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Crystallization behaviour of isotactic polypropylene blended with *trans*-octenylene rubber

W. WENIG
Laboratorium für Angewandte Physik, Universität-GH-Duisburg, 4100 Duisburg 1, Germany

The crystallization behaviour of isotactic polypropylene (iPP) blended with *trans*-octenylene rubber (TOR) has been investigated by optical microscopy. It is found that crystallization kinetical parameters like nucleation densities, Avrami exponents and spherulitic growth rates are strongly dependent on the TOR concentration in the blend. While at 10% TOR content the nucleation density passes through a maximum, both the Avrami exponent and the spherulitic growth rate are minimal. Due to an increased dispersion of TOR in iPP at 10% TOR concentration and the subsequent formation of interfaces, the nucleation changes from preferentially homogeneous to preferentially heterogeneous. The concentration of *trans* double bonds in the TOR chain has no influence on the crystallization behaviour of the samples.

1. Introduction

When isotactic polypropylene (iPP) is solution-blended with *trans*-octenylene rubber (TOR. systematic name: *trans*-polyoctenylene), it exhibits mechanical and morphological properties which are strongly dependent on sample composition: the elastic modulus, which is generally (as observed for all rubber-modified thermoplastics [1–6]) a monotonically decreasing function of increasing TOR-concentration, passes through a maximum between 10 and 20 wt % TOR.

In a recently published paper [7] we have investigated the correlation between the mechanical behaviour and morphological properties of iPP blended with TOR containing 80% *trans* double bonds. X-ray investigations revealed that the order of the lamellar domains (number of orientation-correlated lamellae) is well correlated with the composition dependence of the elastic modulus. This order seems to be a consequence of a higher dispersion of TOR at concentrations of about 10%, which is concluded from a steep increase of the stack height at this particular composition.

It can be expected that this change of the supermolecular order is a consequence of the crystallization kinetics of the blend. In this paper we present the results of investigation of the crystallization behaviour of blends of iPP with two types of TOR differing in the concentration of *trans* double bonds.

2. Experimental procedure

2.1. Sample preparation

Isotactic polypropylene with a molecular weight $\bar{M}_w = 468\,000$ and two samples of *trans*-octenylene rubber with a molecular weight $\bar{M}_w = 123\,000$ (60% *trans*) and $\bar{M}_w = 89\,000$ (80% *trans*) were dissolved in hot xylene and precipitated into a large excess of methanol. A quantity of the dried material was placed between the plates of a hydraulic press and heated to a temperature well above the melting point of polypropylene at a pressure of 10 kN. After switching off the press the sample was allowed to cool down to room temperature. The resulting thickness of the sample amounted to $\simeq$ 30 μm.

2.2. Measurements

The crystallization of the samples was observed in an optical microscope (Leitz Metallux II). For this purpose the samples were placed between microscope slides and put in a Mettler hot stage. Here they were heated up to 200 °C for 5 min and then cooled down to the chosen crystallization temperature. Crossed polarizers were used and the crystallization was monitored on a video screen and recorded on tape. For quantitative investigations the microscope image was digitized and fed into a computer. From these images, the growth of the spherulites as well as the development of the number of nuclei as a function of time was determined. The crystallization temperatures for the isothermal crystallization were chosen between 120 and 139 °C. Each crystallization experiment was carried out five times at different locations of the sample to allow an error analysis. It turned out that both the spherulitic growth rate as well as the number of nuclei as a function of time could be measured with great accuracy.

3. Results and discussion

In microscopic experiments, for a given crystallization temperature the number of nuclei develops as a function of time in the observed volume [8, 11–15]

$$N(t) = M[1 - \exp(-\nu t)] \qquad (1)$$

with M the nucleation density and ν the probability of nuclei development per unit time. The crystallization half-time is then calculated as

$$t_{1/2} = \frac{\ln 2}{\nu} \qquad (2)$$

The number of nuclei can be determined by determination of the number and size of the growing spherulites and extrapolation of their sizes (radii) to $r = 0$ [16].

