Controlled shear-induced molecular orientation and crystallization in polypropylene/talc microcomposites — Effects of the talc nature

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ABSTRACT

Nowadays, innovation in the materials field, particularly for polymer materials undoubtedly requires the control of their structure at the nanoscale. Moreover, in the polymer processing tools, the material generally undergoes high strains. In our case, the goal is to determine the interactions between the filler and the matrix on the crystallization processes, especially for a high aspect ratio nucleating filler embedded in a semi-crystalline matrix submitted to a controlled strain field. In this study, PP/talc blends were developed by compounding in the melt state using a mini-extruder. Several talcs, different in morphology and particles size, have been studied to determine the influence of their dispersion and of their aspect ratio on the matrix crystallization kinetics. Particularly, one is natural talc and the other is synthetic. The dispersion and orientation of the talc lamellae were characterized by scanning electron microscopy (SEM) and Wide Angle X-Ray Scattering (WAXS). Moreover, the crystallization of the microcomposites polypropylene matrix was thoroughly analyzed in terms of kinetics and crystalline orientation. Experiments were performed using both a rheometer and a shearing hot stage mounted on a polarized light microscope or in a synchrotron X-ray beam. They revealed the influence of the nucleating effect depending on the filler, as well as of the shear conditions on both crystallization kinetics and crystalline orientation. Particularly, it was shown that there are two possible crystalline orientations with mother-daughter lamellar structure: one orientation is promoted by the nucleating effect of the aligned talc platelets and the other is directly due to the shear.

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1. Introduction

For many applications, the properties of filled polymer materials are obviously dependent on the filler amount but above all, they are very linked to the quality and the amount of the generated interface between the matrix and the filler. Therefore, most of works are devoted to the dispersion quality of the preformed fillers. Three main methods are usually used for preparing such micro or nanocomposites. Fillers can be directly added to a monomer and mechanically dispersed by dispersive mixing. Hence, polyamide 6 nanocomposite were prepared from the polymerization of ε-caprolactam inserted in the interlayer space of montmorillonite [1]. Besides, in situ polymerization makes thermosetting nanocomposites possible as for example epoxy-clay nanocomposites [2].

A second method consists in previously dispersing the clay in a solvent in which the polymer is soluble [3,4]. Nevertheless, the use of some solvents in a production environment often incurs higher costs and environmentally benign and easily-removed solvents are not always available. Thus, a third method is developed which consists in directly mixing the polymer melt with clay while allowing the migration of macromolecules into the galleries [5,6]. This melt intercalation method is preferred for bulk processing and makes use of conventional industrial equipment like extruder, blowing extruder, injection or rotomolding [6,7]. However, in the case of a micro or nanocomposite material with a semi-crystalline matrix, although the effect of the filler on the material properties is obvious, it lies sometimes less with the filler itself than with the modification of the matrix crystalline structure due to the presence of the filler. This issue is generally disregarded since ascribing the properties alteration to one or the other is difficult because of their synergistic contributions [8]. A heterogenous phase in a semi-crystalline polymer matrix very commonly acts as a nucleating

agent [9] and obviously it can be the case for a filler or a nano-filler, even if it was not incorporated in that perspective. Hence, the crystalline structure and/or the crystallization kinetics of the matrix can be affected by the filler, and this, in a scale range largely greater than the filler itself [10–12]. Besides, since the crystallization cannot occur across the filler that act as walls, a variation of the growth kinetics can also be expected [13,14]. Moreover, in the presence of fibers, a transcrystalline phase can appear around the fiber [15,16] (activated nuclei are so numerous that they are forced to grow in the perpendicular direction of the fiber showing columnar morphologies). In the case of nucleating fibers, spherulites size can be decreased with increasing fiber content [10–12]. Fillers can also influence the crystalline phase structure of the polymer as for example by generating the β-crystalline form in polypropylene [17].

Moreover, high strains are generally undergo by the material during its processing and it is now well established that the polymer crystallization can be enhanced by the flow [18–22]. Indeed, the macromolecular chains orientation due to the flow promotes the crystalline nucleation. Thus, when this nucleation phenomenon largely exceeds the primary nucleation of the unsheared quiescent melt, the shear-induced crystallization becomes faster. Moreover, it has been shown that the shear effect is more dependent on the shear rate than on the shearing time [22,23] and the existence of a critical shear rate linked to the relaxation time of the polymer [24,25], to efficiently accelerate the crystallization was often reported. Hence, the resulting morphologies of flow induced crystallization can spread from very numerous spherulites up to very oriented structures (shish-kebabs) when the shear rates are very high. Consequently, the mechanical properties can be very affected [26].

Therefore, it results from these considerations that a competition is established between the nucleating mechanism of the filler on the one hand, and the flow induced nucleation on the second hand [23,26–30]. This opposition will govern the crystallization in terms of kinetics but also in terms of resulting crystalline orientation. Moreover, it becomes even more interesting in the case of nucleating filler presenting a high aspect ratio because it can be oriented itself [26,28,29], leading to a subsequent crystalline orientation different from that due to the flow induced nucleation. This issue is precisely the main topic of the present work.

