Crystallization of glass-fiber-reinforced polyamide 66 composites: Influence of glass-fiber content and cooling rate

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ABSTRACT

This paper reports the effect of glass fibers (GF) and carbon black powder (CB) on the crystallization behavior of polyamide66 (PA66). Particular attention was paid to erasing the thermo-mechanical history related to processing conditions of the composites in order to probe the intrinsic effect of the fillers. The statistical analysis of the experimental data delivers an analytical relationship for the crystallinity ratio as a function of both GF content and cooling rate. Glass fibers are shown to promote a nucleating effect that significantly increases the crystallization kinetics and crystallinity ratio of the PA66 matrix in the composites up to a GF weight fraction of about 30% before to depress both properties above this threshold value. In parallel, CB particles generate a synergistic nucleation effect that increases crystallinity. However, this effect does not compensate the detrimental effect on crystallinity of GF at high content. A discussion is made on the physical origins of the drop of the crystallinity ratio that occurs above the GF threshold content.

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1. Introduction

Polyamides have much better thermo-mechanical properties than polyolefins which make them suitable for applications requiring creep and fatigue resistance in the automotive industry more particularly above room temperature for parts in the engine compartments [1–12]. Polyamides also have intrinsic good tribological properties which make them suitable for manufacturing sliding parts such as bearings or gears [13–15].

Short glass fibers (GF) are known for long to be an efficient filler for improving the thermo-mechanical performances of thermoplastic polymers. Regarding polyamides, GF provide a great increase of elastic modulus above the glass transition temperature of semi-crystalline polymers which results in an improvement of the so-called heat deflection temperature property that is used for qualifying thermoplastics for high temperature applications. This is the case of polyamide66 (PA66), otherwise nylon66.

Carbon black (CB) is often used for improving the electrical

conductivity of polymers in the case of applications requiring electrical charge dissipation or electromagnetic wave shielding [16,17]. CB is also well known to improves the resistance to sliding wear of all kinds of polymers including polyamides. However CB contributes in the degradation of impact strength as evidenced in the case of PA66/GF composites [5].

A secondary effect of reinforcing fillers and additives in composites based on a semi-crystalline polymer matrix is the modification of the crystallization capabilities of the polymer matrix, i.e. crystallization kinetics, crystal perfection and crystallinity index. The presence of solids particles in such materials was often shown to play a nucleating role in the process of crystallization. This is likely to have an impact of the mechanical properties of the composites.

In spite of the emergence in recent years of polyamide/clay nanocomposites [18–20], PA66/GF composites have continuously been under experimental studies regarding mechanical properties [1–7,21–26] owing to their high rank in technological domains demanding high thermo-mechanical performances and weight reduction. Modelling has also attracted a lot of attention in the aim of predicting the mechanical behavior of PA66/GF parts in service [8–12]. However, investigations regarding the effect of additives

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and fillers on the crystallization kinetics and the morphogenesis of the PA66 matrix have been rather scarce, a situation which contrasts with that of composites and nanocomposites based on polyamide6 or polypropylene matrices, and some other semi-crystalline polymers as well. A general trend is that most fillers display a nucleating role for the semi-crystalline matrix [27—34] that generally promotes a preferred orientation of the crystal growth normal to the surface of the filler particles. In the case of fibers, including nanofibers, this effect generates a *trans*-crystalline microstructure along the individual fibers [35—42]. However, the occurrence and extent of the phenomenon are strongly dependent on the nature of both the polymer matrix and the filler.

When nucleating phenomena occur in fiber-reinforced composites, the resulting anisotropic *trans*-crystalline morphology displays a mechanical behavior different to the isotropic crystalline matrix that is likely to influence the global mechanical behavior of the composite [43—47]. Moreover, the *trans*-crystalline morphology is likely to promote a stiff percolating network between the crystalline phase and the fibers that may significantly influence the macroscopic mechanical properties of the composite when the amorphous phase in soft, i.e. at $T > T_g$. Indeed, as already shown in the case of clay-filled polymer nanocomposites [28,48—51], the crystal-filler interconnectivity can significantly improve the mechanical coupling between matrix and filler towards the highest bond of the so-called *parallel-coupling*.

However, doubts have been cast on the actual nucleating effect of fiber fillers. For instance, no *trans*-crystallization was reported for PA66/GF injection-molded samples [52]. *Trans*-crystallization was absent for quiescent molten polypropylene/aramid-fiber composites for temperatures close to the melting point of the polymer matrix, whereas *trans*-crystallization was shown to re-appear upon drawing the fibers [37]. As a matter of fact, it is now well known that shear may improve the crystallization by the generation of local molecular ordered regions that play the role of homogeneous nuclei [32,37,53,54]. Furthermore, in the case of composites reinforced with high aspect ratio filler particles, the shear amplification effect [55] at the surface of the particles is likely to bias the actual nucleating effect of the filler by enhancing the shear-induced nucleation close to the surface of the particles [56,57].

