A study on the crystallization behaviour of polypropylene, polyethylene and their blends by dynamic mechanical and thermal methods

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Studies on the crystallization of polymers are usually carried out by dilatometry, differential scanning calorimetry (d.s.c.) and optical microscopy. These methods have been widely used in the analysis of crystallization kinetics using the Avrami equation. Direct determination of nucleation rate and density is only possible by the optical microscope technique. We have employed a new technique for studying the crystallization behaviour of polymers by using a dynamic mechanical method. This method is capable of detecting the onset of nucleation. Semiquantitative data on the nucleation density and the initial crystallization rate may also be deduced by this method. Results from the dynamic mechanical method are cross-compared with d.s.c. and optical microscope data for polypropylene, polyethylene and their blends, and are shown to be mutually consistent.

(Keywords: crystallization behaviour; dynamic mechanical method; blends)

INTRODUCTION

Crystallization kinetics studies of polymers are commonly carried out with dilatometry, optical microscopy and differential scanning calorimetry[1-3]. These methods follow the crystallization process by monitoring the changes in physical properties of density (dilatometry), spherulite size (optical microscopy) and enthalpy of fusion (d.s.c.), and the data are usually interpreted and analysed with the aid of the Avrami equation. Out of these three methods, only the optical microscopy technique allows direct determination of the nucleation density. Even in this case, measurement of the nucleation density could be a tedious process, although the method could be improved by utilizing a video recorder and a computerized digital imaging analysis technique[4,5].

Dynamic mechanical testing has long been employed in the study of the viscoelastic response of polymers. The technique has recently been extended to the study of entanglement spacing of polystyrene melts[6], crosslinking in polyethylenes[7], fusion of poly(vinyl chloride)[8] and gelation of thermoplastic elastomer[9]. We report here a preliminary study on the crystallization behaviour of polyethylene (PE), polypropylene (PP) and PE/PP blends using a new dynamic mechanical technique.

THEORY

A Rheometrics RMS 605 mechanical spectrometer allows continuous monitoring of the rheological response of a polymer during a temperature-sweep test (either for a constant-cooling-rate or constant-heating-rate experiment) or a time-sweep test (isothermal 'cure' experiment). At temperatures well above the glass transition temperature and melting point of a polymer, the plateau elastic modulus measured represents the state of the physical entanglements and chemical crosslinks of the system. From the theory of rubber elasticity, the modulus is proportional to the total number of physical and chemical crosslinks and may be expressed (without allowance for dangling chain ends) as[10]:

$$G = n\rho RT \tag{1}$$

where G = elastic shear modulus (Pa), n = total number of crosslinks (mol kg^{-1}), ρ = density (kg m^{-3}), R = universal gas constant = 8.322 mol kg^{-1} K^{-1} and T = temperature (K).

Table 1 summarizes the typical values of modulus for low and high crosslink densities for peroxide-vulcanized natural rubber and computed number of crosslinks, n, for polypropylene melt and solid polypropylene from their elastic shear modulus. The predicted molecular weight between crosslinks ($M_c = 1/n$) for PP is in the range of 2×10^6 g mol^{-1} for the melt at 212°C. It can be seen that, for the PP melt, the theory of rubber elasticity predicts an M_c value much higher than the M_n of the PP ($\approx 40\,000$), indicating that there are very few entanglements in the melt at that temperature.

It is envisaged that, during the crystallization process, the nuclei formed will act like physical entanglements, hence increasing the modulus of the melt. However, the change in modulus from 10^3 to 10^8 Pa from the melt to the solid is not entirely due to the formation of nuclei or entanglements. As crystallization proceeds, the nuclei develop into spherulites, which increase in size with time.

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Table 1 Typical values of crosslink density for vulcanized natural rubber and polypropylene

	n (mol kg^{-1})	ρ (kg m^{-3})	Temperature (K)	Modulus, G (MPa)
Natural rubber (low cross-link density)	0.01	920	298	0.0230
Natural rubber (high cross-link density)	1	920	298	2.280
Polypropylene (melt)	0.0005	750	485	0.00150
Polypropylene (solid)	–	905	298	110

With the complete development of the spherulites from nuclei, the crystallizing system may now be envisaged as a composite composed of a matrix of polymer melt of modulus of elasticity in the range of 10^3–10^4 Pa and a dispersed spherical hard phase of modulus in the range of 10^8 Pa. In this case, the analysis of Nielsen[11] for particulate-filled polymers may be employed. Here, in the simplest case, for rigid particles in very dilute concentrations, Einstein's equation gives:

$$\eta = \eta_1(1 + k_E\phi_s) \quad (2)$$

or

$$G = G_1(1 + k_E\phi_s) \quad (3)$$

where η = viscosity of suspension, η_1 = viscosity of melt, k_E = Einstein coefficient ($k_E = 2.5$ for dispersed spheres), ϕ_s = volume fraction of the solid phase (spherulites), G = shear modulus of the suspension and G_1 = shear modulus of the melt.

