EFFECTS OF SILICA NANOFIBERS AND MMT CLAY ON MECHANICAL PROPERTIES OF POLYAMIDE 6: A COMPARATIVE STUDY

Data de submissão: 06/10/2023 *Data de aceite: 01/12/2023*

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ABSTRACT: Polymeric nanocomposites have been outstanding in recent years. The most used fillers have been montmorillonite clay (MMT) and silica nanoparticles due to their high aspect ratio. However, the tendency to agglomeration during the process has made it difficult to obtain nanocomposites with desired properties. The use of fillers as nanofibers may prevent such aggregation. This study aims to obtain silica nanofibers, comparing their mechanical properties with MMT as fillers into a polymeric matrix. Nanofibers were obtained by Solution Blow Spinning (SBS) followed calcination process. SEM analyzes was performed indicating the silica fibers in nanoscale. The nanofibers were incorporated in polyamide 6 film-forming solution and the hybrids were submitted to mechanical tests. The best mechanical resistances were obtained with the 1.5% content for both fillers. There was a decrease in the ductility with the increase of the MMT content, but such influence was not observed for silica nanofibers.

KEYWORDS: Silica nanofibers, solution blow spinning, polyamide 6, montmorillonite clay.

1 I INTRODUCTION

The incorporation of inorganic fillers in polymers makes it possible to obtain hybrid materials with greater mechanical resistance, greater thermal stability or with superior optical, magnetic or electrical properties [1]. Among the usual fillers in thermoplastic polymers, montmorillonite clay (MMT) and spherical silica nanoparticles have been the most used. In this context, MMT has stood out in recent years due to its high aspect ratio and the possibility of intercalating/exfoliating its lamellae [2], which promote a greater contact filler/surface of the matrix. However, the tendency to agglomerate during the process has made it difficult to obtain predominantly delaminated nanocomposites. Silica nanoparticles with high surface area also generate expectations of a good interaction with the matrix, and may provide, in addition to better mechanical and barrier properties, flame retardancy characteristics and resistance to chemical agents. [1, 3, 4]. However, the agglomeration of nanoparticles has also limited the obtainment of nanocomposites with the desired properties. An alternative would be to use the load in the nanofibers form, since their high anisotropy associated with high aspect ratio can prevent the aggregation of nanoloads in composite materials [5, 6].

Among the usual spinning techniques, electrospinning has been considered the most used for producing ceramic fibers on a nanometric scale. However, recent studies [7-10] reported the production of ceramic nanofibers by solution blow spinning method (SBS). This method uses a polymeric solution (which may contain ceramic precursors), a spinning matrix composed of concentric nozzles with special geometry (which allows the production of nanofibers analogous to electrospinning), a pressurized gas system (which replaces the high voltage used in electrospinning) and a pressure regulator to control the gas outlet. The solution is pumped at a predetermined and constant rate, until it reaches the tip of the internal nozzle of the matrix. Simultaneously, the pressurized gas flows through the external nozzle. Upon reaching the tip of the nozzle, it drags the solution towards the collector. At this point, the solution is pressed and the polymer chains are stretched, promoting the formation of fibers and evaporation of the solvent. [11, 12].

In this sense, the present work aimed to produce silica nanofibers by SBS and incorporate them in a Polyamide 6 (PA6) matrix to obtain PA6/nanofiber hybrids. In addition, MMT clay was also incorporated into a Polyamide 6 matrix to obtain PA6/MMT hybrids. The hybrids materials were compared from the perspective of mechanical properties. There are few publications in the specialized literature report the use of silica nanofibers as filler in thermoplastics, therefore, a comparative study with a filler widely investigated as MMT has its justified relevance.

2 I EXPERIMENTAL

Polyamide 6 (PA6), supplied by Radici in the form of pellets, was used as a polymeric matrix, which was solubilized in formic acid (85% P.A.) to obtain dense films. Fillers used:

i) commercial montomorilonitic clay, encoded as Cloisite Na^+, from Southern Clay Products (Texas/USA) ii); silica nanofibers, synthesized at laboratory from a precursor solution containing polyvinyl chloride (PVC), tetrahydrofuran (THF), hydrochloric acid (HCl) and tetraethylortosilicate (TEOS). An unmodified lamellar nanofiller was used to avoid the effect of the surfactant, as the fibrous nanofiller used did not have surface treatment as well.

