IN-SITU FIBRILLATION FOR IMPROVED MECHANICAL PROPERTIES IN ARAMID-GLASS FIBRE REINFORCED POLYAMIDES

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Keywords: Hybrid composites, fibrillation, mechanical properties, digital image correlation

Abstract

A new class of Hybrid glass / para-aramid reinforced composites has been processed by melt-blending of an aliphatic polyamide (PA6,10) and solid fibers during co-extrusion at high temperature. In situ fibrillation mechanisms occurring during such process result in well dispersed nano-fibres covalently bonded to the matrix due to a rapid compatibilization of the matrix-fiber interface by transamidation reactions. After injection moulding, cooling from the melt results in a network of aramid nanofibers acting as nucleation sites for the crystallization of the polyamide matrix. The presence of this mechanically rigid network is expected to favor stress distribution when the material is deformed. This in turn delays void localization at the glass fibre / polyamide interface in the hybrid composites and yields to improvement of their mechanical properties as compared to conventional glass fibre thermoplastic composites.

1. Introduction

Thanks to their excellent heat resistance, strength and stiffness, short fiber reinforced polyamide thermoplastics are among the most sought-after engineering materials for lightweighting in the automotive industry, accounting for about one third of global polyamide production. There is particular interest in the use of hybrid composites containing chopped aramid fibers for improved impact performance without compromising specific tensile and compressive strength. However, obtaining a strong fiber-matrix interface remains difficult in such materials, in spite of the similar chemical functionality of aramids and typical polyamides [1].

In the present work we describe for the first-time hybrid polyamide composites containing highly dispersed fibrillated aramid fibers that are covalently bonded to the matrix. This is achieved by *in situ* fibrillation of chopped aramid fibers during high temperature extrusion compounding, such that the matrix-fiber interface is reactively compatibilized by rapid transamidation reactions – like those occurring in copolyamide matrices [2] – as the fibers break up to form fibrils, promoting further dispersion. Cooling from the melt then results in a network of aramid nanofibers, which in turn act as nucleation sites during crystallization of the polyamide matrix. The presence of dispersed covalently bonded aramid nanofibrils leads to remarkable improvements in the mechanical properties of glass fiber reinforced polyamide 6,10 (PA 6,10) composites in which part of the glass fiber is substituted by an equal volume of fibrillated aramid fiber. The reduced density results in maintained specific stiffness. Tensile strength increases at intermediate aramid contents. Moreover, there is a significant improvement in ductility, consistent with a delay in the onset of glass fiber debonding. *In situ* fibrillation of aramid assisted by transamidation may hence pave the way to the design of a new class of composite materials with strongly enhanced thermo-mechanical performance.

2. Materials and methods

2.1. Melt coupounding of the composites

The polyamides used in this work were provided by EMS Chemie AG and stored under vacuum for at least 48 h before processing. Poly(hexamethylene sebacoamide) (PA610, M_n = 16’000 g/mol, M_w = 32’000 g/mol), was melt compounded with para-aramid and glass fibre in a co-rotating twin-screw micro-compounder (DSM Micro 5). The barrel temperature was set to 260 °C, and the polymers were compounded for about 10 min at a screw speed of 100 rpm. The resulting blends were then injected using a DSM injection-moulding machine to form dog-bone shaped tensile test-bars of 20 mm length, 2 mm thickness and 4 mm width. The cylinder and mold temperatures were 260 °C and 130 °C, respectively, and the injection pressure was 6 bars. The test-bars were dried for 1 h at 180°C (i.e. well above Tg) under vacuum and stored at room temperature under vacuum before further testing and analysis.

