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Review
Melt crystallisation of polymer materials: The role of the thermal conductivity and its influence on the microstructure

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Even though many characteristics of the quiescent crystallisation process of polymers have been deeply investigated in the long run, some subjects are still open. Indeed, the theory of nucleation and growth, originally developed for metals and low molecular weight materials, have been extended to polymers without taking into account all the characteristics of macromolecules that can induce a crystallisation behaviour different from that of atoms or small molecules. This paper, within the framework of nucleation and growth, reviews the main aspects of the crystallisation process of polymers and discusses its influence on the microstructure, also in comparison with metallic and ceramic materials. Additional factors, often neglected, affecting the crystallisation process have been also identified. In particular, consideration is given to heat flow from solid to melt during polymer crystallisation that can provide an explanation for modified spherulitic morphologies found in fibre based composite materials and blends. Moreover, the circumstances under which thermal gradients within polymer samples may play a dominant role in crystallisation are underlined. Finally, several examples of polymer textures, that could have been originated by heat transfer anisotropy inside samples, are shown.

1. Introduction

The description of the crystallisation process was originally developed to correlate the phase transformation mechanism of metals and alloys with their microstructure [1, 2], which strongly affects the physico-chemical properties of the materials.

Successively, the model of nucleation and growth of crystals was applied to polymer crystallisation, although the considerable length and the statistical nature of macromolecules had to be taken into account to explain some differences in crystallisation behaviour of polymers relative to low molecular weight substances. Indeed, polymerisation reactions are statistical processes leading to more or less broad distributions of the molecular weight, constitution and configuration of macromolecules. Differently from metals, which are almost entirely crystalline materials, macromolecules are not able to crystallise up to 100% and their solid state may be described in terms of crystalline regions strictly interconnected by means of amorphous segments of polymer chains [3]. Moreover, because of the inherent difference between macromolecules and metals, they show different thermal behaviours, especially respect to the heat transport. Indeed, polymers are generally not efficient conductors of heat whereas crystallisation is an exothermal process, occurring with heat development. Therefore, as a consequence of the slow rate of polymers in approaching thermal equilibrium, the temperature inside a sample may not be uniform even during apparently isothermal crystallisation [4, 5], except in the case of very thin films. As a matter of fact, depending on many factors such as crystallisation conditions, amount of heat developed during solidification, geometry and size of the samples, presence of secondary phases, it is possible to achieve a condition of fairly high thermal gradients within a sample [6].

Wu *et al.* [7] reported that curves obtained by differential scanning calorimetry (DSC) have an appearance diverse from that expected under the ideal condition of no temperature difference among sample, pan and furnace. Namely, they found that the shape and especially the positions of the DSC peaks for materials with low thermal conductivity, like polymers, are largely affected by the cooling rate. The authors carried out several simulation models, concluding that the DSC curves cannot be correctly interpreted if internal heat transfer problems are ignored.

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Recently, there have been a renewed interest towards thermal conductivity [8–14], probably because of the diffusion of the temperature modulated differential scanning calorimetry (TMDSC). This relatively new technique has arisen the idea of a complex heat capacity. However, Buehler *et al.* [13] noticed that, differently from thermal conductivity, heat capacity is a scalar and therefore is not able to generate gradients inside homogeneous specimens. Therefore they concluded that a complex heat capacity has not a well-founded thermodynamical interpretation and might be an artefact owing to inadequate mathematical models describing heat transport inside TMDSC specimens. These authors have also derived an equation for thermal diffusion in TMDSC specimens that takes into account both thermal conductivity and temperature gradients.

Moreover, Wunderlich *et al.* [14] admitted that the calculation of heat capacities by TMDSC are valuable provided that no temperature gradient exist within the calorimeter and also recognised the need of special experiments to measure the true temperature inside the samples.

Examining the experimental work and the theories concerning polymer crystallisation, it comes out that the influence of the thermal conductivity on polymer crystallisation has been often underestimated and several examples of thermal and morphological properties reported in the literature might be attributed to the occurrence of neglected heat flow inside polymer samples.

This paper has been undertaken with the aim at clarifying the role of thermal conductivity in polymer crystallisation and gathering evidences of the influence of thermal gradients on the microstructure.

