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THE INFLUENCE OF RECYCLED MATERIAL ON THE CRYSTALLIZATION KINETICS OF THERMOPLASTIC POLYMERS

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The injection moulding of semi-crystalline thermoplastic polymers requires an exact knowledge of the thermodynamic data and of the crystallization kinetics. The behaviour of the polymer melt during rapid cooling in the mould determines, to a great extent, the quality and usability of a final product.

Technical raw materials are often equipped with nucleating agents in order to obtain crystallization within the desired temperature range and at the required rate.

The use of recycled material (regranulate) shows an analogous effect such as the addition of nucleating agents, i.e. crystallization begins at a higher temperature and a higher crystallization rate is detected compared to materials without added regranulate.

Heat flux DSC was used to study the crystallization of polyamides, polyolefins and polyoxymethylene during cooling at various cooling rates.

Although the temperature gradients and pressures which occur in the processing machine cannot be realised in DSC tests, the DSC results reproduce the direction of influence of the regranulate additive very clearly.

Keywords: crystallization kinetics, thermoplastic polymers

Introduction

For ecological and economic reasons, regranulate is used nowadays in the recycling of polymeric materials. DSC makes it possible to determine the changed crystallization kinetics of semi-crystalline thermoplastics. Ecology demands the reuse of materials, and the cost conscious use of recycled materials is also highly economical in polymer technology. Fulfilling this demand is easiest in the primary cycle (Fig. 1), e.g. when reusing a firm's own regranulate of the same type and composition.

When reusing regranulate in the primary cycle, high quality products can generally be produced. This is only possible in a limited way when using regenerated material from the secondary cycle. Re-use of unsorted waste material, however, results in products of a definitely low quality.

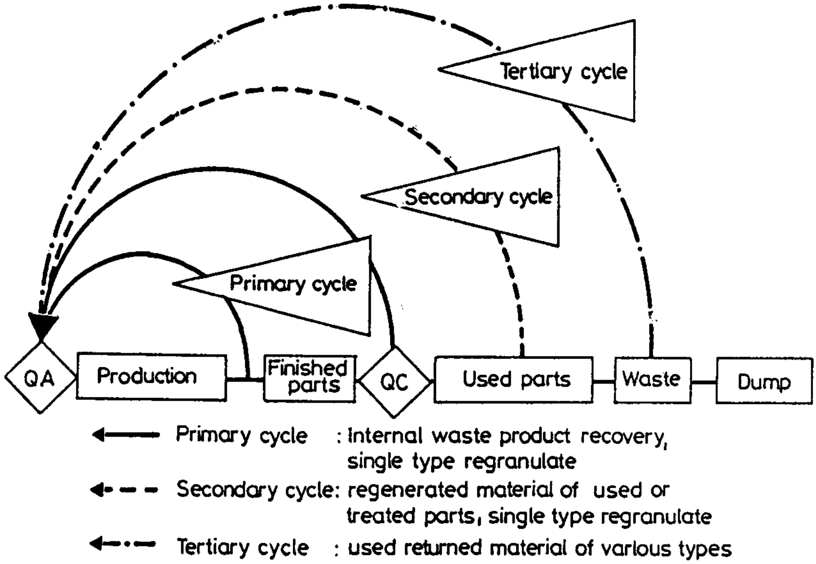

Fig. 1 Polymer recycling, three possible cycles for reuse of polymeric materials

DSC can be successfully used to solve the problems that arise due to the addition of regranulate. Surface defects in the finished product, poor or uneven varnishing and insufficient mould filling are the most frequent problems found during quality control. From the point of view of the thermal analyst, the crystallization of the semi-crystalline thermoplastics is responsible for the behaviour of the material during thermal processing: differences can be detected in the temperature at the start of crystallization and during the course of crystallization (crystallization kinetics). For amorphous thermoplastic polymers no systematic change of a characteristic thermal effect could be detected by DSC after the addition of recycled material.

Experimental

Polyamides, polyolefins and polyoxymethylene of a technical grade and with a different content of regranulate of the same material were tested in the heat flux

DSC (NETZSCH model DSC 200) in heating/cooling cycles. The experimental conditions are given in the corresponding figure captions. Also moulded parts and materials with added nucleating agents were included in the comparison test to show the influence on the crystallization behaviour of previous thermal treatment and of nucleus formers.

Results and discussion

In comparison to the crystallization process of a fresh polyamide 66 granulate, the start of the crystallization of material with a regranulate content is shifted to a higher temperature and the crystallization rate is drastically increased (Fig. 2).