2.2. Mechnanical testing (UTS) and Digital Image Correlation (DIC)

The tensile test bars were tested using a universal testing machine (Walterbai UTM) at a nominal strain rate of 10 % min^{-1}. The strain was measured using a clip-on extensometer with a gauge length of 20 mm. A minimum of 5 specimens were tested for each material. Young’s modulus is calculated as the slope of the nominal stress-strain curve in the linear elastic regime (i.e. for strains ranging from 0% to 1%). Two stereovision systems have been chosen to measure displacement field in front and side surfaces of the specimens, to avoid using transverse isotropy assumption, which generates non-negligible errors in the estimate of volumetric strain. Front and side surfaces of the samples were coated with a white spray paint to generate a random speckle pattern. The images are recorded using PIKE cameras system. The images are then post-processed using VIC-3D software package. The strain field in both front and side faces are obtained in the central part of the sample. Stress-strain and volumetric strain data are extracted from such domains.

2.3. Scanning Electron microscopy (SEM) and Transmission Electron Microscopy (TEM)

SEM. Fractured surfaces of specimens subjected to tensile test were analyzed by a Gemini electron scanning microscope (SEM). Electrons are collected by in-lens detector. The acceleration voltage is 3kV, and samples coated with carbon to avoid charging.

TEM. 200nm thin films were prepared by cryo-microtome at -50°C and cutting speed of 0.2mm.s^{-1} of cross sections from the dogbone shaped specimens. The films were deposited on a copper grid. They were then heat treated under nitrogen in a differential scanning calorimetry (DSC) cell, allowing for good control of temperature and avoiding oxidation. The specimen was heated to 300°C at a heating rate of 10°C min^{-1}, held at 300°C for 2 min and then cooled to ambient temperature at 10°C.min^{-1}. TEM experiments were performed on a TALOS machine with an electron voltage of 200kV.

3. Results and discussion

3.1. Fibrillation

Fibrillation is the processing of solid fibers in a manner that splits the main fiber into its constituent nanofibrils, which remain solid. The degree of fibrillation of para-Aramid increases with the volume fraction of fibers, resulting in higher spatial dispersion of fibrils in the polyamide matrix (figure 1). The fibers can conserve their initial shape (figure 1a), being partially fibrillated (figure 1b), or totally fibrillated (figure 1c). For same processing conditions, the higher degree of fibrillation for materials containing a higher proportion of fibers is likely due to the fiber-fiber interactions or friction during processing associated with higher shearing forces.

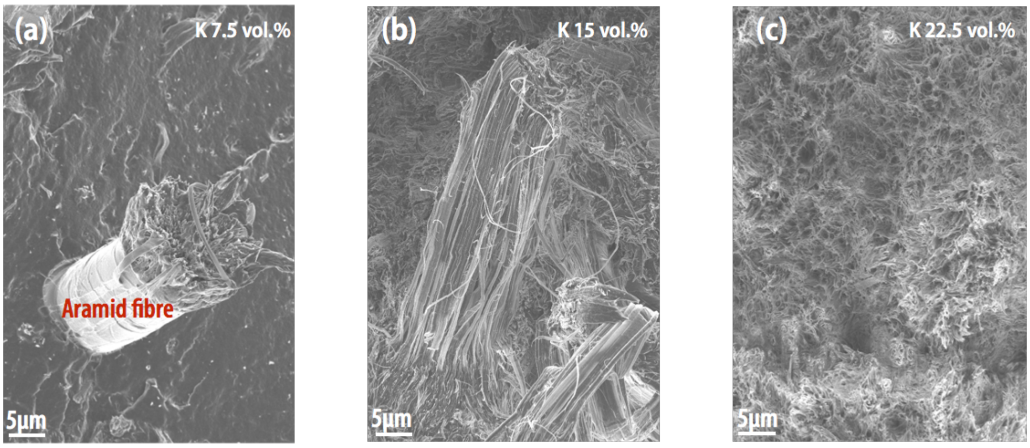

Figure1. SEM images of fractured surfaces of composites with 7.5% vol. of para-aramid fibers (a), with 15% vol. of para-aramid fibers (b), 7.5%, 15% and 22.5% vol. (c).