For the synthesis of the nanofibers, the precursor solution was submitted to the SBS process using compressed air and the following spinning parameters: injection rate of 7.2 mL h-1, gas pressure of 50 psi, working distance of 30 cm and protrusion of 2 mm [13]. The as-spun fibers were calcined at 700 ºC to remove organics and other volatiles. The morphology of the fibers was analyzed by a scanning electron microscope (SEM) (Shimadzu SSX-550). The diameters of the fibers were measured using ImageJ (software of National Institutes of Health USA).

The specimens were prepared using PA6 films, which were dissolved in formic acid (13% m/v) under magnetic stirring at room temperature until its solubilization was complete. After the solubilization, the fillers were added. The amount of fillers was determined as being 0%, 1%, 1.5%, 2.5% and 5% in mass. The final solution was deposited in a petri dish for evaporation of the solvent in an oven at 100 °C. The specimens were subjected to tensile tests in TIRATEST 24250 equipment, with a traverse displacement rate of 5 mm/min. The resulting materials were PA6/nanofiber and PA6/MMT hybrids.

3 | RESULTS AND DISCUSSION

Fig. 1a and 1b shows macroscopic images of nanofibers obtained by SBS before and after calcination process. It is observed that the macroscopic appearence not change after the polymer removal, resuting in silica nanofibers mats as cotton-wool-like. SEM image was perfomed only for calcined fibers, which is possible to evaluate the morphology of the fibers as well as to calculate their average diameter (Fig. 1c). As it can see, the obtained silica fibers were cylindrical and elongated similar to that produced by electrospining. Fibers diameters were measured by ImageJ softwere. Fig. 1d illustrates the graph of fibers diameter distribution. Results revealed an average value of 527 nm with a standard deviation of 235 nm. Moreover, through the histogram a wide distribution range is observed, however, approximately 70% of the fibers are found with diameters below 700 nm, a condition that, according to literature observations [14], nanometric fibers can be considered.

