

# The rheological and crystallization behavior of polyoxymethylene



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## ABSTRACT

In the polymer melt processing, the solidification has a huge importance on the properties of the resulting part. For a semi-crystalline resin, this phenomenon involves a complex interplay between crystallization and the material rheology. In this work, an investigation is carried out on the influence of thermal conditions on crystallization kinetics and rheology of two commercial polyoxymethylene (POM) copolymers. In particular, isothermal crystallization experiments using differential scanning calorimetry (DSC) and rotational rheometry to measure the dynamic viscosity are performed. The evolution of the relative crystallinity and Normalized Rheological Function (NRF) are correlated by a recent technique which allows simultaneous analysis of several measurements, even if they are not carried out at same temperatures. On this basis, a relationship between the crystallinity and the hardening, i.e. the sharp increase in the viscosity, is obtained.

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## 1. Introduction

Polyoxymethylene (POM), also known as acetal resin, is an engineering thermoplastic material used in the processing of precision parts that require high stiffness and low friction. POM homopolymer is a semi-crystalline polymer (75–85% crystalline) with a nominal melting point of 175 °C. The POM copolymer has a slightly lower melting point of 162–173 °C.

Despite its interesting properties, POM processing is difficult and requires specific expertise. Indeed, its high crystallinity degree and density difference between the crystal (1.49 g cm<sup>-3</sup>) and amorphous phases (1.21 g cm<sup>-3</sup>) induce significant volume reduction and cavity formation during solidification. Because of chemical degradation above the melting point [1] and significant shrinkage, the polyoxymethylene processing is generally limited.

Although many papers have been reported so far about the crystallization kinetics and rheology of POM from the molecular level to the higher-order structure level [2–8], the details of the hardening process have not yet been clarified. Pelzbauer and Galeski [4] reported that the crystallization, in a quiescent condition, occurred in the spherulite form below 158 °C; above this temperature, hedrites and, sporadically, ovoids were observed in acetal resins. Hama, and Tashiro [9] investigated the structural

evolution in the isothermal crystallization processes of POM at 130 and 150 °C from the melt by a combination of various experimental techniques as DSC, FTIR, WAXS and SAXS.

In general, the knowledge of how the rheology of a polymer changes during the solidification is an essential information for reliable modeling of the polymer processing. But the experimental data reported in the literature regarding the increase of viscosity as a consequence of the solidification usually show a large dispersion [10].

The effect of the molecular weight on crystallization has been investigated by Bove and Nobile [11]. They used rheological measurements to study the evolution of crystallization either in quiescent conditions as well as after the application of a shear flow. To follow both the cooling and the isothermal crystallization process, the evolution of the storage modulus,  $G'$ , was monitored by an oscillatory test at constant stress and constant frequency. The choice of the values for both these parameters is crucial in order to reduce, as much as possible, the disturbance related to the flow during the crystallization, as discussed in detail in the work of Bove and Nobile [11]. It was verified that the values of 1000 Pa and 1 rad s<sup>-1</sup> ensured that the resin crystallization process occurred in quiescent conditions, i.e. without any effect on the crystallization kinetics. Therefore, the static crystallization tests were carried out using these values of stress and frequency. The storage modulus, detected during the measurements, represents a probe to follow the quiescent crystallization process, because of its sensitivity to follow the structural changes in the samples during the crystallization.

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The main drawback is due to the experimental procedures, which usually requires two separate tests to evaluate the rheology and the crystallinity evolution, thus both time dependent, trying to reproduce the same thermal history in the different devices. The evolution of rheology with progressing crystallization (described as a Normalized Rheological Function, NRF, i.e. the ratio of the complex viscosity with the initial value for the amorphous melt material at the same temperature) was thus obtained [12].

Lamberti et al. [10,12] proposed an analysis of the hardening experiments with two standard devices, i.e. a rheometer and a differential scanning calorimeter, even if the tests are not performed at same temperatures. As a result, the combination of these measurements allows to obtain the NRF change in the isothermal crystallization process, and this analysis was reported for the isothermal crystallization phenomenon of polypropylene but has never been applied to POM.

Janssens et al. [13,14] presented new hybrid technique able to perform simultaneously rheological and thermal measurements in the same device. It is worth noticing that, working with isotactic polypropylene, the novel apparatus give results close to the ones obtained by Lamberti [12]: a significant increase of NRF for crystallinity not below the 10% was found.

Recently Pantani et al. [15,16] carried out rheological measurements on an isotactic polypropylene and simultaneously the evolving morphology was assessed by adopting a rheometer equipped with an optical module. The spherulitic nucleation density and growth rate were found consistent with a quiescent crystallization, and the effect of crystallinity on complex viscosity was relevant.

In this work crystallization kinetics and associated hardening of two commercial polyoxymethylene copolymers are explored with standard instrumentations analyzing the results to link the viscosity evolution to the solidification.