For the entire concentration range, the more appropriate Mooney equation is usually used[12]:

$$\ln(G/G_1) = k_E\phi_s/(1 - \phi_s/\phi_m) \quad (4)$$

where ϕ_m = packing factor for maximum volume fraction. Another commonly used equation is the Kerner–Halpin–Tsai equation in the following form[13]:

$$G/G_1 = (1 + AB\phi_s)/(1 - B\Phi\phi_s) \quad (5)$$

where A, B and Φ are functions of Poisson's ratio, modulus ratio and maximum packing fraction of the solid and melt.

Hence by monitoring the shear modulus of the system as it cools from the melt, we can compute ϕ_s, and hence the amount of crystalline phase. The theoretical plots of Einstein equation, Mooney equation and Kerner–Halpin–Tsai equation for a PP melt matrix ($G_1 = 10^3$ Pa) and PP spherulite dispersed phase ($G = 10^8$ Pa) are shown in *Figure 1*. Here the melt is assumed to be incompressible, with a Poisson's ratio $v_1 = 0.5$, and random loose packing of spherulites is assumed where $\phi_m = 0.601$. It should be noted that for $\phi_s \geq \phi_m$, phase inversion is taking place, and this corresponds to spherulite impingement in the case of a crystallizing mass. The theory also predicts an initial increase of an order of magnitude in modulus for $\phi_s = 0.38$ in the case of the Mooney equation and $\phi_s = 0.60$ in the case of the Kerner–Halpin–Tsai model. It should also be noted that the theories did not take into consideration the effect of particle size and particle size distribution.

The dependence of G and G_1 on temperature is given by equation (1). In the case of constant rate of cooling, a change in the temperature over a range of 40°C corresponds to a change of 10% in modulus, and is negligible compared with a change of three to four orders in magnitude of the measured values.

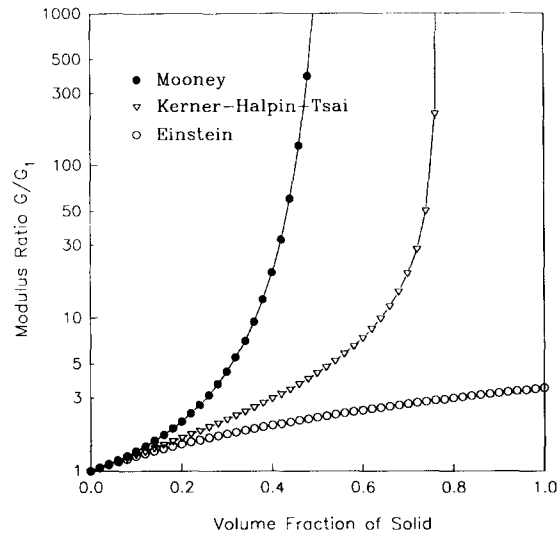

Figure 1 Theoretical predictions of the relative modulus of a composite as a function of the volume fraction of the rigid phase by Einstein, Mooney and Kerner–Halpin–Tsai equations

From the above discussion, it is postulated that, in the case of a crystallizing mass, the initial increase in modulus is due to the formation of nuclei (nucleation process) where the nuclei act as entanglement points, and any subsequent further increase in modulus is the result of the development and growth of the spherulites where the modulus change is mainly due to an increase in ϕ_s.

EXPERIMENTAL

Injection-moulding-grade Shell polypropylene (PP) ($MFI = 20$, at 230°C) and DuPont high-density polyethylene (HDPE) ($MFI = 13$, at 190°C) were used in the present study. Pelletized blends of PP and HDPE of compositions from 0 to 25 wt% HDPE were obtained by melt blending the PP and HDPE in a co-rotating twin-screw extruder as described previously[14]. Dumbbell tensile specimens (ASTM D638 Type 1) were injection moulded directly from the physically mixed pellets and also from the melt-blended pellets.

The pellets (approximately 1.0 g) were introduced between the 25 mm diameter parallel plates of the Rheometrics 605, and compression moulded into a molten disc of 2 mm thickness at a temperature of 180°C. The sample was held at the melt temperature of 180°C for 20 to 30 min to ensure complete melting and destruction of the crystallites. The sample was enclosed by the parallel plates and surrounded by nitrogen gas,

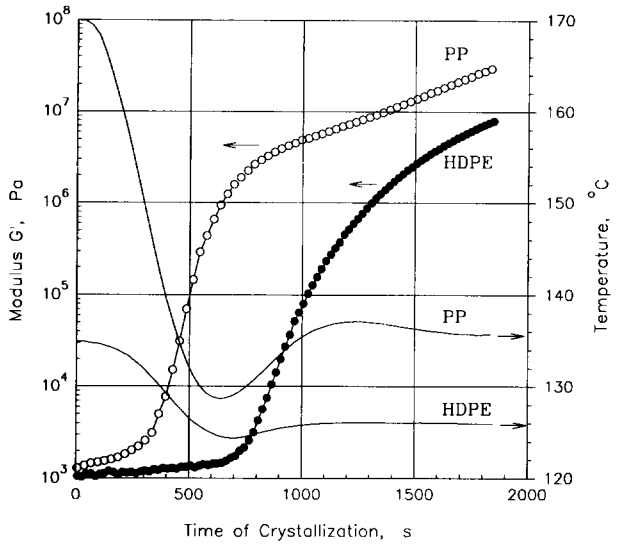

Figure 2 Dynamic mechanical curves showing the change in shear modulus with time for isothermal crystallization test for polypropylene and high-density polyethylene