2. Crystalline texture

All the crystalline materials, whatever their chemical nature, are thought to share the same mechanism of solidification, univocally described as a double step process consisting in nucleation of individual crystals and their subsequent growth. Contrary to other solids, whose structure can be derived from the three-dimensional repetition of a structural cell, metals and polymers crystallised from the melt are polycrystalline materials, i.e. each macroscopic piece of condensed matter consists of agglomerates of crystals developed from the growth of several nuclei [15]. Thus metals are constituted by a myriad of crystalline grains with different orientation separated by borders which represent an element of discontinuity. In metals, crystallisation occurs by rapid depositions of atoms on uneven interfaces and hence proceeds fast. However, structure on a scale wider than atomic is strongly influenced by heat diffusion and, particularly for alloys, also by diffusion of materials. Therefore, according to experimental conditions, crystals with different size and microstructure may arise. On cooling metals from melt, if the growth of crystals is equally probable in all space directions (i.e. it is equiaxial), grains having a spherulitic structure are formed. During the growth, metallic crystals develop heat, which dissipation takes place through a negative gradient at the solid-liquid interface [16]. Analogously, crystalline polymers show a microspherulitic structure crossed by extensive interspherulitic broken lines. However, spherulites are not definable as crystals in the classical sense [17]. As a matter of fact, they are themselves polycrystalline entities, built up of lamellar crystals with finite thickness.

The texture fineness of polycrystalline materials depends on the nucleation process. From a microscopic point of view, it is assumed that during nucleation small aggregates of a few atoms (i.e. crystalline nuclei), having the configuration of the solid phase, are formed in the liquid as a consequence of random fluctuations. The construction of crystalline nuclei may also be induced by impurities, reducing energy cost for surface generation and thus favouring the array of atoms or molecules around them. These two kinds of nucleation are classified as *homogeneous* and *heterogeneous* respectively, according to the composition of the nuclei. Once formed, a nucleus may grow incorporating material close to its surface. The homogeneous nucleation involves the sporadic development of nuclei as a function of time and is actually rare for two reasons. First of all, homogeneous nucleation requires very high undercooling to occur at an appreciable rate and, secondly, almost all substances contain microheterogenities that act as substrates for crystalline germs, lowering energy cost for surface creation. Being homogeneous nucleation characterised by a certain frequency, the concept of nucleation rate may be defined: it represents the number of nuclei formed per unit of time and unit of volume during crystallisation. For polymers, nucleation rate as a function of crystallisation temperature is represented by a bell-shaped curve within the temperature range delimited by the glass transition temperature T_g and the melting temperature T_m [18]. Indeed, nucleation rate increases up to a maximum value with decreasing the temperature owing to the reduction of the critical size of the nuclei, then begins to decrease because of the reduction of the molecular mobility at lower temperatures. Besides polymers, a similar decrease in crystallisation rate, due to mass transport, has been observed for liquids showing molecular association (glycerine, water, etc.) but never for metals.

As said above, the most common birth of the solid phase implies heterogeneous nucleation and takes place by cooling at a temperature higher than that required by homogeneous nucleation. In the presence of impurities, all the crystals nucleated from particles of a foreign substance appear simultaneously, while their number remains constant in the long run. In this case, a parameter inversely related to the undercooling may be defined: the induction time, i.e. the time needed for the appearance of crystallisation germs in the molten material.

For both homogeneous and heterogeneous crystallisation a useful parameter for properties-structure correlation is the nucleation density, i.e. the total number of nuclei developed per unit of volume of crystalline materials. At low temperatures, a small critical size is required for crystallisation and hence many more nuclei may reach such a dimension and subsequently grow. Thus samples nucleated at lower temperatures have a crystalline texture finer than those crystallised at higher temperatures.

3. Dependence of phase transition processes on thermal conductivity

3.1. Relevance to polymer crystallisation

Although the crystallisation rate of polymers has been established to depend on several factors (composition, molecular weight, molecular weight distribution, presence of branching, degree of stereoregularity, chain flexibility, melt viscosity etc.), the influence of thermal gradients within samples has not been sufficiently envisaged. However, we believe that thermal conductivity of the crystallising medium has to be taken into account in order to interpret phenomena not yet explained. Amongst these latter, can be enumerated the origin of spherulitic morphologies [19], the formation of banded structure of spherulites [20–22] or the differences in the growth rate of spherulites in immiscible blends [23].