In the present work, the talc was used as filler presenting a high aspect ratio and a polypropylene was the semi-crystalline matrix. This type of filler is generally used in applications of automobile, household appliances, and construction industries. More precisely, in talc-filled PP compounds, the presence of this plate like filler contributes towards improved stiffness-impact properties balance, increased heat-deflection temperatures (HDT), and also improved processing properties such as reduced and uniform molding shrinkage, besides acting as a heterogenous nucleating agent in the PP matrix, these improvements being more relevant with ultra-fine filler particles size. That filler, with a high aspect ratio, can also be oriented and modify the crystallization of the polymer [31,32].

In this work, the crystallization of the matrix was studied with the focus on the understanding of the competition between the crystalline orientation in the matrix due to the filler itself and this resulting of the shear induced crystallization. Thus, experiments were performed with the purpose of very well controlling all the strain and temperature conditions before analyzing the crystalline orientation.

2. Experimental section

2.1. Materials

The iPP used in this study is a commercial polypropylene supplied by LyonDellBasell under the reference MOPLEN HP500N. It is a homopolymer with a weight-average molar mass Mw of 2.4×10^5 g/mol and a polydispersity Mw/Mn of 6,9 determined by high temperature size exclusion chromatography. The melt rheological characterization is given in Fig. 1 showing the dynamic modulus measured at 200 °C with an ARES device (TA Instruments) equipped with a parallel plates cell (diameter 25 mm, gap 1 mm). Moreover, considering a classical Maxwell N modes model [25,33] (N relaxation times λ_i of modulus contribution G_i), a discrete relaxation spectrum was adjusted to describe the dynamic modulus. The consistency of the obtained 5 modes spectrum is also shown by the calculated curves in Fig. 1. Interestingly, from the relaxation spectrum, characteristic values are deduced: the zero-shear viscosity ($\eta_0 = 1880$ Pa s) and the number average relaxation time ($\lambda_n = 5.35 \times 10^{-2}$ s) and the weight average ($\lambda_w = 1.49$ s) relaxation time which is also viewed as the longest relaxation time [34]. This relaxation time will be considered when discussing the shear effect on the crystallization kinetics.

Two kinds of talcs with different shapes, crystallinity, and way of production were used. One was a powder talc, Luzenac A3, called natural talc (NT). It was manufactured by Imerys Talc with a composition of SiO_2 60.3%, MgO 31.5%, Na_2O 0.21% and 7.99% of moisture content. The characteristic diameters D25, D50 and D75 of the particles were 2.8; 3.9 and 5.2 μm respectively. The other talc also developed by Imerys Talc was a synthetic talc (ST) of the following composition: SiO_2 59.9%, MgO 28.1%, Na_2O 3.71% and 8.29% of moisture content. This talc was synthesized in an autoclave at 300 °C under 100 bars during 6 h. The characteristic diameters D25, D50 and D75 of the particles were 11.3; 19.6 and 31.7 μm respectively. One of the particularities of this filler was its conditioning as a suspension composed of 20%wt of synthetic talc and 80%wt of demineralized water. The powder X-ray diffractograms of both natural and synthetic talcs are compared in Fig. 2 showing that the crystalline cell for the ST is different than the NT crystalline cell. Moreover, the low-amplitude and broad XRD peaks for the ST is due to very fine grain size and poor crystallinity compared to NT.

2.2. Preparation of microcomposites

The talc/PP composites were prepared using a DSM Micro 15 twin-screw extruder at a barrel temperature of 200 °C, with a screw
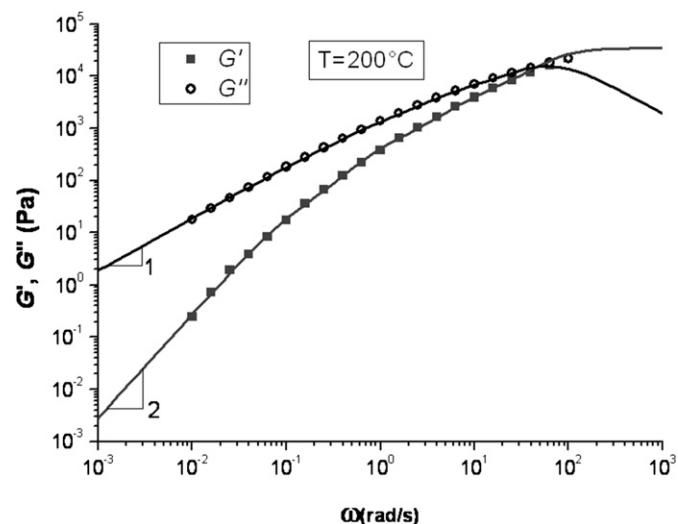

Fig. 1. Dynamic modulus of the studied polypropylene as a function of the frequency obtained at 200 °C (symbols: experimental data, lines: calculated curves).