The nucleation density is a function of the temperature. This dependence can be described by a cumulated Gauss function [11]

$$\begin{aligned} M(T) &= M_0[1 - \mathrm{erf}(T_c - \bar{T})] \\ &= M_0\left[1 - \frac{1}{\sigma(2\pi)^{1/2}} \times \int_{-\infty}^{T_c} \exp\left(-\frac{x - \bar{T}}{2\sigma^2}\right) \mathrm{d}x\right] \end{aligned} \qquad (3)$$

with T_c the crystallization temperature and $\bar{T}$ the mean temperature at which sites nucleate. Fig. 1 shows $M(T)$ for the sample containing 15% TOR (60% *trans*). We see that the total nucleation density M_0 is taken from the maximum and $\bar{T}$ from the point of inflection of the curve.

The total nucleation density, M_0, is displayed in Fig. 2 as a function of TOR concentration. It shows a characteristic dependence on the TOR content: up to $c_{TOR} = 0.05$ and for $c_{TOR} > 0.15$, M_0 is smaller than the value for iPP. For TOR concentrations $0.05 < c_{TOR} < 0.15$ the total nucleation density passes through a maximum. This may indicate a change of the kind of the nucleation from thermal to athermal.

A measure for the kind of nucleation is the Avrami exponent [17–19]. It can be derived from the Avrami equation which describes the development of the crystallinity in a crystallizing spherulite as a function of time [9, 10, 17–20]

$$X_c(t) = 1 - \exp(-kt^n) \qquad (4)$$

where $X(t)$ is the volume crystallinity at time t, k is the characteristic constant and n is the Avrami exponent.

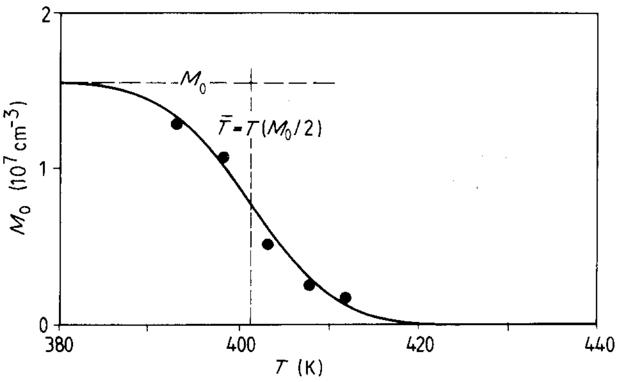

Figure 1 Nucleation density as a function of temperature for the sample containing 15% TOR (60% *trans* content).

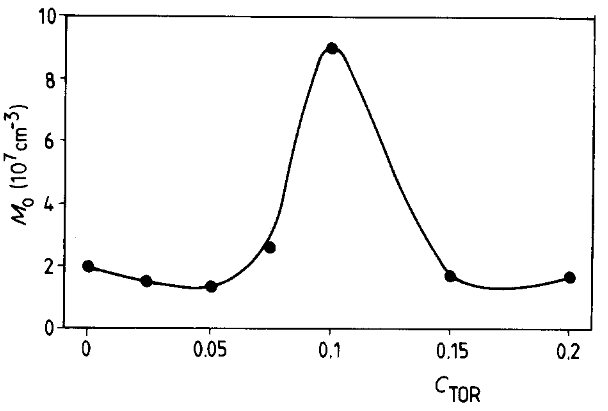

Figure 2 Total nucleation density taken from the maximum of the curve $M(T)$ (cf. Fig. 1) for the sample containing 15% TOR (60% *trans* content).

The parameters n and k can be determined by plotting

$$\log[-\ln(1 - V_{sph})] = n \log t + \log k \qquad (5)$$

with $V_{sph} = V_{sph.abs}/V_{obs}$ where $V_{sph.abs}$ is the absolute volume of crystallized spherulitic material and V_{obs} is the observed volume fraction of spherulites. Equation 5 yields a straight line from whcih n can be taken from the slope and k from the intercept.

In our experiments the volume of the spherulites was determined from the area of their cross-sections. In this case the crystallinity of the spherulites has to be taken into account. By determining the crystallization half-time $t_{c.1/2}$ – the time elapsed when half the volume is crystallized – the Avrami exponent can be correlated with $t_{c.1/2}$

$$n = \frac{\log(3 \ln 2/4\pi G^3 N)}{\log t_{c.1/2}} \qquad (6)$$

where G is the spherulitic growth rate and N is the number of nuclei.