Heat conduction in polymers has been reviewed in detail by Choy [24], that focused on three essential aspects of the thermal conductivity: the temperature dependence, the crystallinity dependence and the orientation effect. The thermal conductivity of amorphous polymers is typically in the range of 0.1–0.2 $\mathrm{Wm^{-1}\ K^{-1}}$, although for semicrystalline polymers it reaches 0.5 $\mathrm{Wm^{-1}\ K^{-1}}$ [25]. Moreover, orientation in semicrystalline polymers produces a very large anisotropy with respect to heat propagation, especially at higher temperature [24]. For instance, polyethylene fibres may exhibit a thermal conductivity along the fibre axis comparable to that of stainless steel [16, 24]. Therefore, the incorporation of reinforcing particles or fibres into polymer materials, may be expected to affect the thermal conductivity of the system, depending on size, shape, orientation, distribution and thermal conductivity of the reinforcement, as well as on the nature of the interface between the matrix and the filler [25–30].

There are several literature data testifying to the importance of heat conduction in the polymer crystallisation processes. The heat flow under isotropic and steady state conditions, assuming the density and the specific heat as constants in the considered temperature range and uni-dimensional heat propagation, may be evaluated by the following equation:

$$-k\frac{\partial^2 T}{\partial x^2} = Q_g \tag{1}$$

where T is the absolute temperature, Q_g is the heat developed (conventionally positive) or absorbed (negative) by the material per time and volume units and k is the thermal conductivity.

According to the above equation, when a phase exchanging heat is simultaneously involved in a physicochemical phenomenon developing or absorbing heat, such as a phase transition or a chemical reaction, the heat transmission may be remarkably modified. Indeed, if the rate of development or absorption of heat is slower than the rate of heat transmission, thermal gradients will not be high. On the contrary, if the rate of heat evolution or absorption is higher, considerable variation of thermal gradients arises. However, in most cases the possibility of local variations in temperature is not taken into account and only few authors [31–33] mention the development of heat during crystallisation. Among these, Foks studied the effect of the temperature on the morphological features of spherulites of polyethylene adipate glycol in order to find out whether local temperature changes at the crystal-liquid boundary could take place. He observed an unexpected change of morphology during isothermal crystallisation accompanied by the variation of both growth rate and melting temperature of spherulites. These changes were correlated to local variations of the temperature and the final spherulites morphology attributed to a competition between crystallisation rate and heat removal rate.

Another example of the importance of heat diffusion is provided by poly(3-hydroxy butyrate) (PHB), a polymer with rather low thermal conductivity and crystallisation rate. Whereas the relatively high T_g and the high purity of PHB, have been invocated to explain its crystallisation behaviour [34, 35], little importance has been given to its high resistance to heat transmission. Indeed, the high purity reduces the number of nuclei developed on cooling from a rather viscous melt, as well as the poor tendency to transfer heat slows the growth of spherulites obstructing the removal of heat from their boundaries. Hobbs *et al.* [36], observing the growth of poly(hydroxybutyrate-co-valerate) (PHBV) spherulites on a lamellar scale by atomic force microscopy, concluded that the accepted models for the growth of spherulites, predicting that the lamellae grow continuously out with a constant growth rate, are not consistent with their observations. The authors evidenced a rough spherulite growth front in a system where the growth front appears smooth and moving at a constant growth rate on an optical scale. Protruding dominant lamellae have been observed that do not grow forward at a constant rate, maintaining dominance until they stop growing or continue growing with a substantially reduced growth rate. In many cases, the average growth rate of a particular lamella, which has stopped growing, is significantly higher than the overall rate of advance of the growth front.

This unexpected deceleration or cessation of growth of the PHBV lamellae could be ascribed to the accumulation of the heat developed during the crystallisation at the growing end of lamellae because of the low thermal conductivity of PHBV. Moreover, in agreement with Bassett [37], the thermal stress acting on the lamellae could induce the twisting of the lamellae, accounting for the banded structure of PHBV spherulites. Indeed, temperature difference between surfaces of the lamellae could arise from heat transfer anisotropy during their growth.

