ALUMINA WHISKERS / BISMALEIMIDE COMPOSITES: PROCESSING STRATEGIES, STRUCTURE AND PROPERTIES

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Keywords: Bismaleimide (BMI), corundum whiskers, RTM

Abstract
This paper investigates the structure and thermo-mechanical properties of a reinforced bismaleimide-based hybrid composite material.
The morphology (filler-matrix interface), thermal and mechanical behavior of the resulting hybrid material have been evaluated as function of the type of whisker and/or of the type of mixing strategy by means of different techniques: SEM, TGA, DSC, DMA, Compression test, Tensile test.

1. Introduction

Monocrystalline α-Alumina whiskers have been mixed with Bismaleimide resin to obtain new composite matrix with higher performance properties and similar processability to neat bismaleimide.

In polymer systems, the addition of nano- and micro-fibers leads to a great improvement in the properties of the matrix such as thermal stability and mechanical performance with very low filler contents. This is because the high surface area of these particles with nano/micrometric dimensions increases the interfacial interactions between matrix and filler [1,2,3]. Therefore, the key factor for the enhancement in performance of the polymer/filler composites is the dispersion of the filler in the matrix since the final properties depend on the structure and morphology generated during the processing. Treatments to modify the filler surface are usually used in both polar and non-polar matrices to improve interactions between the organic polymer and the inorganic filler [2,3].

Alumina (Al_2O_3) and other ceramic oxides are among the commonly used mineral fillers in composite industry in combination with different polymer matrices [4,5,6]. Whiskers are short fiber-shaped single crystals with high perfection and very large length-to-diameter ratio. Owing to its perfect crystal structure, the tensile strength of a whisker is extremely high and close to the binding force of adjacent atoms [7]. Therefore, they are considered an attractive alternative for reinforcing polymers.

NKR® Alumina Oxide monocrystalline micro-fibers are a particular kind of these fillers [8]. They are grown in one direction with no discontinuities or faults providing them more mechanical strength and higher thermal resistance. They are used as additives to make different composites, with different matrixes: metals, ceramics and polymers. For example, when these Alumina whiskers were melt-mixed with polyamide 12 (PA 12) resulted in an interconnected structure with moduli enhancement, higher crystallinity (nucleating effect of fibers,) and improved the thermal stability of the PA 12 matrix [9].

Bismaleimide (BMI) resins are a relatively young class of thermosetting polymers. Even though epoxy resins are the most widely used composite materials in aerospace industry, their used is limited for high temperatures. With epoxy-like processing and mechanical properties, higher service temperature, excellent physical property retention at elevated temperatures and in wet environments, and nonflammability properties, BMI composites are an excellent alternative for high temperature and high performance applications. The principal concern with BMI resins has been their inherent brittleness owing to their high cross-linking density [10,11]. The development of this hybrid composite material has as main objective to improve the thermal stability and mechanical performance, aiming to lower the brittleness at low temperatures and the composite residual stress, since both phenomena are believed to be related with the micro-crack nucleation and propagation frequently observed in carbon fiber/bismaleimide composites after standard manufacturing conditions.

Different mixing strategies are explored: several blending techniques, aspect ratios, purification methods and surface treatments of the alumina whiskers.

2. Experimental Section

2.1. Materials

The α-alumina (α-Al_2O_3, corumdum) (NKR™) fibers were supplied and produced by NEOKER S.L. following a patented process (“purified fibers with short aspect ratio”). The technology for the production of the whiskers involves the reaction between aluminum and powdered silica in Ar atmospheres containing metal vapors.
Three types of α-Al_2O_3 were supplied (un-purified fibers, purified fibers and functionalized (NaOH) fibers) that differed in their level of purification or in modifications introduced during and after their manufacture.
Un-purified fibers: They are fibers with a Si drop at their tips (Figure 1). These α-Al_2O_3 whiskers were prepared by a vapour-liquid-solid deposition method (VLS) with a fibre ending drop mechanism under inert atmospheres and the addition of selected transition metals that improves the amount of produced α-Al_2O_3 fibres. Each fibre has a hexagonal section, drops at one of its ends, and one basal hexagonal pyramid. The drops at the ends of the fibres demonstrate that the fibres had grown via VLS deposition.
They present good chemical stability, high hardness excellent mechanical properties and a melting point of 2050 º C.