Fig. 3 displays the results of the calculations. n is averaged over all crystallization temperatures. We see that n assumes values around 3.5 for low TOR concentrations but drops down to $n \sim 3$ for $c_{TOR} = 0.1$. For higher TOR concentrations n increases again. For the given crystallization conditions, the Avrami exponent should assume the value $n = 3$ for athermal and $n = 4$ for thermal nucleation [10, 21]. Obviously, for the sample containing 10% TOR the nucleation is athermal but for all other TOR concentrations preferably thermal. We can assume that for this kind of iPP nucleation foreign pre-existing surfaces are present in the samples, which can only be provided by the TOR component. Nucleation at PP–TOR interfaces then means that at $c_{TOR} = 0.1$ the nucleation is preferentially heterogeneous, while it is preferentially homogeneous for all other TOR concentrations.

It is difficult to determine the absolute value of the Avrami exponent with great accuracy. A possible truncation effect of spherulitic growth [21, 22] would lower the Avrami exponent so that we have a mixture of homogeneous and heterogeneous nucleation in the samples at all compositions. It is, however, possible to conclude that the drop of n at 10% TOR content is connected with an increase of the TOR surface area.

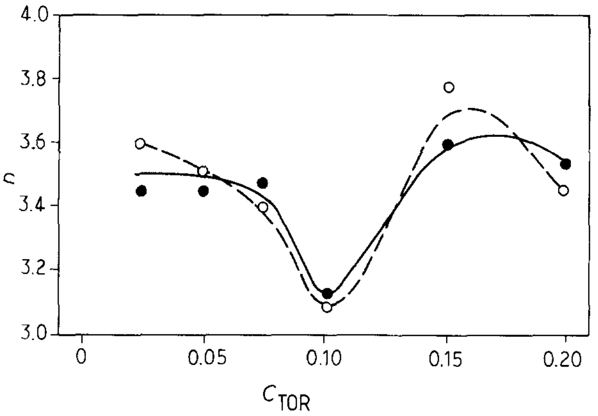

Figure 3 Avrami exponent (average over all crystallization temperatures) for iPP blended with (——) 60%-*trans* TOR and (---) 80%-*trans* TOR.

At this composition the TOR component is less agglomerated than at other concentrations, thus providing (through enhanced dispersion) a higher interface area.

If this concept proves to be correct, we should expect that an increasing dispersion of TOR in iPP leads to a hindrance of the spherulitic growth. The spherulitic growth rate, G, should therefore be minimal at $c_{TOR} = 0.1$.

A growing spherulite changes its radius linearly as a function of time

$$r(t) = r_0 + Gt \qquad (7)$$

where r_0 is the radius of the spherulite at $t = 0$ and G is the growth rate. G is a function of the crystallization temperature. This dependence can be calculated from the following expression [23–25]:

$$G(T_c) = G_0 \exp\left(\frac{-C_1 C_2}{C_2 + T_c - T_g}\right) \exp\left(\frac{-C_3}{T_c(T_m - T_c)}\right) \qquad (8)$$

where T_g is the glass transition temperature, T_m is the melting temperature and G_0, C_1, C_2 and C_3 are constants. G_0 and C_3 can be determined from a plot of $\ln G + C_1C_2/(C_2 + T_c - T_g)$ against $1/[T_c(T_m - T_c)]$, while the values for C_1 and C_2 are taken from the literature ($C_1 = 25$, $C_2 = 30$ K) [11].

The result is shown in Fig. 4 for two crystallization temperatures. Indeed the growth rate drops down for samples containing 10% TOR. Together with the other results we can thus conclude that the dispersion of TOR in iPP is strongly dependent on sample composition. While for most compositions we find a mixture of homogeneous and heterogeneous nucleation with a preference of homogeneous nucleation within the PP phase and heterogeneous nucleation at the iPP–TOR interfaces, heterogeneous nucleation becomes predominant in the sample containing 10% TOR. The distribution of TOR changes drastically at this composition, leading to a finer dispersion of the rubber in the iPP matrix. Possibly, this is an effect of the phase inversion of the system. Considering the molecular weights of the two components ($\bar{M}_{w,iPP} = 468\,000$, $\bar{M}_{w,TOR} = 123\,000$) related to their densities ($\rho_{iPP} = 0.905$ g cm^{-3}, $\rho_{TOR} = 0.91$ g cm^{-3}), we expect the phase inversion at $c_{TOR} = 0.13$. Taking into account that the molecular weight distribution of TOR is bimodal with a first maximum at very low molecular weights (< 1000) [26], we find the phase inversion around $c_{TOR} = 0.1$. This leads to an enhanced distribution of TOR in the sample at this particular composition.