De Carvalho *et al.* [38], followed the crystalline development and the microstructure in compression moulded specimens of isotactic polypropylene (iPP). The specimens were placed in an oven at 200 °C for about 15 min, then quenched at 25 °C, a temperature still above the glass transition temperature of iPP. The temperature profile as a function of time for both heating and quenching processes was recorded. For a typical heating process, it has been shown that, upon melting, the rate of temperature rise decreases, whereas after complete fusion it increases again up to 200 °C. For a typical quenching process instead the temperature profile shows a change of slope in correspondence to the crystallisation. This change has been associated to the heat release during crystallisation. In particular, if the crystallisation is faster than the heat removal by the quenching medium, a maximum will be observed. When the two rates are comparable, a flat segment in the temperature profile is observed, whereas if the quenching agent effectively remove the heat developed during the crystallisation, a negative slope is observed. The authors thus determined the heat transfer coefficient for the iPP quenching in various media and the induction times as a function of the cooling rate for non-isothermal crystallisation. At high cooling rate thin samples of about 400 μm thickness were used. These samples allowed an easier determination of the beginning of the crystallization, at the same time ensuring a uniform temperature along the thickness. The experimental distribution of spherulites diameters was obtained by means of an optical microscope, while calculated values of spherulites diameters were obtained by combining several equations [38] exploiting both theoretical and experimental data. The comparison of the predicted spherulites dimensions and their present size led the authors to conclude that the nuclei concentration is not only a function of the induction temperature at which the crystallisation starts, but also depends on the average temperature of the remaining melt during the whole crystallisation. Therefore, the heat release during crystallisation affects the nuclei concentration and hence the texture fineness of specimens.

3.2. Influence of thermal gradients on microstructure of polymer composites and blends

3.2.1. *Composites*

As the crystallisation of individual polymers, also the solidification of heterogeneous systems is affected by the heat diffusion rate. For instance, a strong reduction in the size of spherulites is evident in polypropylene/silicon carbide whiskers in comparison with neat polypropylene crystallised in a DSC cell on cooling from the melt under the same conditions (Fig. 1). Indeed, the presence of short silicon carbide whiskers has been demonstrated to affect the crystallisation rate of polypropylene and the dimensions of its spherulites [39], likely because of the increase in thermal conductivity of the composite and hence of the improvement of the overall level of heat transfer. Especially during industrial polymer processing, the crystallisation temperature is normally a function of depth; thus it is possible to observe differences in spherulitic texture between surfaces and interior of products. A common modification of spherulites is known as "transcrystallinity" [40] and consists in a massive nucleation along lines, which hinders the lateral growth of spherulites and forces them to grow transversely. Intensive transcrystallinity has been shown, for example, in external layers of polypropylene fibres, on the surface of isotactic polypropylene crystallised in contact to polytetrafluoroethylene and in other appropriately nucleated sheets of polypropylene [37, 41, 42]. Similar effects have been also observed in polymer blends [37, 43, 44], where nucleation may be produced at interphase boundaries. The occurrence of transcrystallinity in commercial materials is known to be due to flow within the samples or to cooling of the external surface of the products during processing. However, in isothermal procedures of quiescent polymer crystallisation, the crystallisation temperature is usually assumed to be uniform and equal to that indicated by the thermostating device [31] and thus the appearance of texture modifications is seldom ascribed to the anisotropy of heat propagation inward materials.