3.2. Fibre network

The nanofibre diameter ranges from 50 nm to 200 nm, as observed in the TEM cross sections of thin films (figure 2). They show well dispersed fibrils and the fibre-fibre distance decreases by increasing both the fibrillation degree and the overall fibre content. A semi-crystalline structure is observed for the polyamide matrix, which consists of regular alterning of nano-size crystalline lamellas and amorphous domains. While the semi-crystalline structure of the polyamide matrix is spatially homogeneous, a part of the lamellar structures nucleates and grows from the fibre surface in the composite materials. Crystalline growth is limited for the composites with the highest content of para-Aramid due close neighboring nano-fibres. Contrarily to localized transcrystaline zones of several decades of microns at the surfaces of nonfibrillated microfiber in polyamide based composites [3], the crystalline domains nucleated from the nanofiber surface is spread enougth in the polyamide matrix to be connected from a fibre to another for sufficiently high quantity of fibres.

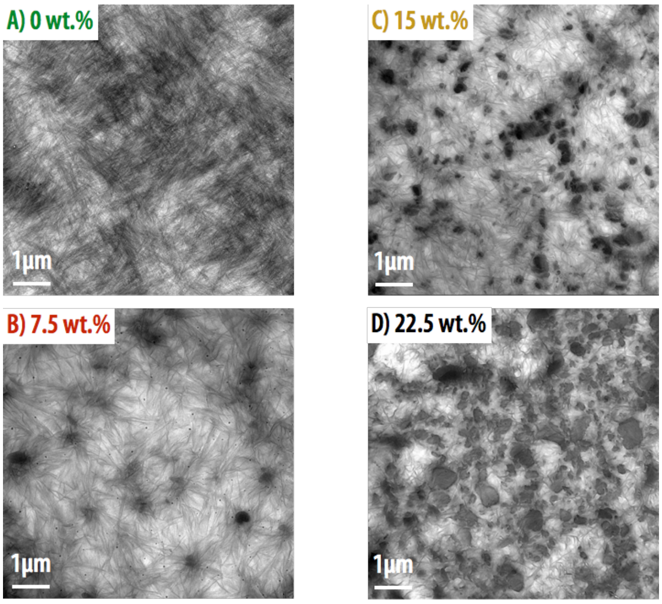

Figure 2. TEM images of thin films prepared from the cross section of the injection molded dogbones for materials with 0%, 7.5%, 15% and 22.5% vol. of para-aramid fibers.

3.3. Mechanical properties of the hybrid composites

Glass fibre composites, para-Aramid fibre composites and hybrid Glass fibre / para-Aramid composites have been tested mechanically during uniaxial stretching up to failure. For all composite, strain localization is observed in the central part of the specimens before macroscopic failure, which is related to the localization of plastic mechanisms. Plasticity is accompanied by a volumetric strain localization that are likely due to acceleration of nucleation and growth of cavitation in the specimen. Larger values of longitudinal strain onset at volumetric strain localization in hybrid composites would prevent premature macroscopic failure (figure 3e). Consequently, both stress and strain at failure are increased for hybrid composites (25% or 50% of GF replacement) and compared to both pure Glass fibre and pure para-Aramid fibre composites.