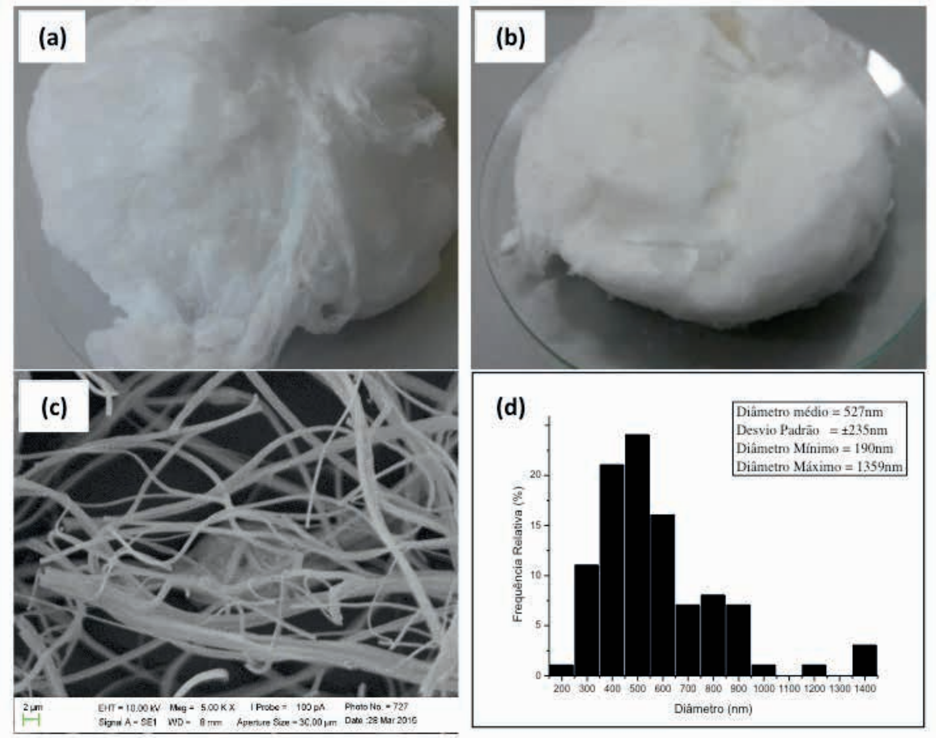

Figure 1. Silica nanofibers obtained by SBS: a) macroscopic image of as-spun nanofibers (PVC/silica); b) macroscopic image of calcined nanofibers (700 °C); c) SEM image of calcined nanofibers; d) graph of the diameter.

It is also observed that, although most fibers obtained are isolated, they can be grouped forming nanofiber “bundles” (Fig. 1c), which impairs the establishment of the average diameter, justifying the value for the standard deviation. This can also be harmful when incorporating such fibers in a polymeric matrix because if the “deinterlacing” does not occur, the “bundles” can provide the same effect of agglomeration of spherical and lamellar nanofillers. To verify this effect, nanofibers were incorporated into a PA6 matrix at different levels and the mechanical properties of the material under tension were measured. As a comparison, a non-organophilized lamellar nanofiller (MMT Na^+) was used since there is less tendency for this filler to be dispersed in the matrix, facilitating the verification of the agglomeration effect. The results are shown in Figures 2 and 3.

Figure 2 shows that the addition of fillers to the polymer in concentration up to 2.5% follows a similar trend for the two types of fillers studied: mechanical resistance decay with 1% of filler, followed by recovery with 1.5% and subsequent decay with 2.5%. For these filler content, the decrease in mechanical strength was considerable for specimens with nanofibers, reaching up to about 35%, suggesting that the high anisotropy of the nanofibers was not sufficient to avoid the effects of the agglomeration of fillers in those concentrations – possibly the “nanofiber bundles” previously observed are influencing the tension concentration caused by the charge. However, at higher amount (5% of nanofiber) there is a recovery in mechanical strength of about 20%, making evident the need to study the influence of higher concentrations of nanofiber. It may be that the effect of anisotropy is favored at higher amounts, or it may be that, it acts as a conventional filler, requiring greater concentrations to provide improved properties. As for the lamellar filler, when comparing the pure polymer with the hybrid with 1 and 2.5%, the maximum tension was not very divergent, and it can be said that the clay, although not organophilized, did not negatively influence the mechanic resistance of the material. For 1.5% filler content, the tension increased over than 5 MPa, which indicates that, for this specific concentration, the clay interacted better with the matrix due to a larger surface area available (although without forming greater agglomerates, which will happen in larger quantities) and, consequently, improved the mechanical resistance of the PA6/MMT hybrid. When the clay concentration was 5%, the mechanical strength decreased considerably (~40%), indicating that the clay in this concentration started to act as a stress concentrator, possibly due to the agglomeration of the filler.