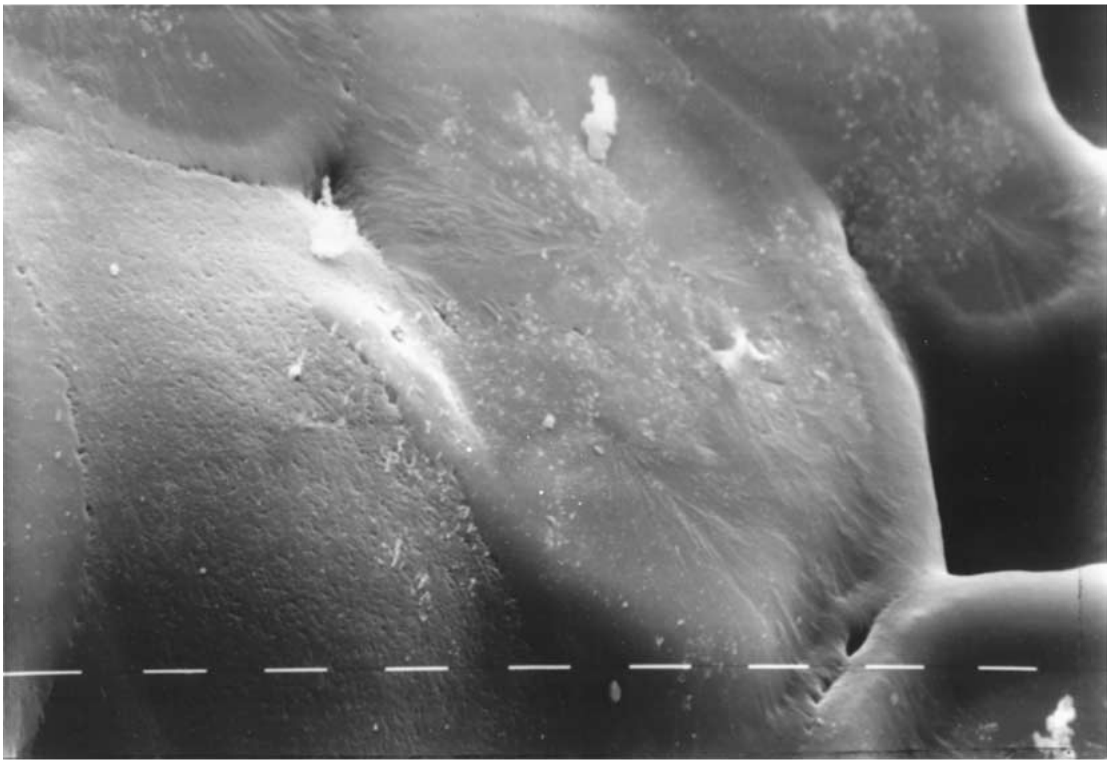
Although the role of thermal gradients is generally a not exhaustively covered issue in polymer crystallisation, the possibility of circumstantial temperature variations need to be stated for multiphase systems such as composite materials. For example, in discussing the origin of transcrystallinity inside fibre based thermoplastic composites (Figs 2 and 3), a strong "nucleating ability" of fibres [45–52] has been generically invocated, without giving a clear reason for this capability. Nevertheless, the columnar spherulitic growth along fibre axes shows a strong resemblance to modified spherulitic textures, which are univocally attributed to the effect of thermal gradients during manufacturing. This analogy makes one think that in specimens of composite materials prepared for optical observations, fibres must be responsible for heat flow inside the samples, even under apparent isothermal conditions. As a matter of fact, at least two properties of fibres, connected to transcrystallinity growth, may be mentioned to explain the local temperature variations at the fibre-matrix interface: their anisotropy with respect to heat conduction and the different value of thermal conductivity of fibres with respect to polymer matrices. As an example, in Table I the thermal conductivity along the fibre axis of carbon, kevlar and glass is reported, evidencing that only glass fibres have a thermal conductivity value comparable to that of thermoplastic materials. Among fibres, glass fibres represent an exception being isotropic as consequence of their three-dimensional network structure, and thus not showing a different value of conductivity in the direction of the transverse axis.

Let us consider a specimen composed by a single fibre whose ends are able to exchange heat with the surrounding environment, whereas a small portion embedded in a polymer is inserted in a hot stage device. Crystallisation procedures of polymer matrices from melt require a preliminary stage of heating at a temperature higher than T_m, followed by a sudden cooling to

