Heterogeneous Nucleation at Interfaces in Isotactic Polypropylene

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Investigations of the efficiency of various nucleating additives for isotactic polypropylene showed that heterogeneous nucleation can exhibit a double character. In addition to conventional heterogeneous nucleation arising because of interaction of the solid surface of the additive with the crystallizing polymer, it is necessary to take into account heterogeneous nucleation at interfaces between the crystallizing polymer and gas or vapour pores and bubbles. Minute holes or pores produced by such gases or vapours present in polymer are able to act as efficient nucleating centres.

ONE often finds efforts to modify the number and size of spherulites by adding artificial nucleating agents; especially with isotactic polypropylene[1–11]. Many substances have been shown to be effective nucleating agents for polypropylene, those most often quoted being organic acids and their sodium, potassium and aluminium salts[8–10]. The exact correlations between the chemical composition, crystal structure, and physical properties of the nucleating agent and the polymer have not yet been established. The mechanism of heterogeneous nucleation is also not fully elucidated. Our investigations of the nucleation of polypropylene reveal two distinct mechanisms.

EXPERIMENTAL

Materials

Commercial isotactic polypropylene, Moplene AT-50 (Montecatini Edison, SpA Italy) was used for this research. The characteristics of this specimen were as follows: viscosity number 192 ml/g. 2·8% (w/w) of the naphthalene–ether extract (solid solution of polypropylene in naphthalene extracted with ether), 6% of the naphthalene–chloroform extract, and 0·09% ash content.

Nucleating ability

This was determined by examining films, prepared from a 4% xylene solution, under a microscope. Polypropylene was dissolved in xylene at 125°C for 6 h, nucleating agents being added either before or after dissolving the polymer. Three drops of the polypropylene solution containing the additive were dropped onto a microscopic cover glass and the solvent evaporated at room temperature. The film was then melted for 15 min at 195°C and crystallized for 30 min at 120°C in a carbon dioxide atmosphere. The spherulitic structure of a standard crystallized base specimen was compared with specimens containing nucleating agents by microscopy in the polarized light between crossed polarizers.

RESULTS AND DISCUSSION

This type of heterogeneous nucleation depends upon the interaction of the polymer with the surface of a solid nucleating agent, where the wetting of the additive by the polymer plays an important role. The mechanism of nucleation and its dependence on the structure of the additive are complicated and our knowledge is predominantly empirical. The situation is complicated further by our observation, described elsewhere[12], that a substance can exhibit different nucleating abilities for different commercial types of isotactic polypropylene. Here we shall confine our remarks to another aspect of heterogeneous nucleation in polypropylene.

We have recognized that it is necessary to take into account the effect of surface tension at a polymer–gas, or polymer–vapour interface. Each such interface acts as a nucleation centre. This situation is not confined to the external surface of the specimen, which is the case with the well known surface nucleation (sometimes called transcrystallization), but also applies to the inner surfaces represented by minute bubbles, holes, crevices and pores. If there are substances in the specimen which aid the formation of bubbles and pores, they might also be expected to increase the number of nuclei and thus to decrease the mean size of originating spherulites.

This has been verified using hydrated calcium silicate as the nucleating agent. If the calcium silicate was added before the polypropylene was dissolved then no nucleating effect was observed since, during the dissolution, the water of hydration of the calcium silicate was mostly liberated and hence could not exercise any influence on melting and crystallization. Because of this, we added the hydrated calcium silicate (2%) after dissolving the polypropylene in xylene, stirred the solution for a short time