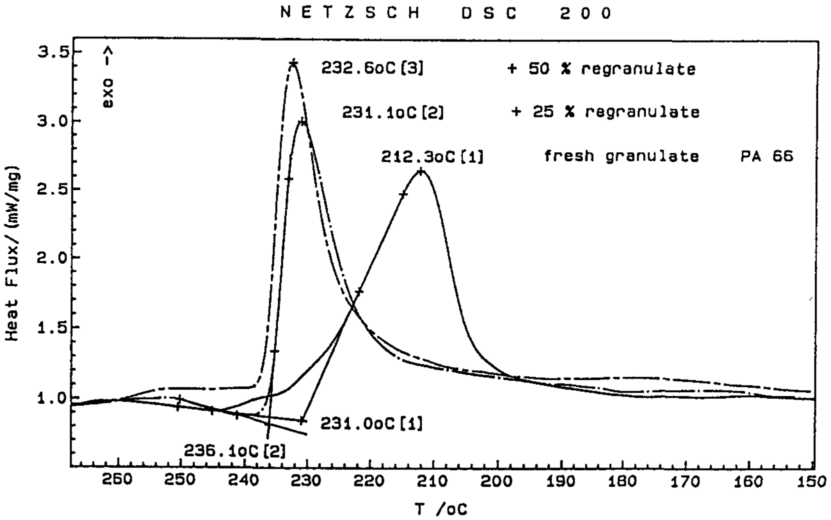

Fig. 2 The influence of regranulate addition on the crystallization of PA 66, cooling rate 20 deg·min^{-1}, air atmosphere

This is shown clearly by DSC experiments during cooling at 20 deg·min^{-1}: the onset of crystallization of the fresh granulate is 231°C, the addition of 25% of a regranulated PA 66 leads to a crystallization onset of 236.1°C. The leading slope of the crystallization peak is significantly increased when adding regranulated material, indicating a faster growth rate for the formation of crystalline domains in the polymer. The changes found in the melting peaks of these polyamides PA 66 during first and second heating revealed no systematic influence of the regranulate addition.

The influence of the content of regranulate on temperature and rate of crystallization for PA 66 is found to be non-linear.

What explanation can be given from the material point of view?

The influence of differing nucleation (content of nucleus formers for starting the crystallization) was determined by DSC during tests of various batches of PA 66 with 35% glass fibre, which had caused problems during injection moulding of motor parts (Fig. 3). The function of the nucleating agent is demonstrated by the start of crystallization at a higher temperature (difference 12.7°C) and by the higher crystallization rate (slope of the peak). This is the desired effect of nucleation: to increase the sites available for crystallization to occur and to control the growth of spherulites for enhancing physical properties. Additionally, faster processing and increased productivity are a result of appropriate nucleation [1].

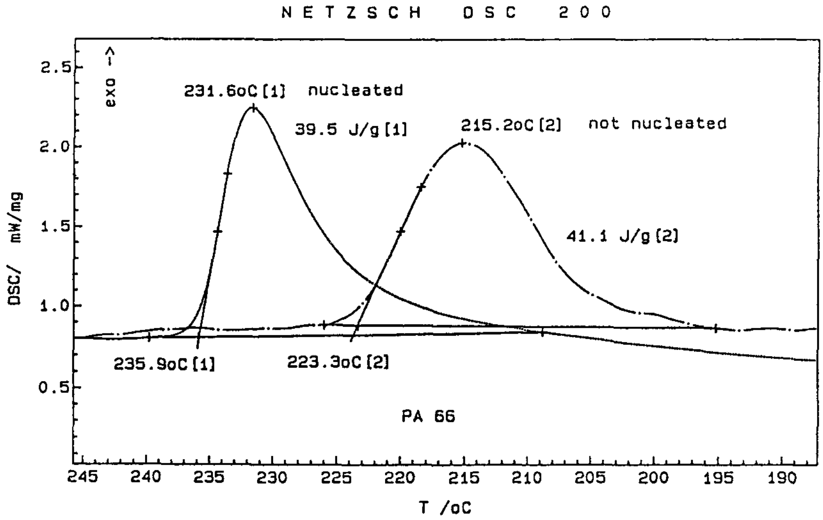

Fig. 3 Crystallization peaks for nucleated and non-nucleated PA 66 with glass fibre, cooling rate 20 deg·min^{-1}, air atmosphere

These conclusions drawn from the nucleation of semi-crystalline thermoplastics are transposed when considering the problems of regranulate additives (Fig. 2). Therefore it can be concluded that an increasing regranulate part in semi-crystalline plastics causes the same sort of change in crystallization behaviour as an increased nucleation, i.e. an earlier and faster solidification of the polymer melt during cooling.