in order to minimize thermo-oxidative degradation. Dynamic mechanical properties were obtained using a low strain of 0.8% at a frequency of 1 rad s^{-1}. The reasons for choosing a low value of frequency and strain were to ensure that the dynamic shearing would not disrupt or disturb the crystallization process, and to ensure that the measurement could be carried out to the largest extent of crystallization before the torque exceeded the maximum value limited by the load transducer.

Isothermal crystallization studies were carried out by rapidly cooling the sample from the initial high melt temperature (170°C in the case of PP and blends, and 135°C in the case of HDPE) down to the crystallization temperature desired. Owing to the large time constant associated with the temperature control system, an ideal step change in temperature was not possible, and an undercooling in temperature due to overshoot (the magnitude of which was dependent on the rate of cooling) was unavoidable. The extent of undercooling has a larger effect on the nucleation in the case of PP than HDPE. The results from the dynamic mechanical test were compared with those obtained from the optical microscopy isothermal crystallization study under the same conditions, assuming that the very low shear rate in the case of dynamic mechanical test has negligible effect.

A constant-cooling-rate study was also carried out. Since both the nucleation and the growth processes were temperature- and time-dependent, the constant-cooling-rate experiment was a non-equilibrium situation. The results were compared with those obtained from the differential scanning calorimetry crystallization study employing the same conditions, ignoring the very low shear-rate effect on crystallization in the case of the dynamic mechanical test.

RESULTS AND DISCUSSION

Isothermal crystallization of homopolymers

The typical isothermal crystallization behaviour of PP and HDPE from the dynamic mechanical tests are shown in *Figure 2*, where the shear modulus was plotted as a function of time of crystallization in a semi-logarithmic plot. Sigmoidal curves were observed. The corresponding change in temperature with time is also shown in the same plot. In the case of PP, the temperature was programmed to cool down from 170°C (initial melt temperature) to 136°C (final isothermal crystallization temperature) at a cooling rate of 10°C min^{-1}. In the case of HDPE, the initial temperature was 135°C, and the final isothermal crystallization temperature was 126°C, at a cooling rate of 2°C min^{-1}.

Figure 3 shows the superimposed curves of the data from the isothermal crystallization studies by the dynamic mechanical method (shear modulus curve *versus* time) and by the hot-stage optical microscopy method (spherulite diameter *versus* time). Initially, the shear modulus curve showed a slight increase as the temperature decreased from 170 to 150°C corresponding to the time from 0 to 300 s (curve a–b). From 300 to 600 s (curve b–c), a rapid increase in modulus from 2.5×10^3 to 4.0×10^5 Pa was observed. In the corresponding hot-stage microscope study, no detectable crystalline entity was observed during this period. For crystallization times from 600 to 1000 s (curve c–d), a gradual slowdown in the increase in modulus was observed. During this same period, a detectable crystalline entity of 2–5 μm size was observed to grow rapidly, initially to 20 μm, forming a fully developed spherulite. From 1000 s onwards (curve d–e), optical microscope observation gave the characteristic result of constant radial growth rate of PP spherulite under isothermal crystallization conditions. The semi-logarithmic plot of the shear modulus *versus* time of crystallization also gave a linear curve after 1000 s.

It is postulated that when the PP melt is cooled to temperatures below 150°C, at point 'b', nucleation of PP commences, and this results in a rapid increase in modulus from 300 to 600 s. After approximately 600 s, at point 'c', the instantaneous nucleation process was completed (as the temperature reached the minimum undercooling), and the increase in modulus from 600 to 1000 s is due to the development of spherulites from the nuclei. From 1000 s onwards, the increase in modulus is due to the spherulite growth, which results in an increase in ϕ_s of the crystallizing mass. Hence it can be seen that the dynamic mechanical method allows detection of the onset of

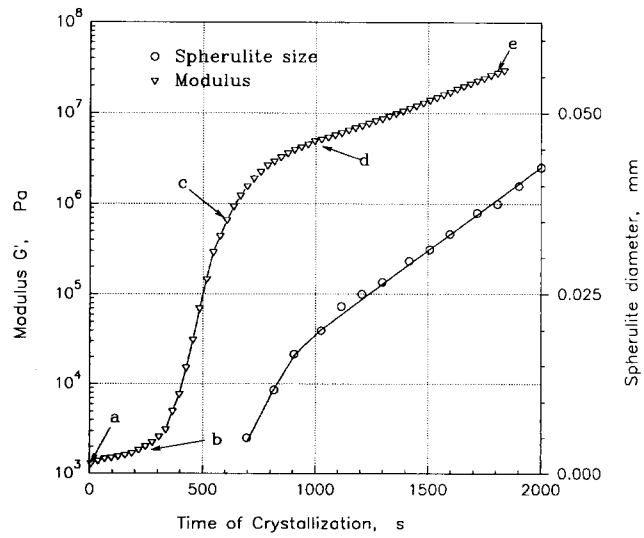

Figure 3 Comparison of isothermal crystallization behaviour of polypropylene at 136°C studied with the dynamic mechanical test (shear modulus) and hot-stage microscope (spherulite diameter)