## 2. Experimental

### 2.1. Materials

Two commercial copolymer acetal resins have been used in this work. The former is an injection molding grade, supplied by Rhodia Engineering Plastics, with the tradename “Sniatal M4”. The latter is a general purpose molding grade, supplied by Asahi Kasei Plastics, with the tradename “Tenac-C”. Both POM copolymers are furnished as pellets. The melting temperature evaluated during DSC heating scan at  $10 \text{ K min}^{-1}$  (peak temperature, standard ISO 11357) is  $165 \text{ }^\circ\text{C}$  and  $164 \text{ }^\circ\text{C}$  for Sniatal and Tenac, respectively. The melt flow index (at  $190 \text{ }^\circ\text{C}$  with weight  $2.160 \text{ kg}$ , standard ISO 1133) is  $5.5 \text{ g/10min}$  and  $2.8 \text{ g/10min}$  for Sniatal and Tenac, respectively. Polyacetal resins, during melt processing at high temperature, could generate gasses, principally formaldehyde, for thermal decomposition. Their decomposition in the cylinder of the molding, extruding, or other processing machines may also cause a dangerous high-pressure buildup inside the cylinder. Furthermore, drying is required before processing (drying conditions: temperature  $80\text{--}90 \text{ }^\circ\text{C}$ , time  $3\text{--}4 \text{ h}$ ).

### 2.2. Methods

The isothermal crystallization behavior of the acetal resins was investigated by differential scanning calorimetry (DSC) using a Mettler Toledo DSC 822™, calibrated with indium ( $T_m = 156.6 \text{ }^\circ\text{C}$ ,  $\Delta H_m = 28.45 \text{ kJ kg}^{-1}$ ). The experiments were carried out, according to the protocol in Fig. 1, in a nitrogen atmosphere at a rate flow of  $50 \text{ ml min}^{-1}$ , in order to prevent oxidative degradation, using approximately  $10 \text{ mg}$  of sample sealed in aluminum pans.

The crystallization kinetics was studied starting from the melt,

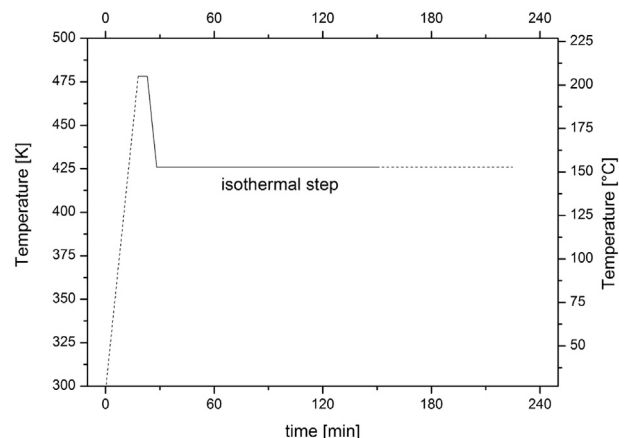


Fig. 1. Experimental protocol for isothermal crystallization.

after holding the sample at  $205 \text{ }^\circ\text{C}$  for 5 min in order to erase the effect of previous thermomechanical history. Preliminary tests were performed holding sample temperature up to  $220 \text{ }^\circ\text{C}$ , or at  $200 \text{ }^\circ\text{C}$  with times up to 30 min to check the material behavior: the “couple”  $205 \text{ }^\circ\text{C}$  for 5 min was selected as the standard procedure to obtain a disordered melt, without thermal degradation.

The crystallization process has been also monitored with rheological investigation performed on both acetal resins by means of a rotational stress rheometer, SR5000, Rheometric Inc., in the cone and plate configuration ( $\varnothing = 25 \text{ mm}$ , cone angle =  $0.1 \text{ rad}$ ). Dynamic oscillatory strain sweep experiments were performed to determine the limit of the linear viscoelastic region of the samples. As for calorimetric tests, the crystallization kinetics was investigated starting from the melt, after holding the sample at  $205 \text{ }^\circ\text{C}$  for 5 min in order to erase the effect of previous thermomechanical history. In order to study melt isothermal crystallization, the experimental protocol, sketched in Fig. 1, was adopted both for differential scanning calorimetry and rheology characterization. In particular, the sample was then cooled from  $205 \text{ }^\circ\text{C}$  directly to isothermal test temperature (crystallization temperature), with a cooling rate of  $10 \text{ K min}^{-1}$ .

This cooling rate is essentially limited by the rheometer features, in order to avoid an appreciable thermal gradient over the thickness of the crystallizing specimens, resulting in a thermal non-homogeneity over the thickness.

## 3. Results and discussions

### 3.1. Calorimetric measurements

Isothermal crystallization kinetics were investigated at different temperatures each  $1 \text{ K}$  apart within the range  $426 \text{ K}\text{--}428 \text{ K}$  and  $425 \text{ K}\text{--}427 \text{ K}$ , for Sniatal and Tenac respectively. In Fig. 2, for both acetal resins, it can be seen that longer time is taken for the samples crystallized at a higher crystallization temperature, i.e. the crystallization rate decreases with increasing crystallization temperature.

The crystallization temperature range is generally limited in calorimetric experiments because for a temperature higher than the explored ones the amount of heat evolved per unit time was really small and for temperature lower than the explored ones crystallization starts during the cooling step before the isothermal crystallization (as could be marginally observed in the experiment on Tenac at  $425 \text{ K}$  in Fig. 2). The analysis of the calorimetric isothermal results lets to evaluate the crystallinity evolution. Partial areas of the peaks in Fig. 2, corresponding to a given percentage of the total transformation, were determined from the data points of the exothermic peak, after a linear baseline subtraction. The

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