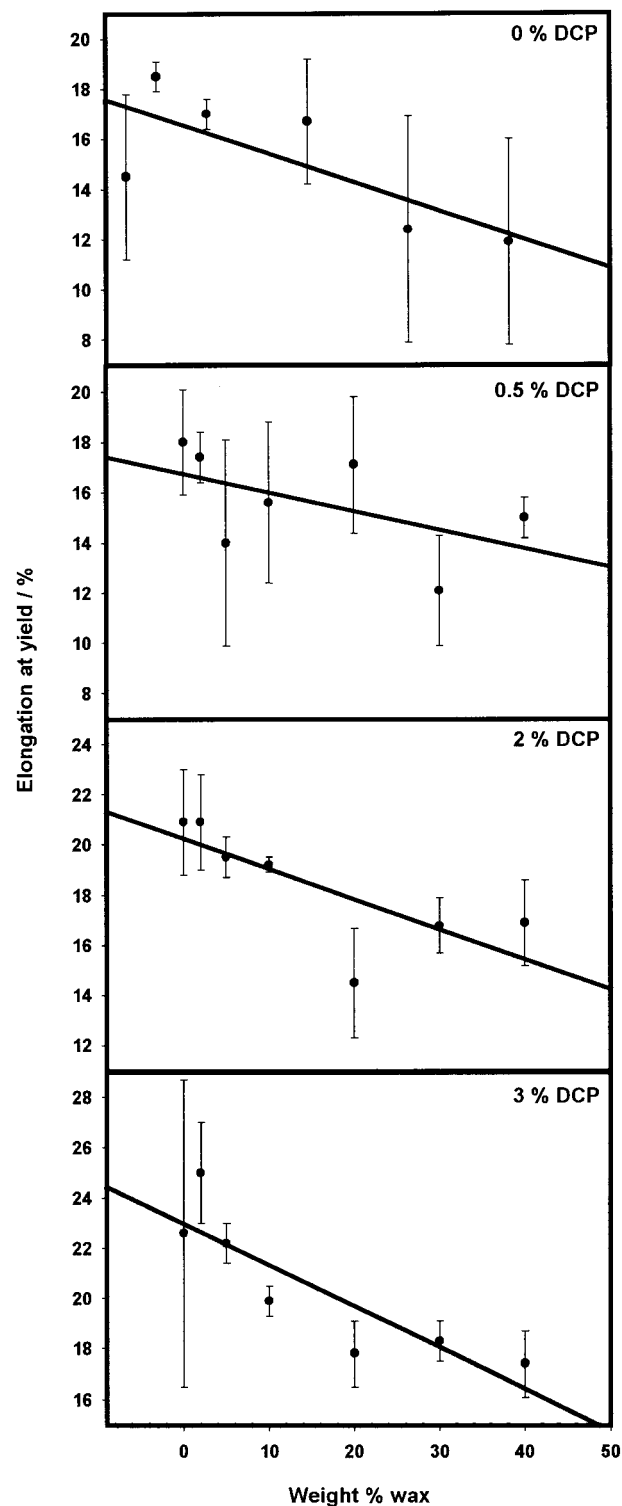

Figure 3 The yield stress as a function of the weight percentage of wax in uncrosslinked and crosslinked LLDPE/wax blends.

the fact that pure wax has three peaks (two of them significant). A probable explanation is that LLDPE and wax are miscible in the crystalline phase.[28]

Figure 4 The elongation at yield as a function of the weight percentage of wax in uncrosslinked and crosslinked LLDPE/wax blends.