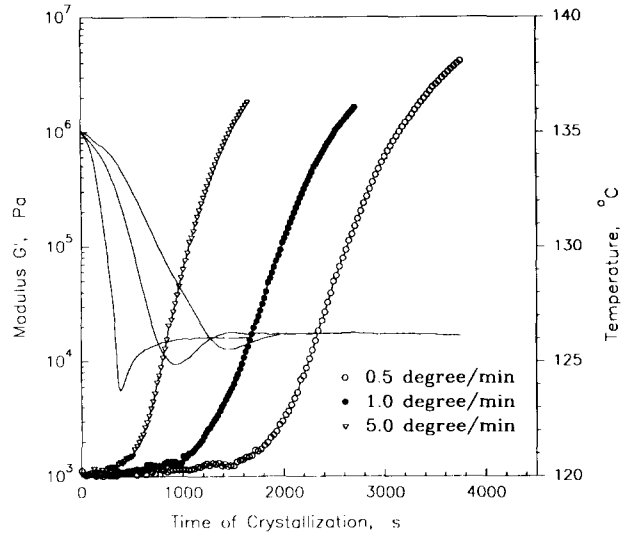

Figure 4 Effect of initial rate of cooling and degree of supercooling on the isothermal crystallization behaviour of high-density polyethylene at 126°C

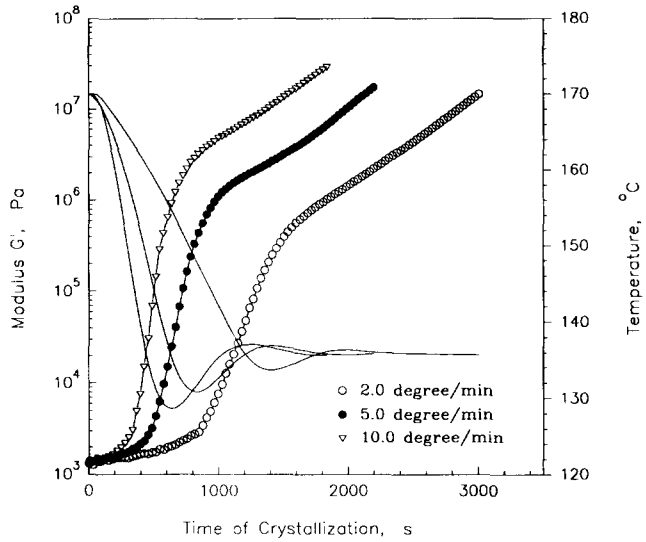

Figure 5 Effect of initial rate of cooling and degree of supercooling on the isothermal crystallization behaviour of polypropylene at 136°C

nucleation, development of spherulites from nuclei, and finally spherulite growth.

In the case of HDPE, nucleation commenced after 650 s, and the modulus increased rapidly to 1×10^5 Pa after 1000 s, after which the nuclei developed into spherulites and continued to grow as shown in *Figure 2*.

Figure 4 shows the effect of different initial cooling rates on the isothermal crystallization of HDPE. Owing to the different cooling rates, the time taken for the melt to reach the temperature at which nucleation began was different. Inherent in the temperature programming control of the Rheometrics 605, different degrees of supercooling were also introduced by different cooling rates. However, the three curves were nearly superimposable with a horizontal shift, indicating that the nucleation process of HDPE was not much affected by the degree of supercooling. However, in the case of PP, the nucleation was found to be more sensitive towards the degree of supercooling and the rate of cooling, as shown in *Figure 5*. Nucleation was observed to begin in all cases when the temperature has dropped to below 150°C. However, in the case of a higher cooling rate and larger degree of supercooling, the initial rate of increase in modulus was higher, and the final modulus reached where the curve turned linear (as in point 'd' of *Figure 3*) was also higher.

The effect of temperature of crystallization on the crystallization behaviour of HDPE is shown in *Figure 6*. The same cooling rate of 2°C min^{-1} was used. For the three different isothermal crystallization temperatures of 127.0, 126.5 and 126.0°C, the lowest temperature (undercooling) reached was 125.5, 124.9 and 124.4°C respectively. If the time taken for the modulus to increase from 1×10^4 to 1×10^5 Pa is taken as a measure of rate of nucleation, the 127°C isothermal crystallization (640 s) is approximately four times slower than that of the 126°C isothermal crystallization (160 s). Comparing *Figure 4* with *Figure 6*, we note that the temperature of crystallization has a greater effect on the crystallization behaviour than the degree of undercooling, in the case of HDPE.