Many single factors are conceivable that could lead to nuclei formation for crystallization resulting from the addition of regranulate, such as the beginning of damage (oxidation, degradation), changes in the molecular structure or in the molecular weight, impurities from processing, fillers, paints, humidity, etc.

Polyamide PA 6 with glass fibre shows an increase of 5.8°C in the crystallization temperature when adding regranulate (Fig. 4). No significant change in the crystallization rate is detected by DSC, if only the peak slope is evaluated, i.e. the growth rate of the crystalline sections of this material is not influenced.

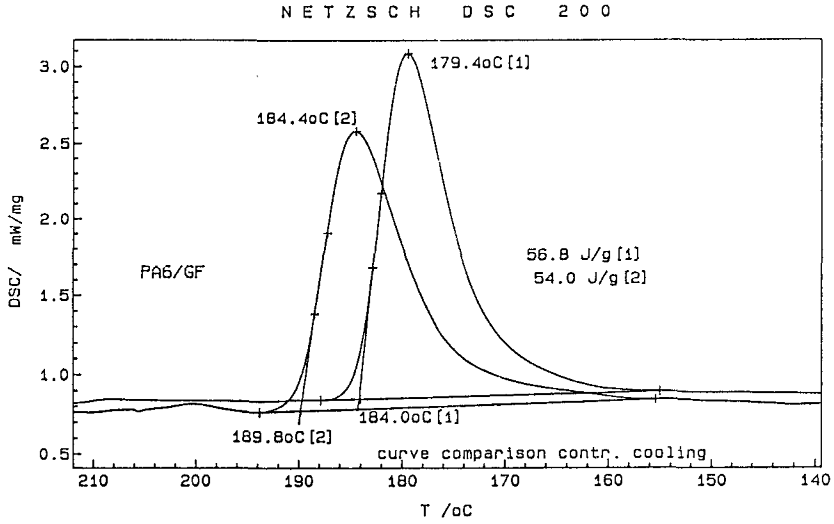

Fig. 4 Crystallization of polyamide PA 6 with content of glass fibre, influence of regranulate addition; [1] fresh granulate; [2] regranulate addition; cooling rate 20 deg·min^{-1}, air atmosphere

This indicates that the influencing factors for the crystallization kinetics could possibly be separated into the function of forming nuclei and of increase the growth rate of these nuclei.

Low-density polyethylene (PE-LD) is very sensitive to processing conditions during injection moulding. A high melt temperature as well as a high temperature gradient between polymer melt and the mould result in an extensive change of crystallization behaviour during controlled cooling in the DSC (Fig. 5). Compared with a fresh granulate, the samples taken from moulded parts show again a higher onset of crystallization, a different peak shape and also a reduced crystallization heat.

Extreme conditions in the processing of a polymer lead to start of degradation. This is especially true for PE-LD with its branched structure. These structural changes are combined with an increase in the nuclei content.

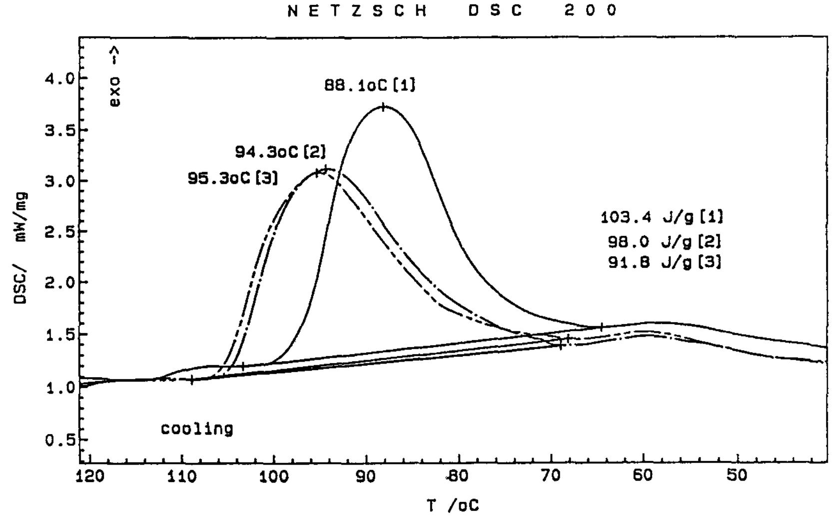

Fig. 5 Influence of processing conditions on the crystallization of PE-LD; [1] fresh granulate; [2] melt temp. 260°C, mould temp. 70°C; [3] melt temp. 160°C, mould temp. 27°C, cooling rate 20 deg·min^{-1}, air atmosphere