meric pairs have usable (usually mechanical) properties.[2] Some authors follow the definition of mechanical compatibility given by Utracki[7]: "If
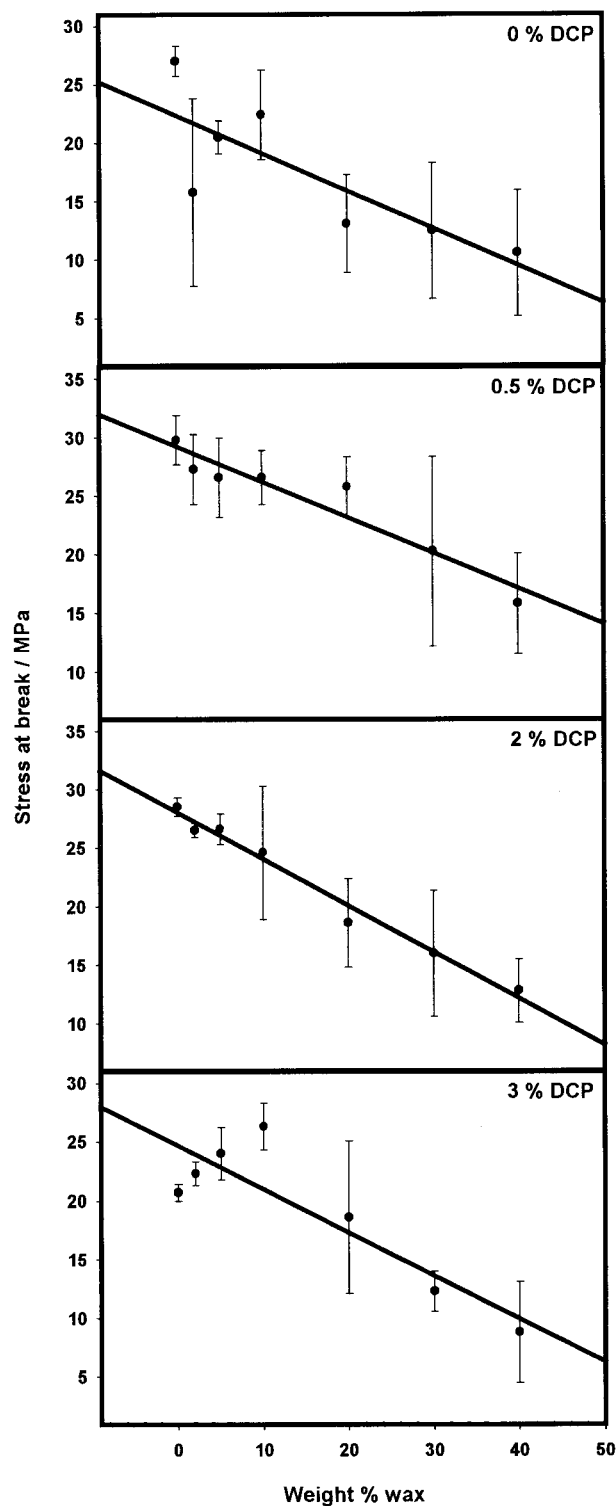

Figure 5 The stress at break as a function of the weight percentage of wax in uncrosslinked and crosslinked LLDPE/wax blends.
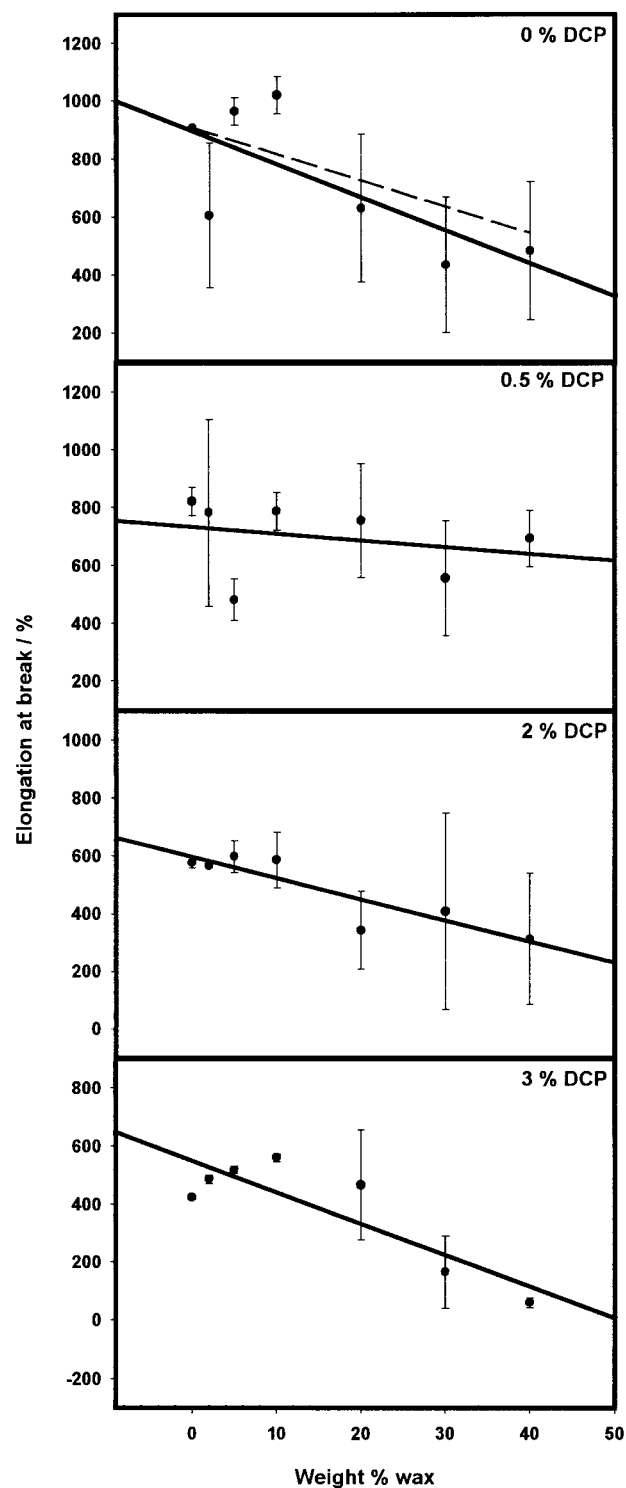