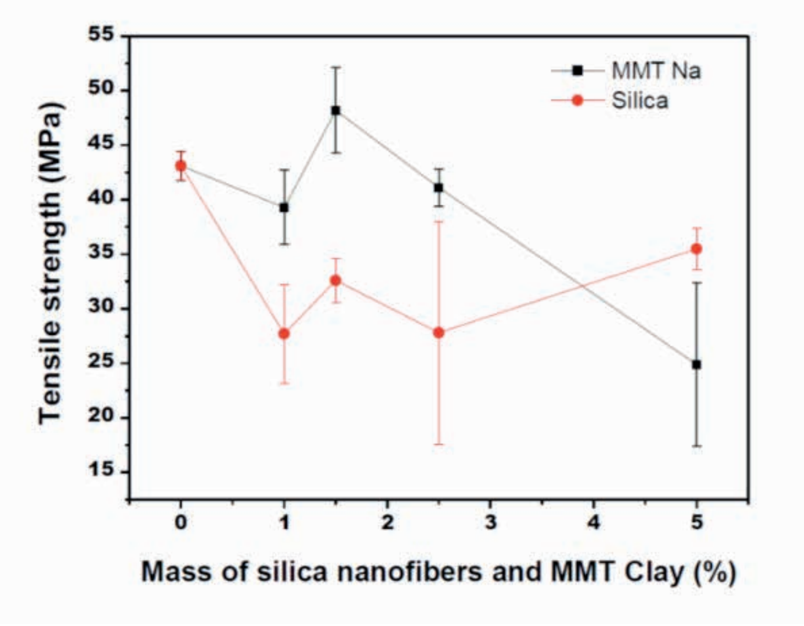

Figure 2. Limit of tensile strength of PA6 with different amount of lamellar (MMT Na+) and fibrous (silica nanofiber) filler.

In Figure 3, there is a noticeable decay of pure material deformation, with the addition of 1% filler, which sums up to about 70% for both charges. However, when increasing filler content, it is possible to notice divergent behaviors for lamellar and fibrous fillers. For instance, silica nanofibers do not show decrease in deformation after subsequent increases in mass. Therefore, it can be said that the ductility remains constant with the additional filler content. As for the clay, it is possible to notice that the more the MMT concentration increases, the more the elongation of the hybrid film decreases. This indicates that the clay concentration both directly and negatively influences the ductility of the material.

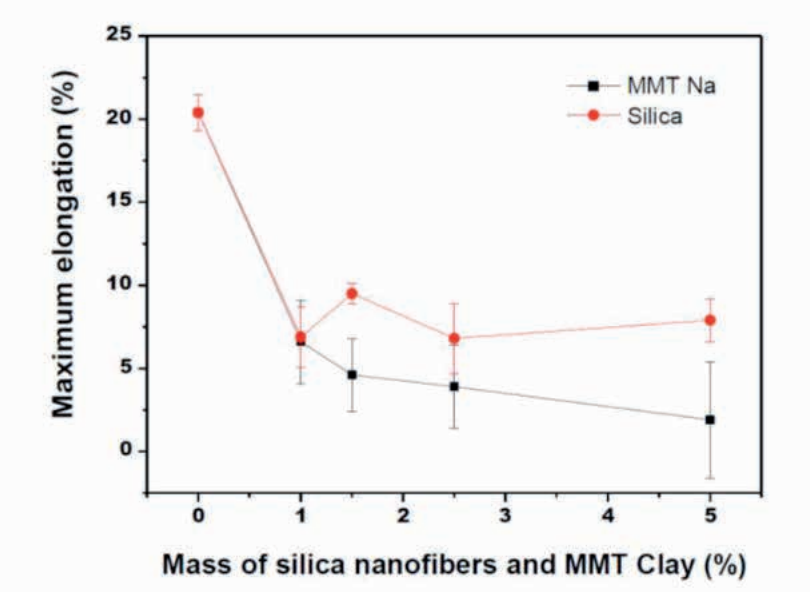

Figure 3. Deformation of PA6 specimens with different amount of lamellar (MMT Na^+) and fibrous (silica nanofiber) at the moment of rupture during the tensile test.

4 I CONCLUSIONS

The silica fibers produced by the SBS method were within the standards necessary for them to be characterized as “nano”. Even so, the addition of these nanofibers to the polymer caused a considerable decrease in the mechanical strength, indicating that the high anisotropy and aspect ratio of the nanofibers were not sufficient to avoid the effects of agglomeration of charges under the studied conditions. For the MMT clay, the stress-concentrating effect was only evident at concentrations above 2.5%. At low concentrations, the best results were obtained with the content of 1.5% for both fillers and the MMT promoted an increase in mechanical strength for this concentration. In relation to the ductility, it was observed that this property decreases as the MMT concentration increases. This influence was not observed with the use of silica nanofibers, keeping the ductility practically constant with the increase in the filler content.

ACKNOWLEDGMENTS

The authors would like to thank the Fundação Cearense de Apoio a Pesquisa

(FUNCAP) for the scholarships granted, to the Faculdade de Tecnologia Cariri (FATEC) for carrying out the mechanical tests and to CNPq for the resources released, which enabled the implementation of the SBS system in the region of Cariri.

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