Figure 7 shows the crystallization behaviour of PP at different isothermal crystallization temperatures when

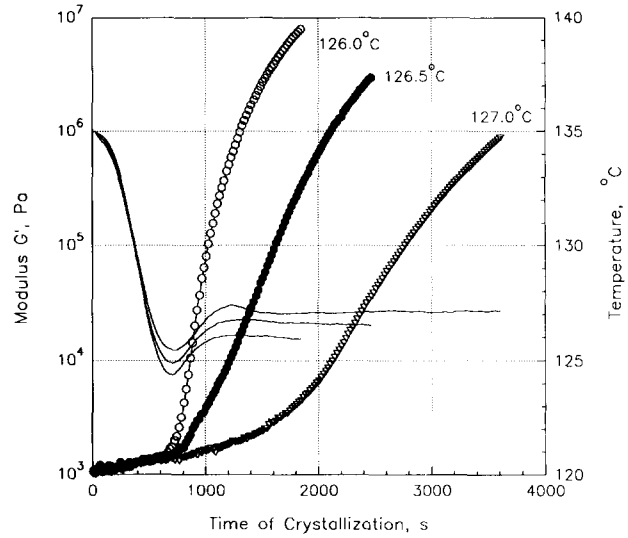

Figure 6 Dynamic mechanical test of high-density polyethylene at different isothermal crystallization temperatures

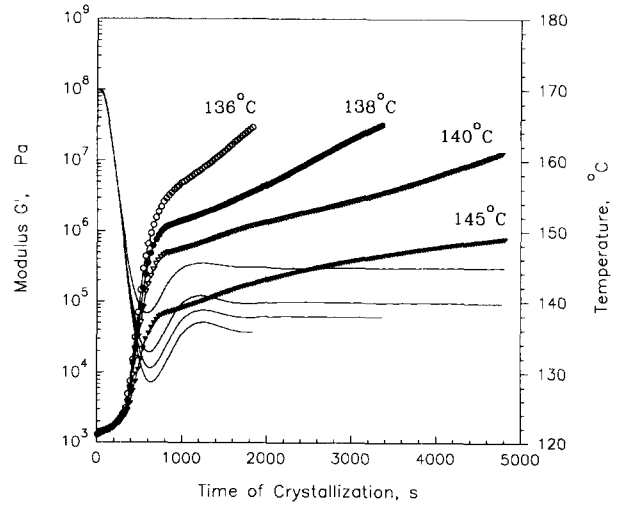

Figure 7 Dynamic mechanical test of polypropylene at different isothermal crystallization temperatures

Table 2 Effect of isothermal crystallization temperature on the nucleation and growth of polypropylene

Isothermal crystallization temperature (°C)	136	138	140	145
Lowest temperature (undercooling) (°C)	128.7	130.6	132.9	138.4
Modulus at point 'c' (MPa)	1.0	0.48	0.20	0.035
Modulus at point 'd' (MPa)	5.0	1.4	0.58	0.085
Time for modulus at point 'd' to increase one order of magnitude (s)	1100	1760	2960	4060

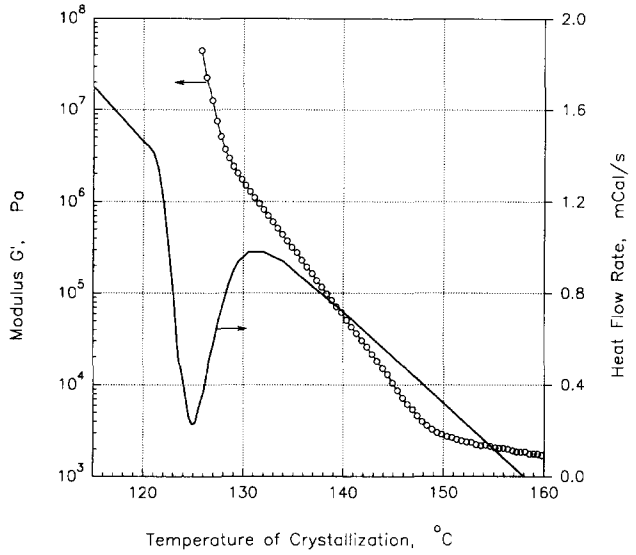

Figure 8 Comparison of crystallization behaviour of polypropylene studied with the dynamic mechanical test and differential scanning calorimeter at the same cooling rate of 1°C min^{-1}

