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CRYSTALLIZATION KINETICS OF LDPE/Ny6 BLENDS

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The crystallization behaviour of low density polyethylene/nylon 6 blends has been investigated as a function of the composition.

The melting points of the polymers are almost uninfluenced by the presence of the other homopolymers except for blends with a nylon content of 75–90%.

Blends with 10% nylon content do not exhibit the crystallization peak during the cooling step probably because of the low concentration and high viscosity of the low density polyethylene matrix.

The crystallinity degree of the polyethylene is independent of the composition, while some variations are shown by the polyamide.

Finally the rate of nucleation is strongly affected by the composition, in particular for the nylon phase.

An attractive way to modify the properties of polymeric materials and improve their cost/performance ratio is to prepare blends of different homopolymers. However, it is well known that the properties of the blends depend on the properties of the pure polymers, on their preparation and on the physical state of each component at a given temperature.

Many works have been performed on the crystallization behaviour of polymeric blends, but only a few studies deal with blends made with components capable of crystallization [1, 2].

Low density polyethylene (LDPE) and nylon 6 (Ny6) form incompatible blends [3–7]. The interest in these blends is now increasing because the incorporation of the LDPE in the polyamidic matrix helps to dissipate energy and then to improve the impact properties of the Ny6.

The aim of this work is to study the crystallization behaviour of low density polyethylene/nylon 6 blends. Several other properties of these blends have already been investigated [5, 6].

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Experimental

The materials used in this investigation were a low density polyethylene and a polycaproamide manufactured by Montedison and SNIA, respectively.

The melt flow index of the LDPE was 0.08 g/10 min (ASTM D 1238/73 method, procedure B) and of the nylon 6 was 10.8 g/10 min (ASTM D 1238/73 method, procedure R).

The blends were prepared by melt mixing the homopolymers in a Brabender Plasticorder mod. PLE 330 at $T = 260°$ and 20 rpm. A mixing time of about 15 min was long enough to get a practically constant value of the torque. Also the homopolymers were subjected to the same treatment.

The wt/wt composition of the blends, φ, was 0, 10, 25, 50, 75, 90 and 100% nylon 6.

All the samples were kept in a vacuum desiccator and in the presence of silica gel for about 7 days before the tests in order to avoid any effect of the moisture.

The calorimetric tests have been performed with a Perkin–Elmer differential scanning calorimeter, DSC 4, linked to a Data Station Perkin–Elmer mod. 3600.

The following standard procedure was used: the sample (about 15–20 mg) was heated up to 250° at a 20 deg/min heating rate; after 2 min they were kept at this annealing temperature, then they were cooled down to 50° at a cooling rate of 20 deg/min. In a further heating run carried out at 20 deg/min, the crystallinity, x_c, and the melting point, T_m, of each component were calculated. The crystallization temperature, T_c, was evaluated during the cooling step.

Specimens of the blend with $\varphi = 10\%$ were analyzed by a light transmission microscope at a magnification of 150 × between crossed polarizers.

The microscope was a Leitz Laborlux 12 POL equipped with a heating stage and photographic equipment.

Results and discussion

The thermal curves of all the investigated blends show two distinct peaks. This feature indicates that the blends are completely incompatible.

The crystallization temperature and the melting points, T_m, taken as the peak temperatures of the thermal curves are reported in Fig. 1 *vs.* the composition.

The crystallization temperatures do not exhibit any change with the composition except for the blend with $\varphi = 10\%$. In this case, in fact, no exothermic peak is revealed for the nylon 6, although the subsequent heating step exhibits the usual melting peak of the nylon phase. This unusual feature can be due both to the low crystallization heat and to the very slow crystallization kinetics of the nylon because

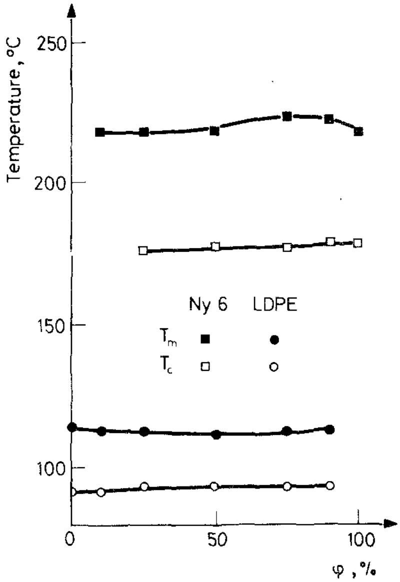

Fig. 1 Melting temperature, T_m, and crystallization temperature, T_c, as a function of the nylon content

of its low concentration and the high viscosity of the low density polyethylene matrix.

Photographs taken during the cooling step in the hot stage of the optical microscope, Fig. 2, show that also for the blend with $\varphi = 10\%$ the crystallization of the nylon phase starts at about 180°.

The melting point of the low density polyethylene is, within the experimental error, independent of the nylon content. The melting point of the nylon is unchanged when the LDPE content is less than 50%, then rises by about 6–7° for nylon contents of about 70–90%.

A zero shift in melting points indicates a complete lack of interaction [7], while some lowering of T_m suggests miscibility of the two crystalline phases [8, 9]. Moreover other properties, electrical [5] and mechanical [6], show some unusual features in this composition range.

A possible explanation of this feature will be given in the following.

The crystallinity degree, x_c, of the two components is reported in Fig. 3 as a function of the nylon content. x_c remains essentially independent of the composition for the low density polyethylene.

As for the polyamide, the blends in the composition range 25–90% show a small inceease of the crystallinity, especially for the blend with $\varphi = 90\%$.