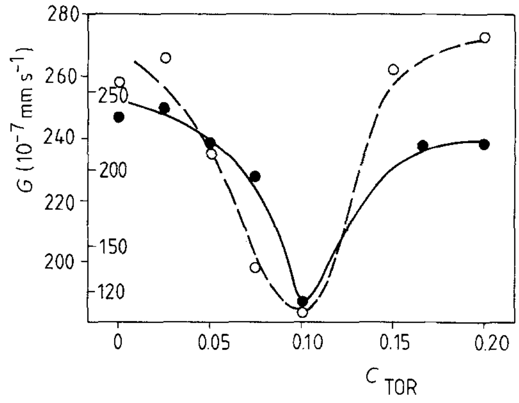

Figure 4 Spherulitic growth rate for the blends iPP–60%-*trans* TOR: (——) $T_c = 125$ °C, (---) $T_c = 135$ °C.

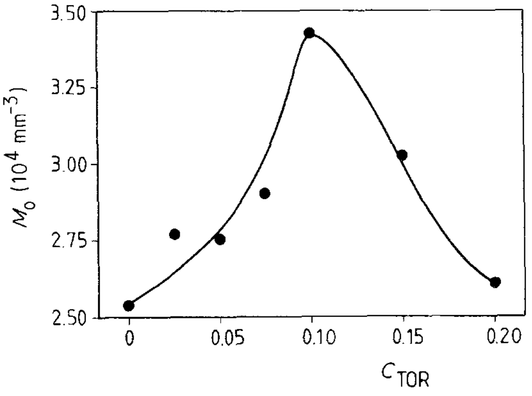

Figure 5 Total nucleation density for the blend iPP–80%-*trans* TOR.

It is possible to investigate the influence of the configuration of the TOR chain, i.e. the concentration of *trans* double bonds, by comparing the results presented above with those obtained from iPP–TOR blends containing TOR with a *trans* content of 80%. This TOR is crystallizable ($X_c = 30\%$) and has a slightly higher melting temperature.

The total nucleation density (Fig. 5) shows in principle the same dependence. The maximum is broader than for the 60%-*trans* TOR, but it also appears at 10% TOR content. Also the Avrami exponent (Fig. 3) shows an almost identical course when plotted versus the TOR concentration. This confirms our assumption that only the presence of a TOR interface is responsible for the observed crystallization effects.

These results agree well with findings of Martuscelli *et al.* [27], who investigated the crystallization of iPP–EPDM and iPP–PIB blends. These authors deduce a semi-compatibility of iPP with both elastomers, although in the case of polyisobutylene this semi-compatibility seems to be dependent on the molecular weight. As for the system iPP–TOR, we would not go so far as to conclude a semi-compatibility. We should then find a specific hindrance of the crystallization and probably the formation of mixed crystals, which is not the case, as we showed by X-ray investigations [7].

4. Conclusions

1. The crystallization behaviour of iPP–TOR blends is strongly dependent on the composition of the samples.

2. At 10% TOR content the total nucleation density passes through a maximum, while the Avrami exponent and the spherulitic growth are at a minimum.

3. For TOR concentrations of 10% the nucleation changes from preferentially homogeneous to preferentially heterogeneous.

4. At this TOR concentration the TOR is more finely dispersed in the sample, providing interfaces for heterogeneous nucleation of iPP nuclei.

5. The concentration of *trans* double bonds in the TOR chain has no influence on the crystallization behaviour of iPP–TOR blends.

6. A possible semi-compatibility of iPP and TOR, as discussed by other authors for blends of iPP with EPDM and PIB, cannot be concluded from the results presented in this paper.

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