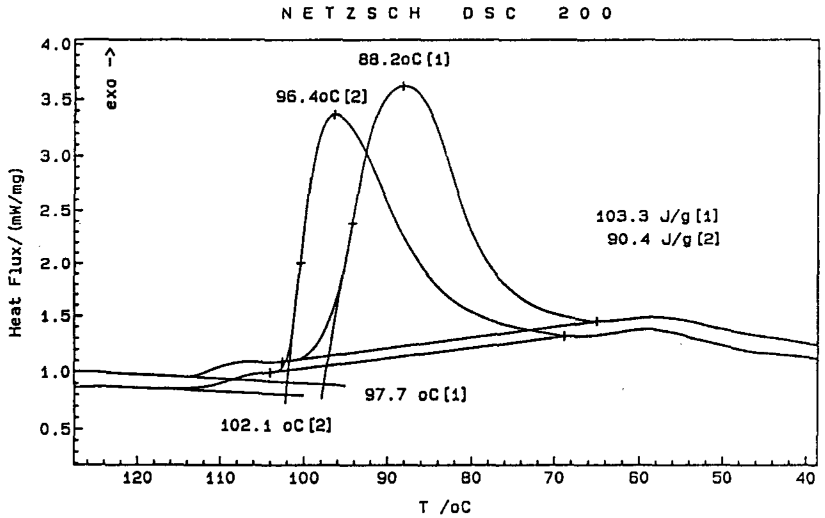

Fig. 6 Influence of regranulate addition on the crystallization of PE-LD; [1] fresh granulate; [2] containing regranulate; cooling rate 20 deg·min^{-1}, air atmosphere

Regenerated PE-LD, also resulting from normal processing, has the effect on the crystallization kinetics (Fig. 6) as shown above: temperature at start and rate of crystallization are changed after the addition of regranulate.

Small exothermal peaks before the main solidification peaks of PE-LD indicate the content of a nucleating agent in both materials.

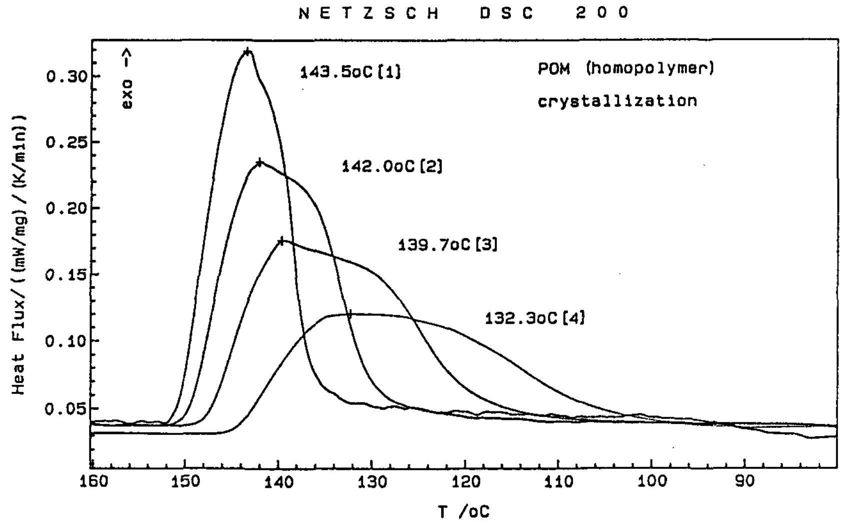

Fig. 7 Crystallization of POM at different cooling rates; [1] 5 deg·min^{-1}; [2] 10 deg·min^{-1}; [3] 20 deg·min^{-1}; [4] 30 deg·min^{-1}; air atmosphere