Figure 6 The elongation at break as a function of the weight percentage of wax in uncrosslinked and crosslinked LLDPE/wax blends.

the mechanical properties of the blend conform to a rule of mixture, or to positive deviations from it, then the system is said to be mechanically com-

patible." If the tensile strength and elongation at break of the blends decrease dramatically, this indicates that the components are immiscible by a discrete phase separation.[7] When applying the additive rule to the results of the elongation at break of uncrosslinked blends (Fig. 6, broken line) and neglecting the elongation at break of the wax, no unambiguous conclusions can be drawn.

The miscibility of blends is often characterized by using the log-additive rule,[29]

$$\log \eta = \sum_i w_i \log \eta_I \qquad (3)$$

or the Hayashida et al. equation,[30]

$$1/\eta = \sum_i w_i/\eta_i \qquad (4)$$

where η and η_i are the melt viscosities of the blend and the ith component, respectively, and w_i is the weight portion of the ith component. A strong negative deviation from the log-additive rule indicates that systems are not miscible in the melt.[28]

We applied an equation to our flow rate measurements. Because the flow rate and viscosity of the melt are connected with each other, we can apply eq. (3) in the following form:

$$\log FR = w_{PE} \log FR_{PE} + w_w \log FR_W \qquad (5)$$

where FR, FR_{PE}, and FR_w are the flow rates of the blends, LLDPE, and wax, respectively; and w_{PE} and w_w are the weight portions of LLDPE and wax in the blends, respectively. As we can see in Figure 7, the dependence of the FR on the w_w is perfectly linear. Linear regression of these data gave the following parameters: $\log FR_{PE} = 0.076 \pm 0.015$, $\log FR_w = 1.842 \pm 0.072$, and $R = 0.996$. This indicated mutual miscibility of LLDPE and wax in the melt.

CONCLUSIONS

The mechanical properties of uncrosslinked and crosslinked LLDPE/wax blends and their dependence on the concentration of the crosslinking agent (DCP) and wax portion were investigated. The flow rate of the melt for uncrosslinked blends was also determined. We further investigated the influence of the DCP concentration on the change in the degree of crystallinity.

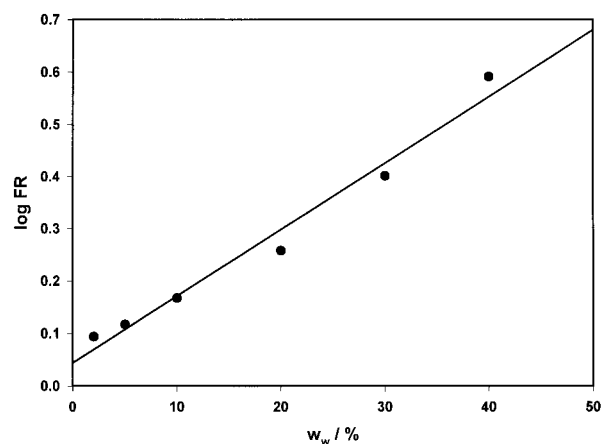A decrease in the degree of crystallinity with an increase in DCP concentration was observed.

Figure 7 The logarithm of the melt flow index (log FR) as a function of the weight percentage of wax (w_w) in uncrosslinked LLDPE/wax blends.

The Young's modulus slowly increased with an increase in the wax portion. This increase was higher for crosslinked blends than for uncrosslinked blends. A small decrease in the yield stress of crosslinked LLDPE was observed when the concentrations of DCP were 0.5 and 2%. If 3% DCP was used, the decrease in yield stress was larger.

Crosslinking caused an increase in the elongation at yield at all concentrations. The increase in the wax portion caused a decrease in the elongation at yield.

Crosslinking had only a small influence on the stress at break for pure LLDPE and blends when the concentrations of DCP were 0.5 and 2%. In the presence of 3% DCP the stress at break increased more. Increasing the wax content caused a decrease in the stress at break at all DCP concentrations.