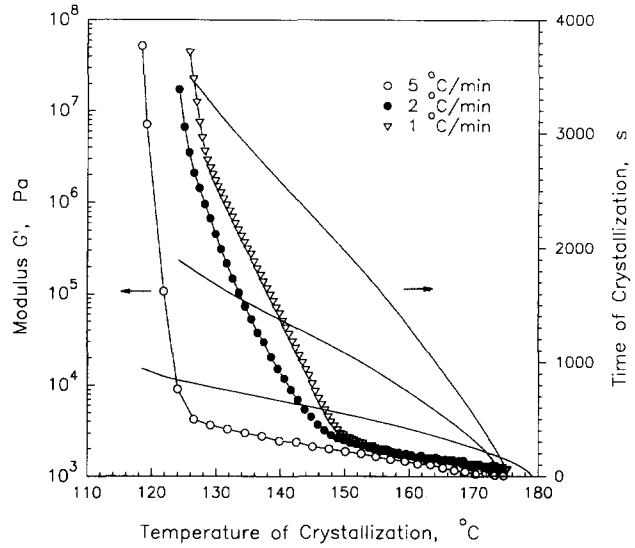

Figure 9 Effect of rate of cooling on the crystallization behaviour of polypropylene as monitored by the dynamic mechanical test

the melt was cooled down from 170°C at 10°C min^{-1}. It is unlikely that different spherulite types will form at different isothermal crystallization temperatures, since the rate of cooling is the same. Formation of β spherulite is unlikely under the present experimental conditions[3,15,16]. The modulus at which the melt temperature first reaches the lowest value (which corresponds closely to point 'c' in *Figure 3*) is used as an arbitrary measure of the nucleation density, and the time taken for the modulus to increase by an order of magnitude for the linear part of curve d–e (see *Figure 3*) is taken to be a measure of rate of spherulite growth. The results are shown in *Table 2*. It is seen clearly here that the nucleation density is dependent on the degree of supercooling, increasing rapidly with increase in degree of supercooling. The rate of spherulite growth also increases with decrease in isothermal crystallization temperature.

Constant-cooling-rate crystallization of polypropylene

The crystallization behaviour of polypropylene at a cooling rate of 1°C min^{-1} as determined by the differential scanning calorimeter and Rheometrics 605 are shown in *Figure 8*. When the melt was cooled down from 180 to 150°C, the melt shear modulus increased slightly as expected, which was a reflection of the change of modulus with temperature. In the temperature range between 150 and 132°C, the modulus was observed to increase rapidly from 0.002 to 1.0 MPa. However, for the same range of temperatures, the d.s.c. did not exhibit any change in enthalpy, indicating that no crystallization was detected. This gives further strong support to the postulate that increase in modulus measured over this range of temperature represents the formation of nuclei that act like crosslinking points in the melt. From 132°C onwards, d.s.c. detected the onset of crystallization, as indicated by the exothermic enthalpy of crystallization, and reached a peak at 125°C. Similarly, in the case of the Rheometrics curve, the modulus is seen to increase more rapidly with further decrease in crystallization temperature, representing the growth of spherulites and increase in ϕ_s reflected by the greater increase in modulus, since now both nucleation and growth process are occurring simultaneously. It is interesting to note that, by combining the d.s.c. and Rheometrics data, the nucleation process can be distinctly separated from the growth process.

Figure 9 shows the dynamic mechanical curve for the crystallization of polypropylene at different cooling rates of 1, 2 and 5°C min^{-1}. It can be seen that, at the very high cooling rate of 5°C min^{-1}, although nucleation is postulated to commence at 150°C, the effect on the modulus was not detected until 130°C. If we look at the dynamic shear modulus curve for the isothermal crystallization case (*Figures 2* and *7*), we observe that it takes approximately 300 s for the completion of nucleation (curve b–c). For a fast cooling rate of 5°C min^{-1}, it takes only 240 s to cool down from 150 to 130°C, and hence no nucleation was 'indicated' before 130°C. It should also be borne in mind that the measured temperature is the temperature of the plate in contact with the polymer melt, and may not be the actual temperature of the melt, especially for this dynamic high constant-cooling-rate case, where the poor thermal conductivity of the polymer may result in a large

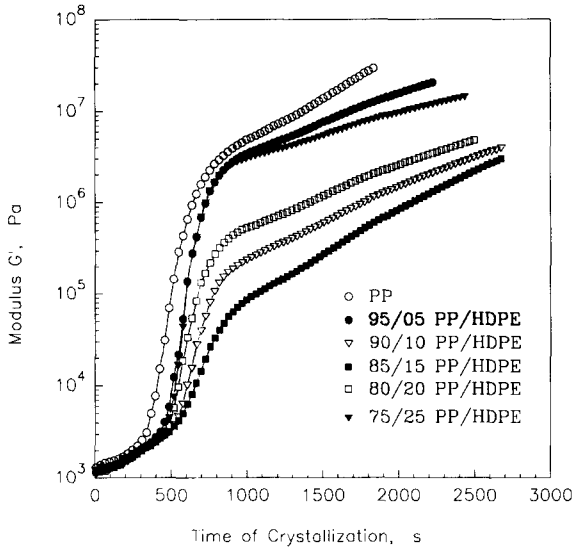

Figure 10 Effect of composition of blend on the isothermal crystallization behaviour of PP/HDPE blends at 136°C obtained by the dynamic mechanical test