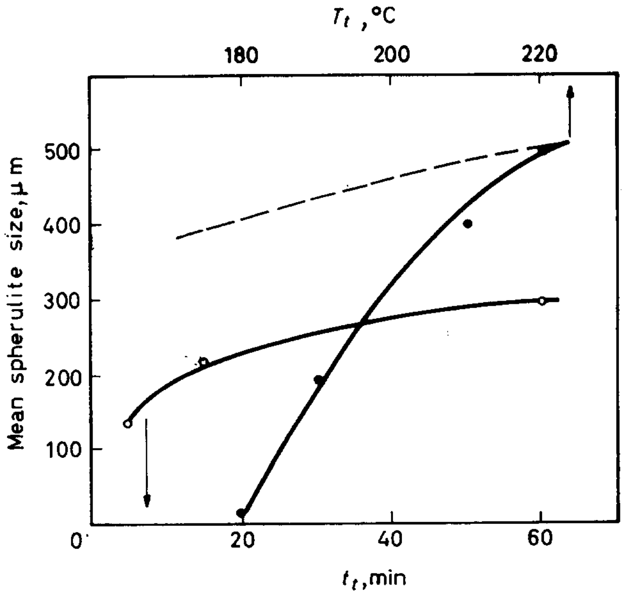

Figure 1—The dependence of the mean spherulite size of polypropylene containing 2% hydrated calcium silicate on melting temperature (melting time 15 min) (●); and melting time (melting temperature 195°C) (○). The dashed curve shows the relationship for polypropylene without nucleating agent.

and then prepare a crystallized film in the usual manner. We expected that, under these conditions, some of the water would be left in the specimen and might exhibit a nucleating effect, especially when the melting was for a short time at relatively low temperatures. This proved to be true, as can be seen from the dependence of mean spherulite size on the melting temperature, and on time (*Figure 1*). Analogous results were obtained with other substances containing water of hydration. In the same way it is possible to explain the nucleating effect of oxidized polypropylene. In dissolving the base polymer together with 5% of oxidised polypropylene for 6 h no nucleating effect was noticed, whereas after 5 min mixing with the solution of polypropylene in xylene the oxidized polypropylene acted as an effective nucleating agent (see *Figure 2*). Polypropylene oxidized in the open air in a thin layer for a shorter period (1 h, 200°C) to a gel consistency showed a much higher nucleating efficiency than polypropylene specimens

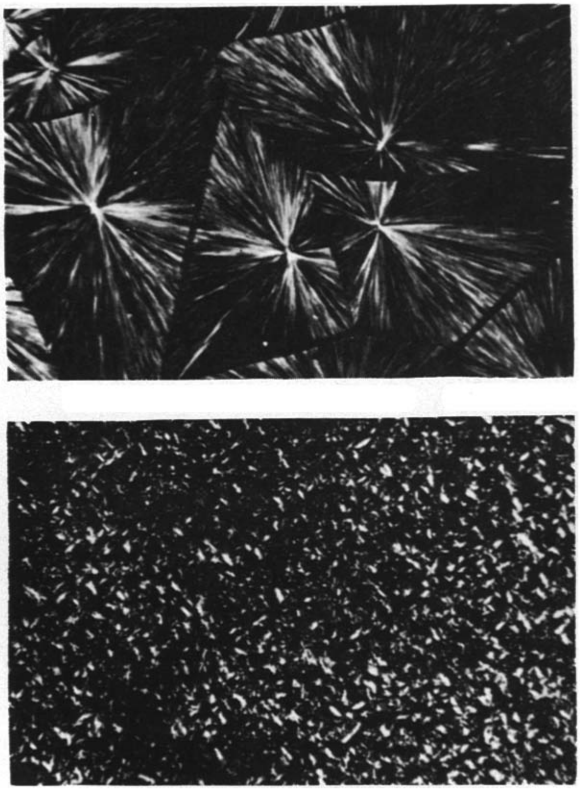

Figure 2—Micrographs of polypropylene containing 5% of polypropylene oxidation products. In case (a) the polypropylene was dissolved together with oxidation products by heating for 6 h at 125°C; in case (b) the solution of polypropylene in xylene was mixed for 10 min at 125°C with oxidation products. (Crossed polarizers, magnification 80×)

oxidized at higher temperatures for a longer period (3 days, 240°); the oxidation product in this case being brittle and fragile. Again we suppose that the actual nucleating agents are volatile decomposition products which create fine bubbles and pores in the crystallizing polymer. At higher temperatures and with prolonged periods of oxidation these volatile products have a better chance of diffusing out. In the same way, we can explain the unexpectedly high number of heterogeneous nuclei in specimens of polypropylene which have been melted and kept at high temperatures for relatively long periods; an observation noted in previous works[13].

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