The present paper aims at studying the combined effect of GF and CB on the crystallization behavior of PA66/GF composites over a large range of GF content. The objective of the present work is to determine to which extent the crystallization capabilities of the PA66 matrix is sensitive to GF and CB and to probe their possible synergistic effect. Special attention is taken to prevent shear-promoted nucleation resulting from the injection-molding.

2. Experimental

2.1. Materials and processing

The study was carried out on a collection of 10 materials of polyamide 66 composites reinforced with short glass fibers (GF) having an average diameter of 10 μm and surface-treated with an amino-silane coupling agent. The virgin PA66 samples and the composites materials having 30 and 50 wt% of GF, with or without carbon black (CB), were supplied by Solvay (Saint Fons - Belle Etoile, Lyon, France). The molecular weight of the PA66 matrix, $M_v \approx 33$ kg/mol, was determined by viscosimetry at 30 °C in formic acid, according to the manufacturer.

The PA66 pellets were dried at 80 °C under vacuum for 48 h prior to compounding in order to prevent hydrolysis during the process. Rectangular bars 2 mm thick were injection-molded by means of a Demag press H200-80 (Sumitomo, Germany) using an average screw temperature of 285 °C under a pressure of about

2 kbars and using a hot mold at 80 °C.

The composites of intermediate GF contents, namely 7 and 15 wt % of GF, were prepared by compounding pellets of the 30% GF composite and the native PA66 in adjusted proportions. This compounding was carried out on a Xplore mini-extruder and a mini-molder from DSM (Netherland). The composites were mixed for 2 min using an average screw temperature of 285 °C before to be injection-molded in the form of rectangular bars.

Composites containing 0.4 wt % of carbon black were also prepared using the same compounding process as in the previous case of composites without CB, using the same GF contents as indicated above.

All samples were quickly stored in sealed bags after compounding for preventing moisture uptake that could generate hydrolysis at high temperature during the DSC experiments.

2.2. Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) was carried out on a Perkin—Elmer DSC7 apparatus using samples of about 7 mg. The temperature and heat flow scales were calibrated using high purity indium. Prior to crystallization experiments, all samples were heated from room temperature (RT) up to 290 °C, and held at 290 °C for 5 min in order to erase thermal history. Indeed, the shear-flow-induced orientation of the chains in the polymer matrix is well known to enhance the nucleation ability of the fibers (see *Introduction* section). The present procedure was performed in order to promote relaxation of the oriented chains and to enable thereby studying the actual nucleation effect of GF on the PA66 matrix. The samples were subsequently cooled down to RT at various cooling rates, C_R, in the range 2—50 °C min^{-1}.

The crystallinity was determined from the DSC heating trace recorded at a heating rate of 10 °C min^{-1}, immediately after the crystallization experiment. All heating traces were corrected by subtraction of the baseline recorded with empty pans in both the sample and the reference ovens. The crystal weight fraction or crystallinity ratio was computed from the relation

$$X_C = \Delta H_f / \Delta H_f^\circ \qquad (1)$$

where ΔH_f is the melting enthalpy of PA66 in the samples and $\Delta H_f^\circ = 195 \pm 5$ Jg^{-1} is the melting enthalpy of perfectly crystalline PA66 in the α-crystal form [58,59]. In the case of composites, the actual content of PA66 matrix was taken into account for the X_C computation.

2.3. Structural characterization

Scanning Electron Microscopy (SEM) experiments were performed on a JOEL 840 A LGS apparatus at an acceleration voltage of 1—5 kV. Observations were made from the metal-coated surface of samples broken in liquid nitrogen.

Wide-Angle X-ray Scattering (WAXS) experiments were carried out at RT in reflection mode on a Bruker D8 Advance System (Germany) operated at 40 kV and 40 mA, using the Cu-Kα radiation (λ = 0.154 nm). The WAXS intensity was collected by a LynxEye linear detector.

2.4. Design of experiments and statistical analysis of data

A design of experiments approach was adopted for this work for optimizing the crystallinity ratio, X_C, using the filler ratio, F_R, and the cooling rate, C_R, as independent variable parameters. For doing this, the ANOVA variance analysis was used to determine the mathematical law. The second order regression used for the