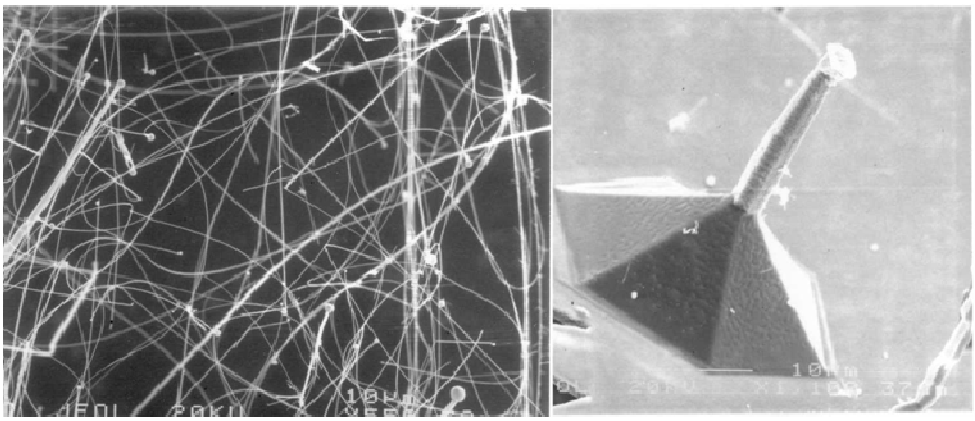

Figure 1. Unpurified NKR single crystal alumina fibers

Purified fibers: (without drop, Figure 2) These fibres are obtained using purified alpha-alumina fibres through the selective volatilization of the metal impurities with low oxygen pressure atmospheres. The volatilization occurs when liquid metal impurities in non-aqueous phase or dissolved in water come into contact with a gaseous phase. The metal impurities then reach their vapour pressure which is the gas pressure in equilibrium with respect to the solid or liquid at a given temperature. In this way, the metal impurities are transferred from the fibre surface to the gaseous phase. To this end, a controlled-atmosphere device is used. The volatilization comprises subjecting the α-Al_2O_3 whiskers at vacuum with an oxygen partial pressure lower than 10^{-1} atm O_2 and at a temperature of 1600ºC for 2h.

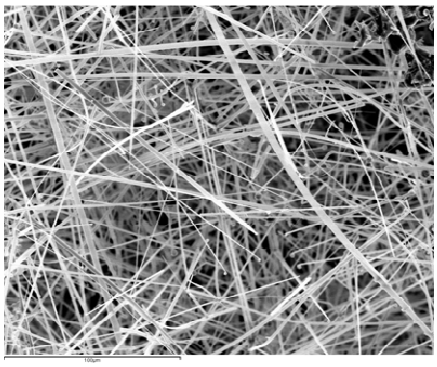

Figure 2. Purified NKR single crystal alumina fibers

Functionalized fibers: Surface treatment with NaOH [Fisher, 2005] was used to functionalize the surface of whiskers and to generate reactive groups (OH groups) in their surface, the fibers were immersed in dissolution of NaOH (1M) at 100ºC during 24 h. Then, they were dried in an oven before the mixing with the resin.

The bismaleimide (BMI) used as matrix is a one-component modified bismaleimide for resin transfer moulding (RTM) with high glass transition temperature (285ºC) for service temperature to 232˚C provided by an external supplier.

2.1. Preparation of BMI - NKR® composites

BMI resin was preheated in a bath at 110ºC. Then, alumina whiskers (10 wt % loading) were pre-dispersed in the resin at the same temperature. Finally, the BMI/whisker mixtures were blended by sonication during 5 minutes.
The different BMI/whisker blends were cured in an oven with the following cure cycle: 4h at 191ºC+16 h at 232ºC, following the supplier's recommendations.
Table 1 shows the different samples prepared with three kinds of alumina whiskers: Un-purifiedd fibers "un-p", purified fibers ''p''and surface modified fibers "pt". In order to study the effect of the sonication in the fiber dispersion and, latterly, in the macroscopically properties of blend, a sample, only mechanically stirred, was prepared "pm".

Nomenclature	BMI (wt.%)	NKR™ (wt.%)	Surface treatment with NaOH
BMI	100	0	-
90/10un-p	90	10	No
90/10p	90	10	No
90/10pt	90	10	Yes
90/10pm	90	10	mechanical stirred

Table 1. Nomenclature of the samples

2. Characterization

To assess the influence of alumina whiskers in the polymerization process of BMI resin, the glass transition temperature (Tg) and the degree of cure of cured blends was measured by Differential Scanning Calorimetry (**DSC**). Analyzes were performed using a DSC 2020 (TA Instruments) between 50 and 350ºC under nitrogen atmosphere at a heating rate of 10ºC/min.

The study of the thermal stability of composites and their degradation mechanis were realized by Thermo Gravimetric Analysis (**TGA**) in a TGA-7 thermo balance (Perkin-Elmer). Dynamic experiments were conducted under Argon and Oxygen atmospheres, from room temperature to 900ºC at heating rate of 10ºC/min.

To study the dispersion of the fibers and the morphology of the composites, specimens were broken under cryogenic conditions and then examined using a JEOL JSM-6400 Scanning Electron Microscope (**SEM**) at an accelerating voltae of 20 kV. The samples were suputter-coated wi9th a thin layer of gold before they were observed.

In order to evaluate the influence of the fibers in the mechanical properties of the matrix **Tensile and Flexural tests** were performed at a crosshead speed of 2 mm/min using a Instron 5566 Universal Testing Machine (Instron 5566, Instron Norwood, USA).
Tensile test were carried out according to ISO 527. The Young modulus (E), the tensile strength (σ_B) and strain (ε_B) at the break point were measured from stress-strain curves.
Three point bending flexural tests were performed following ISO-178 standard. The span length was 64 mm.

3. Results and Discussion

Analyses and tests are currently in progress.

4. Conclusions

Analyses and tests are currently in progress.

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