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Anisotropic compressive properties of multiwall carbon nanotube/polyurethane foams

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ABSTRACT

The anisotropic compressive properties of 0.1, 1 and 2 wt.% multiwall carbon nanotube/polyurethane foam (MWCNT/PUF) composites along the two main directions of transversely isotropic foams are investigated. Special attention is devoted to the anisotropic property-structure relationship of the nanocomposite foams governed by the cell size and morphology, which is investigated by microscopy and the use of existent micromechanical models which consider the cell geometry. Significant enhancement of compression properties with respect to the neat foam occurred for 0.1 and 1 wt.% tested along the foam's free raising direction, while more modest property enhancement occurred along the foam's transverse direction. The cells of the free rising foams are elongated and stronger in the rising direction and the foam's structural anisotropy increases with the addition of small amounts (0.1 wt.%) of MWCNTs. The stiffness and strength ratios of the two main anisotropic directions may be reasonably predicted by using a simple parallelepiped cell model, but more accurate predictions are achieved when a tetrakaidecahedron representation is assumed, albeit more experimental parameters are necessary.

1. Introduction

Foams are commonly used in a wide range of applications ranging from commodities such as thermal insulation and furniture to structural applications such as cores in sandwich composite materials. As cores of sandwich materials, their more relevant loading scenarios are likely compression and shear (Carlsson and Kardomateas, 2011). Polyurethane foams (PUFs) are more economic compared to other polymer foams such as those made of, for example, polyvinyl chloride, but also more limited in their mechanical properties (Carlsson and Kardomateas, 2011; Gibson and Ashby, 1997). By reinforcing PUFs by adding nanoparticles, the applications of such foams are hoped to advance towards more load-bearing scenarios. The mechanical properties of foams are known to be strongly dependent on its density and microstructure, i.e., cell shape and size (Gibson and Ashby, 1997). Therefore, it seems attractive to modify the microstructure of PUFs by the inclusion of nanofillers, modifying in turn their mechanical properties. In this respect, multiwall carbon nanotubes (MWCNTs) are cylindrical nanostructures with high stiffness and strength due to the covalent carbon–carbon bonds that conforms their crystalline structure. Since they can be mass produced nowadays in a fairly economic way, they constitute excellent candidates to investigate the property-microstructure relationship of nano-modified PUFs.

Some research works have been devoted to the incorporation of MWCNTs into PUFs, investigating their resulting mechanical properties. Zhang et al. (2011), for example, report that the addition of 0.2–1 wt.% MWCNTs into PUFs increases their stiffness and strength. Madaleno et al. (2013) report that montmorrillonite/carbon nanotube PUF hybrids ranging from 0.25 up to 1 wt.% modifies the PUF

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microstructure reducing its cell size and increasing its compressive elastic modulus. Dolomanova et al. (2011) found enhanced mechanical properties in PUF composites using MWCNTs with respect to using single-wall ones, due to the better dispersion achieved for the former ones. Yan et al. (2011, 2012) also found that the mechanical properties of PUFs are enhanced with the addition of MWCNTs in weight concentrations below 0.25 wt.%. These results show the potential of MWCNTs as reinforcements for PUFs. However, PUFs are often mechanically anisotropic (Gibson and Ashby, 1997; Huber and Gibson, 1988; Metha and Colombo, 1976; Hamilton et al., 2013) and the changes in the foam's microstructure by the inclusion of MWCNTs, concomitant with the changes in anisotropy, have been very scarcely investigated. Hamilton et al. (2013) are probably the only ones in the open literature that have formally reported on the anisotropy of PUFs reinforced with several nanofillers. They studied the anisotropy of PUFs reinforced with milled glass fibers, montmorillonite and MWCNTs, and found that along the rising direction the elastic modulus increases as much as ~26%, while along the transverse one decreases by ~40%. These findings were supported by an existent tetrakaidecahedron model for the cell geometry.

When synthesized in an open mold, PUFs rise freely. As a result, its microstructural cells are more elongated along the rising direction than along both transverse ones. In this condition, since both transverse directions are assumed to behave equally, the resulting microstructure and consequent mechanical properties of the PUFs are often transversely isotropic (Gibson and Ashby, 1997; Huber and Gibson, 1988; Metha and Colombo, 1976; Hamilton et al., 2013).