An increase in the wax portion resulted in a decrease in the elongation at break for the uncrosslinked and crosslinked blends. This decrease was higher for crosslinked blends, especially for DCP concentrations of 2 and 3%. A general decrease in the elongation at break with an increase in DCP concentration for crosslinked LLDPE and blends was observed, because crosslinking reduced PE drawability.

We also investigated the miscibility or compatibility of LLDPE/wax blends. In another article we discussed the thermal properties of these blends, and we concluded that LLDPE and wax may be miscible in the crystalline phase.[28] For this study we applied the additive rule on the results of the elongation at break of uncrosslinked blends, according to the Utracki[7] definition of me-

chanical compatibility. Unfortunately, no unambiguous conclusions could be drawn.

The miscibility of blends is often characterized by using the log-additive rule. Our measurements of the flow rate of the melt of uncrosslinked blends confirmed linear behavior. It seemed as if the LLDPE/wax blends were mutually miscible in the observed concentration region.

REFERENCES

1. Koning, C.; Van Duin, M.; Pagnoulle, C.; Jerome, R. Prog Polym Sci 1998, 23, 707.
2. Paul, D. R.; Barlow, J. W. J Macromol Sci-Rev Macromol Chem 1980, C18, 109.
3. Vasile, C., Seymour, R. B., Eds. Handbook of Polyolefins; Marcel Dekker: New York, 1993.
4. Hashemi, S.; Williams, J. G. Polymer 1986, 27, 384.
5. Mai, Y. W.; Williams, J. G. J Mater Sci 1997, 12, 1376.
6. Ulrich, H. Introduction to Industrial Polymers, 2nd ed.; Hanser: New York, 1993.
7. Utracki, L. A. Polymer Alloys and Blends: Thermodynamics and Rheology; Hanser: New York, 1989.
8. Speed, C. S. Plast Eng 1982, July, 39.
9. Sax, N. I.; Lewis, R. J., Sr. Hawley's Condensed Chemical Dictionary, 11th ed.; Van Nostrand Reinhold: New York, 1987.
10. Olabisi, O.; Robeson, L. M.; Shaw, M. T. Polymer–Polymer Miscibility; Academic: New York, 1979.
11. Chodak, I. Prog Polym Sci 1998, 23, 1409.
12. Gedde, U. V. Polymer 1986, 27, 269.
13. Borsig, E.; Fiedlerova, A.; Lazar, M. J Macromol Sci Chem 1981, A16, 513.
14. Kampouris, E. M.; Andreopoulos, A. G. J Appl Polym Sci 1987, 34 ,1209.
15. Lazar, M.; Rado, R.; Rychly, J. Adv Polym Sci 1990, 95, 149.
16. Andreopulos, A. G.; Kampouris, E. M. J Appl Polym Sci 1986, 31, 1061.
17. Appleby, R. W.; Busfield, W. K. Polym Commun 1986, 27, 45.
18. Bhateja, S. K.; Andrews, E. H. J Appl Polym Sci 1987, 34, 2809.
19. (a) Efimov, A. V.; Valiotti, N. N.; Dakin, V. J.; Ozerin, V. J.; Bakeev, N. F. Vysokomol Soed 1988, A30, 963; (b) Efimov, A. V.; Valiotti, N. N.; Dakin, V. J.; Ozerin, V. J.; Bakeev, N. F. Vysokomol Soed 1988, A30, 2165.
20. Klein, P. G.; Ladizesky, N. H.; Ward, I. M. Polymer 1987, 28, 393.
21. Brink, A.; Dressler, F. Br Polym J 1969, 1, 37.
22. Nhlapo, N. S.; Luyt, A. S.; Vosloo, H. C. M. J Appl Polym Sci 1998, 70, 1551.
23. Wunderlich, B. Macromolecular Physics II; Academic: New York, 1973.
24. Narkis, M.; Reiter, I.; Shkolnik, S.; Siegmann, A.; Eyerer, P. J Macromol Sci Phys 1987, B26(1), 37.
25. deBoer, J.; Pennings, A. J. Polymer 1982, 23, 1944.
26. Kunert, K. A. J Polym Sci Polym Lett Ed 1981, 19, 479.
27. Krupa, I.; Luyt, A. S. Polym Degrad Stabil 2000, 70, 111.
28. Cho, K.; Ahn, T. K.; Lee, B. H.; Choe, S. J Appl Polym Sci 1997, 63, 1265.
29. Utracki, L. A. In American Chemical Society Symposium; American Chemical Society: Washington, DC, 1989; p 153.
30. Hayashida, T.; Takahashi, T.; Matsu, M. In Proceedings of the Fifth International Congress on Rheology; 1970; Vol. 4, p 525.