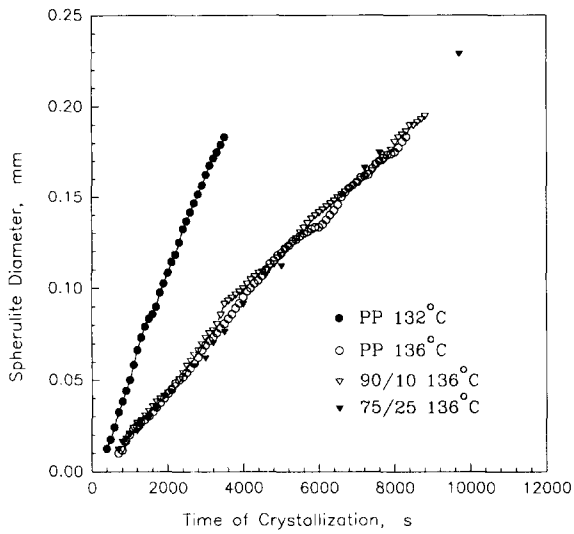

Figure 11 Spherulite growth rate as measured with an optical microscope for PP and PP/HDPE blends

discrepancy between indicated temperature and true temperature of the melt.

Crystallization of PP/HDPE blends

The crystallization behaviour of PP/HDPE blends of composition from 0 to 25 wt% HDPE at 136°C isothermal crystallization temperature when the melt was cooled down from 170°C at 10°C min^{-1} are shown in *Figure 10*. It can be seen that the nucleation density (as measured arbitrarily by the increase in modulus for curve b–c or curve b–d) decreases with increased HDPE content initially up to a composition of 85/15 PP/HDPE, and then increases again with further increase in HDPE content. The rate of nucleation (as measured by the slope of the linear portion of curve b–c) is also seen to follow the same trend. The rate of spherulite growth (slope of curve d–e) remains almost the same for most blends.

The hot-stage optical microscope data for the isothermal crystallization at 136°C for PP and two blends are shown in *Figure 11*. It can be seen that, at the same isothermal crystallization temperature, the neat PP, 90/10 PP/HDPE and 75/25 PP/HDPE all give the same spherulite radial growth rate. The data of the spherulite growth of PP at a lower isothermal crystallization temperature of 132°C are also included for comparison. It has been reported that the radial spherulite growth rate is independent of PP/PE blend compositions[15,17]. The nucleation density as determined from the hot-stage microscope by counting the number of spherulites per square millimetre of crystallizing thin film for the four cases are 34 for PP at 132°C, 25 for PP at 136°C, 8 for 90/10 PP/HDPE at 136°C and 22 for 75/25 PP/HDPE at 136°C. This corresponds to the trend shown by the dynamic mechanical G' curves for the semiquantitative description of the nucleation density.

The constant-cooling-rate crystallization curves from the rheological tests are shown in *Figures 12a* and *12b*. The temperature at which onset of nucleation was detected was found to decrease with increased HDPE content from 150 to 130°C up to a composition of 90/10 PP/HDPE, after which the further addition of HDPE results in an increase in the nucleation onset temperature to 136–138°C. Hence, constant-cooling-rate crystallization and isothermal crystallization yield consistent results.

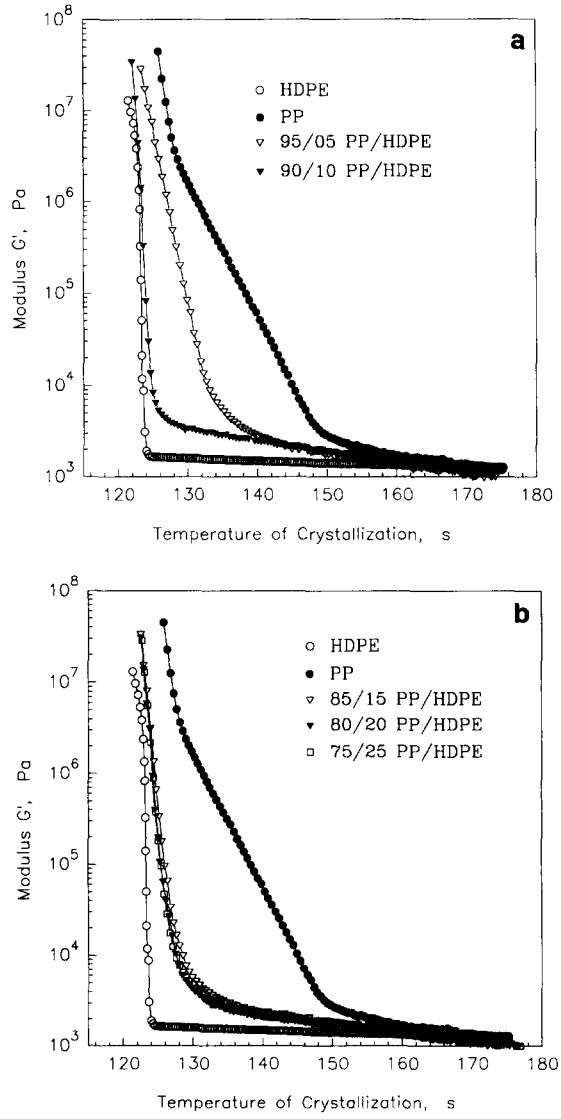

Figure 12 Dynamic mechanical tests on the crystallization behaviour of PP, HDPE and PP/HDPE blends at a constant cooling rate of 1°C min^{-1}