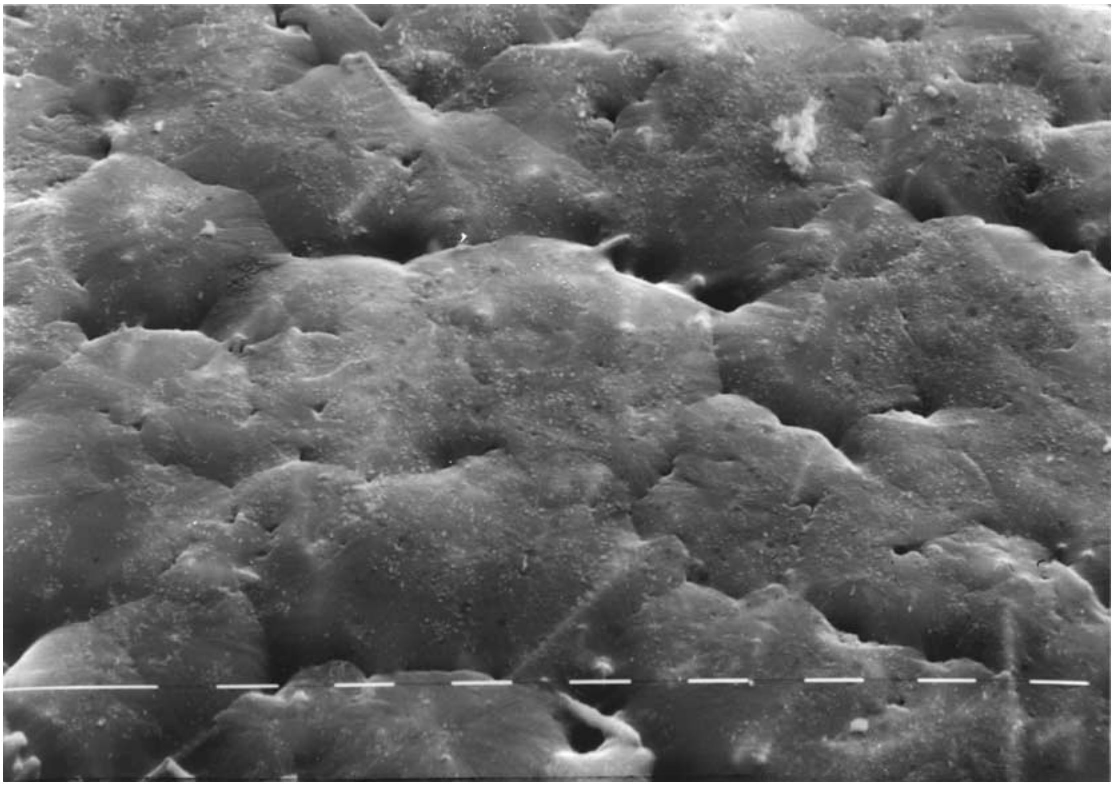
TABLE I Thermal conductivity of fibres*

	Carbon fibre	Glass fibre	Kevlar fibre
Thermal conductivity parallel to fibre axis (Wm^{-1} k^{-1})	24 – 105	1.04	0.04

*Typical range of thermal conductivity of polymers: 0.1–0.5 Wm^{-1} k^{-1}.



(a)



(b)

Figure 1 Scanning electron micrographs of (a) polypropylene and (b) polypropylene containing silicon carbide whiskers (10% by weight). The DSC crystallised specimens were both cooled dynamically from the melt at a scan rate of 10 °C/min. Magnification 1000×.

the crystallisation temperature. The former stage lasts usually a few minutes, a time thought to be enough to destroy any previous crystallinity trace in the matrix. However, this short time may not be sufficient to reach a condition of thermal equilibrium inside a composite specimen. If the thermal conductivity of the fibres is very different from the value pertaining to the polymer matrix, the polymer/fibre system may not reach the uniform temperature settled by the thermostating device, especially in short periods of time. Indeed, on cooling a previously heated composite material, if a fibre propagates heat along the longitudinal axes faster than in the transverse direction, it exchanges heat with the surroundings quicker than with the polymer matrix so that

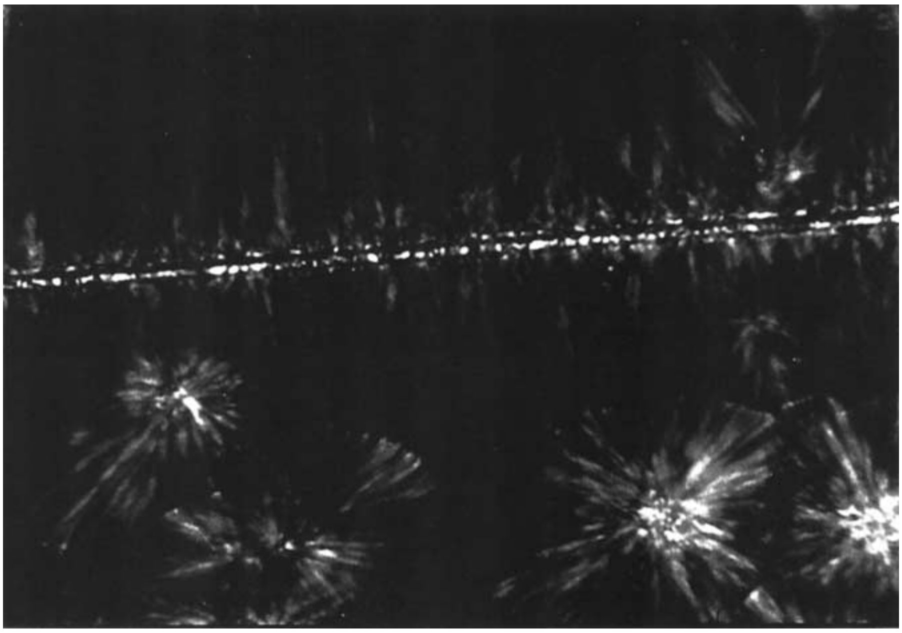


Figure 2 Optical micrograph of polypropylene/kevlar fibre system. Magnification 140×.

