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Carbon nanofibers in polyurethane foams: Experimental evaluation of thermo-hygrometric and mechanical performance

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ABSTRACT

Polymer nanocomposites synergistically combine the good thermal properties of the hosting polymer matrix with the high mechanical performance of the fillers, providing a new class of materials with superior properties.

The present study aims to evaluate in a multidisciplinary way the enhancement in mechanical and thermal-hygrometric properties of low and medium density nanophased polyurethane (PUR) foams with either randomly oriented or aligned nanofibers as compared to the neat ones.

To this aim, 1% weight of carbon nanofibers (CNFs) were homogeneously dispersed into polyol of PUR foam by an ultrasonic cavitation method. In parallel, a small amount of CNFs was functionalized in advance by a co-precipitation method so as to align them into the polymer matrix through an external low intensity magnetic field.

SEM analyses were used to compare the microstructure of the neat and nanophased samples.

Results have shown that the addition of carbon nanofibers in the foams products a closer structure with a more uniform size and shape. Moreover, functionalized CNFs play a significant role in regulating cells shape as well as strengthening cells walls.

Mechanical test results also demonstrated that CNFs increase both strength and stiffness of the samples. The alignment of carbon nanofibers within medium density nanophased foams determines the highest mechanical properties. However, the more noticeable improvement in samples performance occurred in low density nanophased foams.

Finally, carbon nanoparticles decrease the thermal conductivity and increase the resistance against water adsorption.

1. Introduction

Nanoscience and nanotechnology consist of understanding and controlling the materials at a nanoscale which is a billion part of the meter (10^{-9} m). Moreover, the real significance of the nanoscale is that the materials obtain new properties at this level [1].

Polymer nanocomposites have been drawing a great deal of interest due to their high potential to achieve improvements in their performance by adding a small amount of nanoparticles in polymer matrices.

In particular, polyurethane foams belong to lightweight and energy efficient materials for buildings [2], but their application is limited because of low mechanical strength, poor surface quality, low thermal as well as dimensional stability.

The introduction of fillers in the formulation of building materials, thanks to a refinement of the microstructure, leads to an increase in durability and mechanical performance [3].

At present, carbon nanofibers (CNFs), carbon nanotubes (CNTs), nanoclay and oxides such as SiO_2 and TiO_2 are some of the most commonly adopted fillers in the field of polymer nanocomposites.

Therefore, a small amount of well-dispersed nanoparticles in polymer matrix may significantly improve a wide variety of properties without sacrificing the lightweight structure of polymer foams.

Vapor-grown carbon nanofibers (VGCNFs), commonly named CNFs and used in the present study, are multiwall and highly graphitic fibers

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with diameters ranging from 70 to 200 nm and lengths up to a few hundred microns. Due to their high thermal stability, tensile strength and Young's modulus, CNFs have demonstrated their great potential in nanoscale polymer reinforcements.

Indeed, nanofibers act as nucleation sites to facilitate the bubble nucleation process, leading to an enhancement in mechanical and thermal performance because of a finer cell structure of the hosting foam [4–7].

However, due to their high surface energy, nanofibers tend to agglomerate, bundle together and entangle. These drawbacks may lead to many defect sites in the composites having detrimental effects on polymer performances and limiting the efficiency of CNFs in polymer matrices. Thence, it is imperative to well disperse nanofibers into the polymer matrix when they are still in liquid phase so that interactions at the molecular level can be achieved in order to produce a material with superior thermal and mechanical properties [8].

In the literature, there are several techniques to improve the dispersion of nanoparticles in polymer matrices, such as by optimum physical blending, in situ polymerization and chemical functionalization. For polymer/CNFs composites, high power dispersion methods, such as ultrasound and high speed shearing, are considered the simplest and most convenient ones to reach a homogeneous dispersion of CNFs [9,10].

Moreover, apart from achieving a uniform dispersion, the alignment of carbon nanofibers along a predetermined direction has been found to produce outstanding improvements in mechanical and thermal performance when compared to their randomly-oriented counterparts [11]. Several techniques with the aim of aligning nanoparticles have been reported in literature [12–15]. Among them the application of an external magnetic field is recognized as one of the most effective and simple methods.

However, due to the low magnetic susceptibility of nanofibers, an extremely strong magnetic field (ranging from 25 to 30 T) would be required to achieve a satisfying alignment [16]. Thus, the need of employing such high magnetic field limits the practical application of this method.