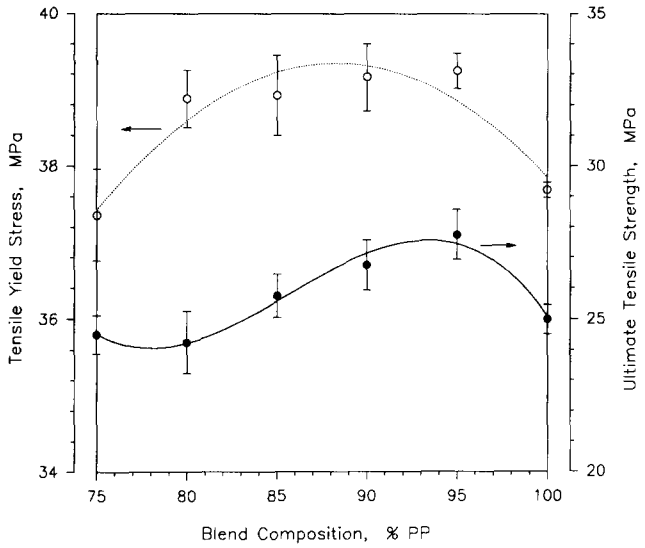

Figure 13 Dependences of tensile yield stress and ultimate tensile strength on composition for PP/HDPE blends

It is interesting to compare the observed change in nucleation behaviour due to the presence of different HDPE contents in the blends with the dependence of mechanical properties on blend compositions. Tensile properties were obtained from a constant-jaw-separation-rate tensile test on injection-moulded dumbbell test specimens (ASTM D638 Type 1) (aged at room temperature for 1 week) with a strain rate of 0.4 s^{-1}. The dependence of tensile yield stress and nominal ultimate tensile strength on composition for the PP/HDPE blends are shown in *Figure 13*. Data shown are for specimens that were injection moulded directly from physically mixed pellets. Results are similar to those which were melt blended with a twin-screw extruder prior to injection moulding, although the latter exhibit a smaller effect. It is seen that a synergistic effect is exhibited where a maximum in properties is observed between the compositions of 5 and 15 wt% HDPE. Similar observations have also been reported by previous workers[15,18–21]. Comparing the mechanical properties data with the crystallization data, it can be seen that the same trend has been observed in both cases. Hence the synergism observed in the blend must be due to a morphological change as a result of different crystallization behaviour. The isothermal crystallization study indicated that there is a reduction in nucleation density of polypropylene at the synergistic composition. This would lead to the conclusion that a larger spherulite size will be obtained at synergistic composition. However, from other studies[15,16,20], the spherulite size of the blends was found to be decreased by the presence of polyethylenes. This apparent contradiction is due to the fact that the isothermal crystallization process is not representative of the actual process when the blends are cooled down from the melt and solidified. If we look at the constant-rate crystallization data given in *Figures 12a* and *12b*, it can be seen clearly that addition of HDPE to PP results in a suppression of the onset temperature of nucleation. At a higher cooling rate, the onset temperature of nucleation of the PP may be further decreased (see *Figure 9* for pure PP), so that simultaneous nucleation and crystallization of HDPE and PP may be taking place. The HDPE spherulites may act as heterogeneous sites for the nucleation of PP, and this will result in a drastic reduction in the PP spherulite size. Hence the synergism effect observed may be predominantly due to the effect of HDPE on the nucleation of PP, where the onset temperature of nucleation is decreased by the presence of HDPE. It has been postulated that this could be due to a migration of heterogeneous nuclei across the interphase boundary from PP melt to HDPE melt[22]. However, this does not explain why, at the optimum synergistic composition, maximum suppression of onset temperature of nucleation was observed (see *Figure 12a*) for 90/10 PP/HDPE blend, and, with further increase in HDPE content, the onset temperature of nucleation was increased.

CONCLUSIONS

The crystallization behaviour of PP, HDPE and their blends under constant-cooling-rate and isothermal conditions have been studied by a dynamic mechanical method. The crystallization process has been followed and monitored from the shear modulus of the melt. Data from the dynamic mechanical method have been compared with the results from the d.s.c. and hot-stage microscopy. The dynamic mechanical method enables the detection of the onset temperature of nucleation, and semiquantitative empirical values based on the shear modulus may be obtained to characterize the nucleation density, the rate of nucleation and the spherulite growth rate. The method has been applied to investigate the synergistic effect of addition of approximately 10 wt% of HDPE to the PP. It has been found that the presence of the synergistic composition of HDPE results in a maximum suppression of the onset temperature of nucleation, minimum nucleation density and maximum decrease of nucleation rate of polypropylene.

ACKNOWLEDGEMENTS

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