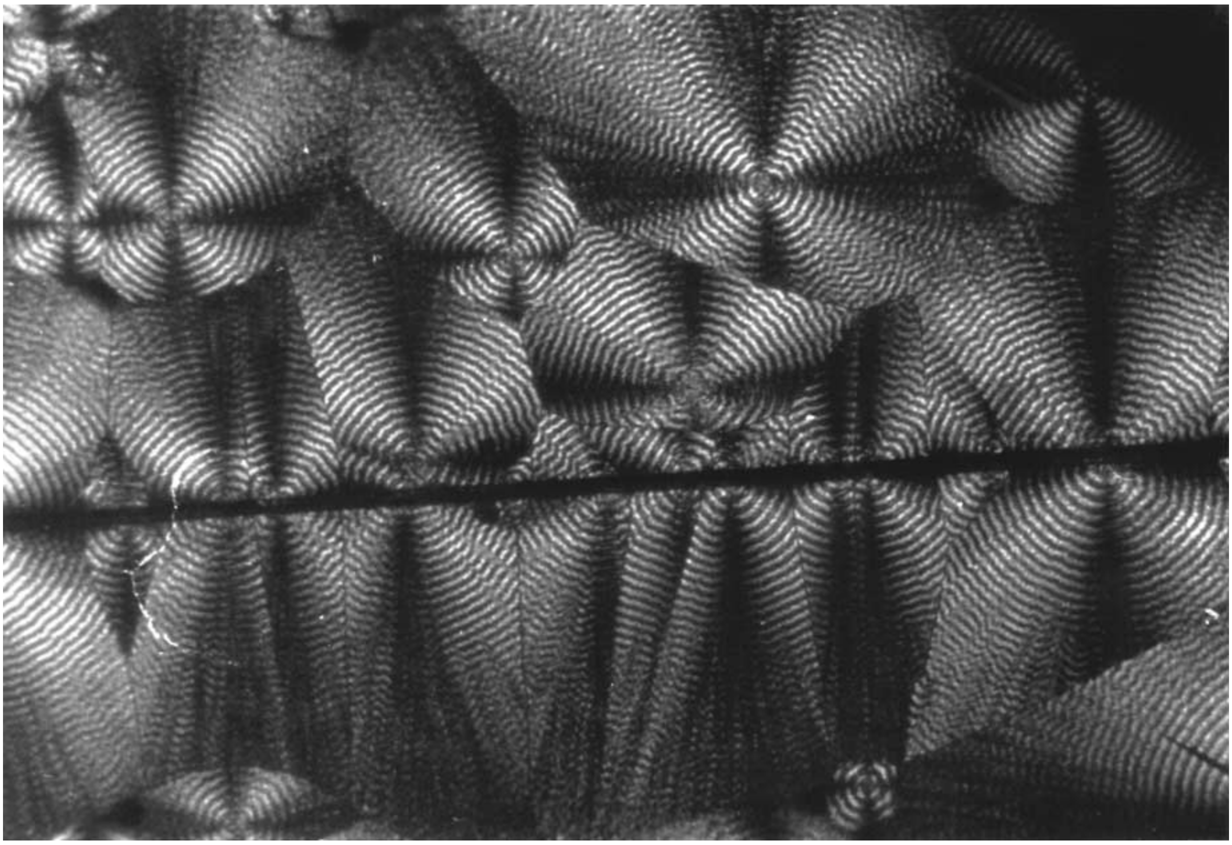


Figure 3 Optical micrograph of PHB/kevlar fibre system. Magnification 180×.

the temperature of the fibre will result lower than that of the bulk polymer. Therefore, the polymer melt in contact to the lateral surface of the fibre will transfer heat to this latter lowering its temperature and thus permitting an easier nucleation. Once nucleated at the matrix-fibre interface, polymer crystals grow far from the interface and thus experience the same temperature of the bulk matrix. This explains why transcrystalline layers of isotactic polypropylene, within iPP/ kevlar and iPP/carbon fibre systems, have been found to grow at the same rate as isolated spherulites in the bulk [53, 54]. The incapability of glass fibres to induce transcrystallinity [53] well agrees with their isotropy and thermal conductivity value comparable to that of polymer matrices. Moreover, glass fibres have the same efficiency as heat dissipators as glass microscope slides and thus cannot provide a preferential way to heat dispersion in specimens for microscopic observation. Therefore, in this case at the polymer-fibre interface there will be a thermal condition of *quasi-equilibrium* rather than a transitory regime. Transcrystallinity may be even recognised in polyethylene reinforced with polyethylene fibres [55], and this is not in contradiction with the possibility of thermal gradients inside the composite. Indeed, fibres may exhibit thermal conductivity values up to thousand times the value of non-fibrous polyethylene [16].