Therefore, it is crucial to functionalize carbon nanofibers in advance by coating them with magnetic materials to align them in a polymer matrix under a relatively weak magnetic field, ranging from 50 mT to 1 T [17,18].

In summary, to the best of our knowledge, the majority of research available in the present literature regards the experimental evaluation of nanocomposites mechanical performance [4,7,10,18,19].

Less common are multidisciplinary studies which synergistically combine both thermal and mechanical aspects of polymer nanocomposites [5,8,11,16].

Moreover, polymers are generally tested in terms of decomposition temperature [20] without addressing the thermal conductivity issue.

Therefore, the present work is intended to quantify the enhancement in mechanical and thermal-hygrometric properties of nanophased foams with low and medium densities, containing both randomly oriented and aligned carbon nanofibers, as compared to neat ones.

To this aim, a small amount of CNFs has been functionalized in advance by a co-precipitation method in accordance with a previous study carried out by Shuying Wu and co-workers [18].

1 wt% of nanofibers were dispersed homogeneously into polyol of PUR foam by an ultrasonic cavitation method.

Subsequently, nanophased foam was obtained by adding diisocyanate to the mixture and pouring it in a mould whilst functionalized CNFs were aligned through an external magnetic field of about 90 mT (value measured in the proximity of the magnetic disks).

Finally, the properties of the samples were compared in terms of microstructure, mechanical performance, thermal conductivity, hygroscopic adsorption and apparent density.

2. Materials

2.1. Polyurethane foams

Polyurethane foams of two different apparent densities were used.

The foam consists of two liquid precursors: part-A is a diphenylmethane diisocyanate polymer and part-B is a polyol. It was supplied by Claudio Foresi s.r.l. and has a density of 30 kg/m^3.

In addition, a higher density PUR foam was obtained from the same precursors by varying the foam production process through the adoption of a closing cap on the top of the mould, thus restraining the foam rise.

2.2. Carbon nanofibers (CNFs)

According to material data supplied by Tech-Star s.r.l., the vapor grown carbon nanofibers (VGCNFs) adopted have an average diameter in the range of 30–50 nm and a length of 10–30 μm.

2.3. Magnetic carbon nanofibers (Fe_3O_4@CNFs)

One of the main aims of this study was to demonstrate the improvement in thermal and mechanical properties of PUR foam by the introduction of CNFs aligned by a weak magnetic field.

However, since the CNFs have low magnetic susceptibility, their surface requires to be covered in advance with materials characterized by strong magnetic properties such as iron oxide.

Therefore, the present section describes the method adopted to functionalize CNFs and the preliminary analysis to evaluate the magnetic properties of Fe_3O_4@CNFs.

The fabrication methods of magnetic CNFs-embedded composites have been extensively investigated in literature. A detailed review could be found in Ref. [9].

For the present study, a simple co-precipitation method, developed by Shuying Wu et al. [18], was adopted to functionalize carbon nanoparticles and align CNFs through a relatively low magnetic field.

Indeed, thanks to the functionalization process, fillers may show excellent magnetic properties.

The original CNFs were first subjected to an oxidation treatment in the nitric acid to modify the surface in order to achieve a better dispersion.

Subsequently, 2 g of as-received CNFs were mixed with 200 mL of concentrated nitric acid whilst stirring vigorously. This mixture was then treated at 100 °C for 6 h under magnetic stirring. Afterwards, the mixture was washed several times using deionized water until reaching a pH value of ~7. The samples were vacuum filtrated and dried in a vacuum oven.

After this acid treatment, the CNFs are expected to possess oxygen-containing functional groups on their surfaces and are denoted by CNFs-OX.

The functionalized nanoparticles were fabricated by a co-precipitation method from the CNFs-OX material, prepared as described above.

Firstly, 0.40 g of the CNFs-OX were dispersed in 355 mL distilled water by sonication for 15 min and 0.40 g of Fe_3O_4 was added whilst stirring.

Subsequently, the mixture was vigorously stirred for 15 min whilst being heated to 50 °C under a nitrogen (N_2) atmosphere. Then 0.32 g of $FeSO_4{\cdot}7H_2O$ were added with continuous stirring under a N_2 atmosphere for 30 min. Next, 27 mL of 8M NH_4OH aqueous solution were added drop-wise to precipitate ferric and ferrous salt.

The pH of the mixture was kept at ~10 and the reaction was carried out at 50 °C for 30 min under vigorous magnetic stirring. N_2 was continuously purged during the reaction to prevent oxidation.

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