Therefore, given this motivation, this study investigates the anisotropic compressive mechanical properties of PUFs modified by small concentrations ($\leqslant$2 wt.%) of MWCNTs with particular focus on the relationship between the foam's microstructure and its resulting anisotropy. Existent micromechanical models considering the foam's cell morphology are used to better understand this relationship and reconstruct a plausible representation of the cell's shape.

2. Materials and methods

2.1. Materials

Commercial MWCNTs with purity greater than 95% produced by chemical vapor deposition with internal diameter ranging between 5 and 10 nm, external diameter of 30–50 nm, and a length ranging between 1 and 6 μm were used (Cheap tubes Inc., 2014; Avilés et al., 2014). For the production of PUFs, commercial DOW resins with 330 mg KOH/g and diisocyanate with 31% NCO were used (The Dow Chemical Company, 2015). Blowing agents, surfactants and catalyst were dissolved in the polyol by the manufacturer.

2.2. Preparation of neat PUF and MWCNT/PUF composites

Preparation of PUFs was achieved by mixing the polyol and isocyanate in a polyol:isocynate weight ratio of 1:1.16. The polyol–isocyanate mixture was manually stirred for 10 s until the foam rose freely in an open mold. For the MWCNT/PUF composites preparation, MWCNTs were previously dried at 100 °C for 24 h in order to remove moisture and used at weight concentrations of 0.1, 1 and 2 wt.%. Then, MWCNTs were added to the polyol and stirred at 1200 rpm for 5 min. This MWCNT/polyol mixture was ultrasonically dispersed for 30 min at 225 W in an ice bath by using an ultrasonic horn, and stirred again at 1200 rpm for 2 h. Finally, the isocyanate was added to the MWCNT/polyol mixture and manually stirred during 10 s, casting the solution in an open mold for free foaming. For 2 wt.%, the high viscosity of the solution and the heat generated during stirring tends to evaporate part of the blowing agent present in the polyol mixture, and then, the resulting density of the produced foam may increase. Since the intention of this study was to keep the density constant, for 2 wt.% the mixture MWCNT/polyol was stirred for only 15 min. The average density of the foams produced was 44.6 kg/m^3 (PUF), 43.8 kg/m^3 (0.1 wt.%), 46.1 kg/m^3 (1 wt.%) and 48.3 kg/m^3 (2 wt.%) with a maximum coefficient of variation of 9%, which was measured based on the procedure reported by the ASTM standard D1622 (ASTM D1622, 1998). This normalizes the studied properties under a similar density, as aimed in this investigation.

2.3. Morphological characterization

The morphology of PUFs was examined extensively using optical and electron microscopy. An stereoscope with 10x magnification lens was used to measure an effective cell size by counting the intersection over a 10 mm long line, based on the procedure reported by the ASTM standard D3576 (ASTM D3576, 1998). To obtain a reliable statistical significance, 250 cells per each direction and MWCNT concentration were measured. Orthogonal directions, indicated as x_1, x_2, x_3 in Fig. 1 are used to refer to the principal directions of the foam. x_3 corresponds to the free raising direction (direction of larger cell elongation) while x_1 and x_2 form the transverse (isotropic, as will be seen) plane.

In the parallelepiped model, cell size was characterized by three cell lengths l_i, where i = 1 2, 3 correspond to x_1, x_2 and x_3, respectively, see Fig. 1. A JEOL JSM-6360 LV scanning electron microscope (SEM) operated at 20 kV was used to image the microstructure and measure the cell edges. The cell density (number of cells per cubic unit) was calculated using a standard formula (Kumar and Suh, 1990; Gosselin and Rodrigue, 2005) but slightly modified to account for transverse isotropy as,

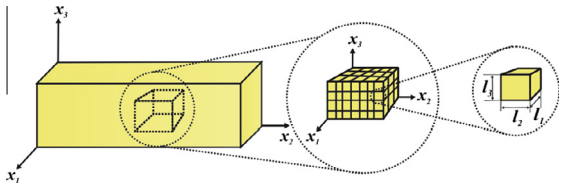

Fig. 1. Schematic of bulk foam, a specimen and a unit cells indicating the x_1, x_2 and x_3 directions.