3.2.2. Blends

It is a common industrial practice to mix a material with another to improve the performance. This procedure has been applied in metallurgy and later successfully extended to polymers resorting to the use of compatibilisers.

When a polymer crystallises in the presence of a miscible amorphous component (i.e. a diluent), chains have a lower probability of aggregation in domains larger than the critical nucleus size; therefore the crystallisation rate is reduced. Moreover, in miscible blends, the composition of the melt close to the growing liquid-solid interface may be different from the composition of the solid phase, owing to the presence of impurities or to the rejection of solute from the solid. This concentration gradient in the melt phase may be an additional source of disturbance of the heat propagation during the crystallisation.

The influence of the diluent is also reflected by the depression of the melting point of the crystalline polymer in the blend [56]. However, a depression of the melting point has been observed also in immiscible polymer blends [57, 58], where the crystalline phase is located in distinct homogeneous domains and thus neither diluent nor solute rejection effects can be involved.

In immiscible blends morphological changes may be observed in dependence on the thermal conductivity values of the blend components and their interfacial layers.

H. Li *et al.* [59] studied the effect of a compatibiliser on the melting process of an immiscible blend based on polypropylene (PP) and polyamide 6 (PA6). The compatibilising agent was a graft copolymer (PP-g-PA6) with PP as the backbone and PA6 as grafted blocks. The melting process of PA6 pellets in a PP matrix was studied in a mixing chamber whose temperature was settled at 220 °C. Under the experimental mixing conditions, the PP melting was almost completed before PA6 started to melt. After specific mixing time, the mixed materials was drawn out of the chamber and rapidly quenched to stop the melting process and freeze the morphology. Afterwards, PP was extracted by xylene, while the molten and unmolten fractions of the remaining PA6 part were distinguishable by sight as a flocculent mass and solid pellets respectively. By extrapolating to zero the weight fraction of the unmolten PA6 as a function of mixing time, the time needed to melt completely the PA6 pellets in both uncompatibilised and compatibilised blends was estimated, showing that PA6 melting is accelerated in the presence of the compatibiliser. The authors concluded that when the melt blending process is conducted so that the rate of melting of PA6 pellets is much lower than the rate of removal of the molten PA6 from PA6 pellets, the thermal conduction is controlled only by the interfacial layer between the blend components. Therefore, they attributed the higher melting rate and the finer dispersion of PP/PP-g-PA6/PA6 blends to the enhancement of the thermal conductivity of the interfacial layer between the components in the presence of the compatibiliser.

Since the melting process of a dispersed phase in a polymer blend is accelerated by a higher thermal conductivity of the surrounding medium, it is reasonable to believe that its crystallisation from melt will be consequently retarded, also causing morphological changes. An example is provided by poly(3-hydroxy butyrate)/poly(methylene oxide) (PMO) blend [26], for which a strong depression of the melting point of the PHB phase is found in the blend, whereas a decrease of the growth rates of the PMO spherulites is also observed. This latter has been attributed to the lower thermal conductivity of the heterogeneous molten medium from which spherulites arise. Indeed, the PHB shows a lower tendency to propagate heat than the PMO and thus the removal of the heat developed during the crystallisation of PMO is even more difficult in PHB/PMO blends.

In conclusion, the illustrations provided by the literature demonstrate the influence of several variables on the final microstructure of blends. Amongst all these variables, a complex heat transfer between distinct phases of the materials plays a fundamental role in determining morphology and microstructure.

4. Conclusion

Up to now, only a few attempts have been made in order to describe the influence of thermal gradients on polymer crystallisation. In this article, a new outlook for polymer crystallisation has been provided combining the classical theory of nucleation and growth of crystals with considerations on heat development and transport inside materials. The proposed approach to polymer crystallisation has provided qualitative explanations for several modified spherulitic morphologies found in heterophasic thermoplastic materials. Starting from analogy with the structure of some materials originated by non-isothermal process of crystallisation, thermal gradients have been suggested to occur even during the apparent isothermal solidification of composite systems and blends. Moreover, the existence of heat flows within the specimens has been correlated to the final microstructure.

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