Only the blend with a nylon content of 10% seems to exhibit a remarkable

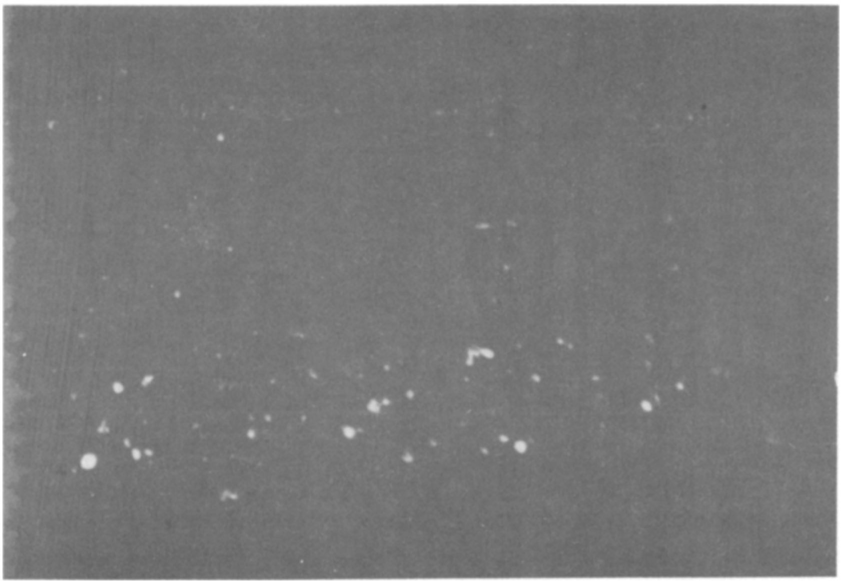

Fig. 2 Optical micrograph of the blends with $\varphi = 10\%$ at 180°

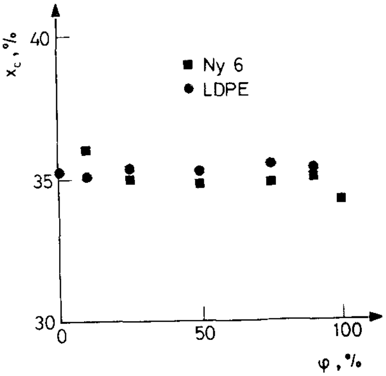

Fig. 3 Crystallinity degree as a function of the nylon content

increase in the crystallinity degree. This is due, probably, to the long time available for the crystallization of this material.

In Fig. 4 the initial slopes of the crystallization exotherms of both components are reported as a function of the nylon content. This quantity, S, has already been used [10] as a measure of the rate of nucleation.

It is evident that the rate of nucleation is strongly dependent on the composition

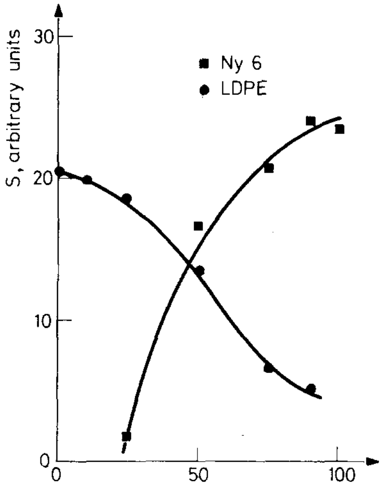

Fig. 4 Rate of nucleation as a function of the nylon content

and, in particular, for each component S falls down quickly with increasing concentration of the other component.

These two curves provide a direct confirmation of the unusual feature shown by the blends with $\varphi = 10\%$. Indeed, the rate of nucleation of the nylon is already very low at a concentration of 25%, and of course becomes still lower on decreasing the content of nylon. As for the low density polyethylene, on the contrary, the rate of nucleation is sufficiently high also for blends with a large nylon content.

It is worth mentioning that at low LDPE content this rate of nucleation is very similar to that of the nylon and for the blend with $\varphi = 90\%$ it is slightly larger than that of the pure polyamide.

The slight increase of the crystallinity accompanied, at least for the blend with $\varphi = 90\%$, by a faster rate of nucleation implies a larger number of small crystalline domains of nylon and a slight elevation of the melting point [11].

* * *

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Zusammenfassung — Die Abhängigkeit des Kristallisationsverhaltens von 6 Polyethylen/Nylon-Gemischen geringer Dichte von der Zusammensetzung wurde untersucht. Der Schmelzpunkt eines jeden Polymers ist nahezu unbeeinflußt von der Anwesenheit des anderen Homopolymers ausgenommen die Gemische mit einem Nylongehalt von 75–90%. Die Gemische mit einem Gehalt von 10% Nylon zeigen während des Abkühlungsschrittes keinen Kristallisationspeak, was wahrscheinlich auf die niedrige Konzentration und auf die hohe Viskosität der Polyethylenmatrix mit geringer Dichte zurückzuführen ist. Der Kristallinitätsgrad des Polyethylens ist unabhängig von der Zusammensetzung, während ein Einfluß des Polyamids festzustellen ist. Die Keimbildungsgeschwindigkeit ist stark von der Zusammenstzung abhängig, was besonders für die Nylonphase gilt.

Резюме — Изучен характер кристаллизации смесей полиэтилен низкой плотности — найлон 6 в зависимости от их состава. В случае смесей, содержащих 75—90% найлона, точка плавления полимеров почти не затрагивается наличием других гомополимеров. Смеси с 10% содержанием найлона при охлаждении не показывают пика кристаллизации, что, повидимому, обусловлено низкой концентрацией найлона и высокой вязкостью полиэтилена низкой плотности. Степень кристалличности полиэтилена не зависит от состава смеси, тогда как для полиамида наблюдаются некоторые изменения. Скорость образования центров кристаллизации, особенно для найлона, сильно зависит от состава смесей.