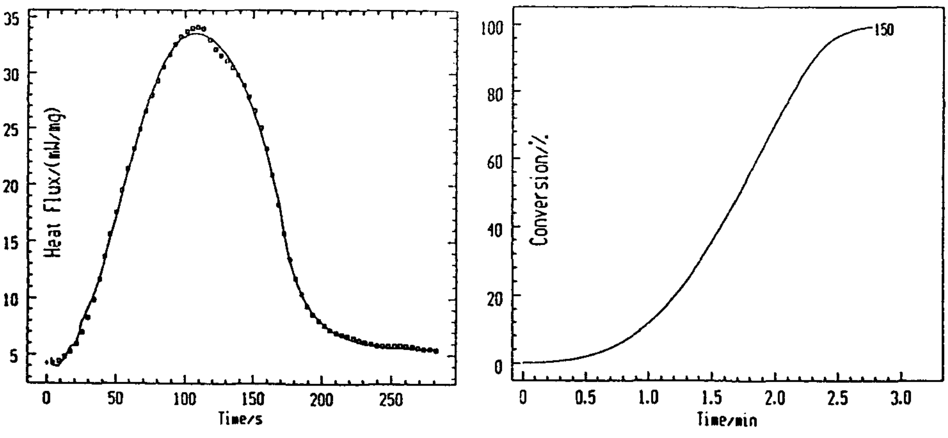

Fig. 8 Curve fit for POM crystallization at 5 deg·min^{-1} (a) and prediction of crystallization behaviour at 150°C (b)

For a formal approach to the calculation of kinetic parameters for the crystallization of polymers with the influence of recycled material, Polyoxymethylene (POM) was crystallized at four different cooling rates (Fig. 7).

The DSC peaks show clearly that the crystallization of this POM (homopolymer) is no homogeneous, single step process. Therefore it is understandable that plots of the logarithm of the cooling rates against any of the characteristic peak parameters (onset or peak temperature) show no linearity.

The isothermal crystallization of polymers is normally described by Avrami's equation or its modifications [2]. The crystallization of POM in isothermal DSC experiments was also recently described by Avrami's or, even better, by Tobin's equations [3]. But for a simulation of the crystallization behaviour of a polymer melt during processing by injection moulding or extrusion, non-isothermal tests are nearer to the real conditions [4, 5].

The set of curves in Fig. 7 cannot be described by multivariate non-linear regression [6] with the same conbination of reaction models for all cooling rates, even assuming a three step process. Further tests are necessary to indicate whether the crystallization behaviour of the POM measured by DSC is controlled by different mechanisms in the selected range of cooling rates.

A separate evaluation of the crystallization at one cooling rate is possible with a combination of a three step consecutive process of an n-dimensional Avrami, followed by an n-th order reaction and a three-dimensional diffusion process (Fig. 8). But this evaluation based on only one DSC result is not taken as being sufficient for a reliable prediction of the crystallization behaviour during technical processing of semi-crystalline polymers.

The changed crystallization behaviour by the addition of recycled polymers requires further systematic tests for a quantitative description of their influence on the crystallization kinetics.

Conclusion

The use of recycled semi-crystalline polymers changes the start temperature and the rate of crystallization. Depending on the pre-treatment of the added recycled material and on the nature of the basic polymer, the influence on the start of crystallization or on the rate of crystallization is predominant. These effects from the addition of recycled semi-crystalline polymers are analogous to the effects from the addition of nucleating agents. A quantitative description of the influence on the crystallization behaviour by corresponding kinetic models and parameters requires further experiments.

DSC clearly indicates the changes in the crystallization behaviour of semicrystalline polymers with added recycled material. This information is a good basis for the engineer to adjust the processing parameters in such a way that good quality products are achieved in the first and also second cycle of polymer recycling.

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Zusammenfassung — Das Spritzgießen von semikristallinen thermoplastischen Polymeren erfordert eine exakte Kenntnis der thermodynamischen Daten und der Kristallisationskinetik. Das Verhalten der Polymerschmelze bei schnellem Abkühlen im Preßwerkzeug bestimmt zu einem großen Anteil Qualität und Nutzbarkeit des Endproduktes.

Technische Rohstoffe werden oft mit Keimbildungsstoffen versehen, um innerhalb des gewünschten Temperaturbereich und mit der gewünschten Geschwindigkeit die Kristallisation zu erreichen.

Die Verwendung von recyceltem Material (Regranulat) zeigt einen ähnlichen Effekt wie der Zusatz von Keimbildungsstoffen, d.h. die Kristallisation setzt bei höherer Temperatur ein und eine höhere Kristallisationsgeschwindigkeit wird beobachtet, als es bei Materialien ohne Regranulatzusatz der Fall ist.

Mittels Wärmefluß-DSC wurde die Kristallisation von Polyamiden, Polyolefinen und Polyoxymethylen während beim Kühlen mit verschiedenen Kühlgeschwindigkeiten untersucht.

Obwohl die in der Fertigungsmaschine vorkommenden Temperaturgradienten und Drücke im DSC-Test nicht verwirklicht werden können, geben die DSC-Ergebnisse die Tendenz des Einflusses des Regranulatzusatzes sehr deutlich wieder.