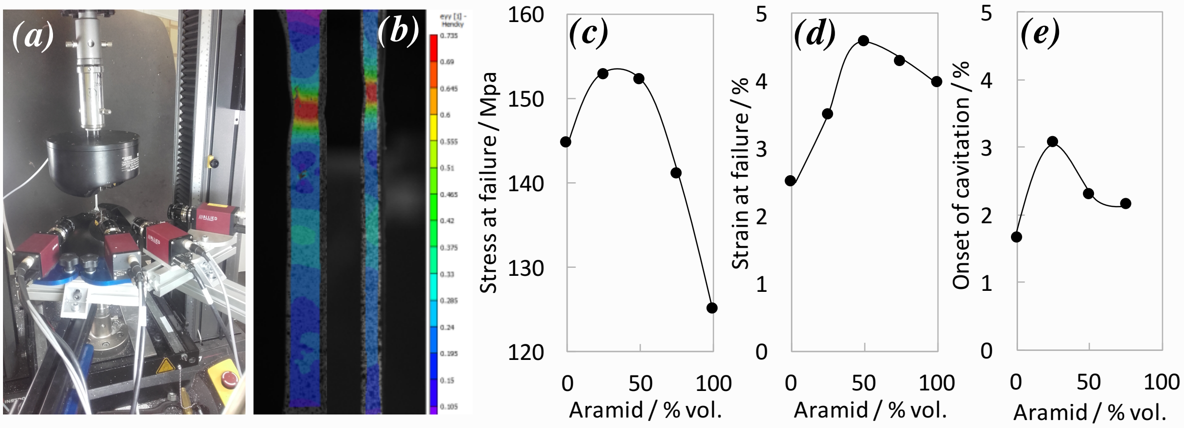

Figure 3. (a) Set-up for volumetric strain measurement during tensile testing; (b) strain field determined by DIC; (c) stress at failure; (d) longitudinal strain at failure and (e) longitudinal strain at the onset of localized volumetric strain during mechanical testing of 30 vol% fiber reinforced polyamide with substitution from 0% to 100% of the Glass fiber by para-Aramid fiber.

SEM preformed on fractured surfaces of pure Glass fibre composites (figure 4a) shows micro-voids mechanisms due to fibre breakage or debonding, eased by high stress gradient at fibre / matrix interface. Contrarily, homogeneously dispersed para-Aramid fibres are subjected to nano-cavitation in pure Kevlar composites and hybrid composites (figure 4b and 4c), which is consistent with delayed volumetric strain localization in these materials. The presence of a percolating crystalline and mechanically rigid network, composed of nano-fibres and crystalline lamellaes, allows distributing the stress. This would delay localization, growth and coalescence of the micro-voids at glass fibre / polyamide surface, that relates to improved mechanical properties in the hybrid composites.

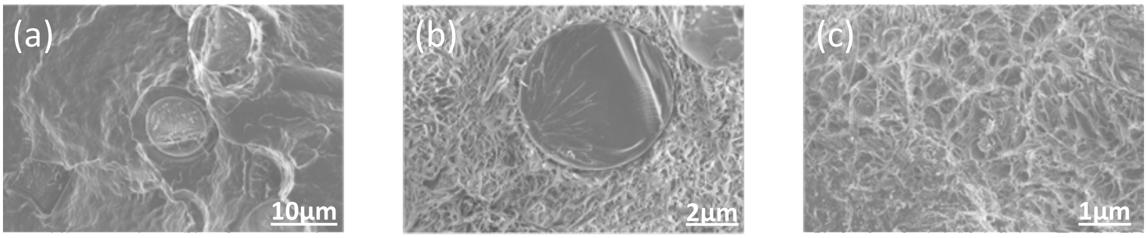

Figure 4. SEM images of fractured surfaces of composites with 30% vol. of glass fibers (a), with 15% vol. of glass fibers and 15% vol. of para-aramid fibers (b), with 30% vol. of para-aramid fibers (c).

4. Conclusions

Hybrid polyamide composites containing solid glass fibres and highly dispersed fibrillated aramid fibers have been prepared by blending with a polyamide matrix (PA6,10) by extrusion process. Thanks to *in situ* fibrillation of chopped aramid fibers during high temperature extrusion compounding, reactive compatibilization of matrix-fiber interface is allowed by rapid transamidation reaction, yielding to the creation of covalent bonds between aramid nano-fibrils and the polyamide matrix. Cooling from the melt after injection-moulding then results in a network of aramid nanofibers, which in turn acts as nucleation sites for crystallization of the polyamide matrix. The presence of the dispersed covalently bonded aramid nanofibrils leads to improvements in the mechanical properties of glass fiber reinforced polyamide composites if glass fiber is replaced by an equal volume of fibrillated aramid fiber. The reduced density results in maintained specific stiffness. Tensile strength increases at intermediate aramid contents. Moreover, there is a significant improvement in ductility, consistent with a delay in the onset of glass fiber debonding.

Current investigations on the microstructure of the global crystalline network – made of para-Aramid crystalline nano-fibres and crystalline lamellae in the polyamide matrix – at macromolecular and crystal lattice scales would help in better understanding and predicting the impact of this network on the mechanical macroscopic properties.

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