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Natural rubber foams with anisotropic cellular structures: Mechanical properties and modeling

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ABSTRACT

Natural rubber foams are biobased and lightweight products which have found their main field of application in comfort products such as mattresses and pillows. They are generally produced from chemical foaming processes in which the expansion of the polymer is isotropic and hence, their properties are not directionally dependent. However, this dependency could be interesting for certain structural and thermal insulating applications. In this work, elastomeric foams based on natural rubber with a medium relative density (around 0.3) and with varied cellular structures in terms of the shape anisotropy ratio of the cells were produced by a chemical foaming process in which expansion was restricted to only one direction inside a mold. The use of solid precursors of different dimensions, the elastomeric properties of natural rubber and the crosslinking by sulfur of the polymer matrix during foaming allowed foams to be obtained with anisotropy ratios between 0.90 and 2.48 at the same density and with the same properties as the polymeric matrix. In this particular case the study was focused on analysing their compressive modulus and its relationship with the anisotropy of the cellular structure by employing analytical models generally used to describe the mechanical behavior of anisotropic foams.

1. Introduction

Natural rubber is a biobased elastomeric polymer which has been mainly applied in the tire industry. As foam, natural rubber is generally used for comfort applications such as in mattresses and pillows. These foams are produced from latex, which is the liquid form of natural rubber and directly extracted from the *Hevea brasiliensis* tree (Ferreira, 2002; Kanokwiroon et al., 2008). However, the homogeneity in properties of latex is not always guaranteed due to the high amount of substances found in it, such as proteins, fatty acids, carbohydrates, phospholipids and inorganic salts (Archer, 1963). Moreover, latex requires chemical stabilization by ammonia prior to being processed because its properties can be affected by the environment during storage. On the contrary, dry natural rubber, which is obtained from latex after centrifugation and drying, is more stable and homogeneous in properties (Najib et al., 2011). Natural rubber foams produced from dry natural rubber have great potential for being employed in several industrial sectors such as in the aeronautics and automotive industries, sports equipment, footwear, toys and packaging.

Natural rubber has been studied in detail as the main polymer matrix in biobased composites (Jong, 2015; Wu et al., 2004) and nanocomposites (Abrahama et al., 2013; Bellucci et al., 2012). However, there are not many works in literature dealing with the production of dry natural rubber foams. The few ones found employed chemical blowing agents, different grades of natural rubber and in some cases the properties of the polymer matrix were modified by the addition of carbon black (Ariff et al., 2008; Joon-Hyung et al., 2006, 2007; Najib et al., 2009, 2011). All these works have in common that dry natural rubber is firstly chemically crosslinked by compression molding and later foamed at temperatures above the decomposition temperature of the blowing agent by free expansion. This produces cellular structures which are mainly isotropic. In this way, the properties of the foams obtained are not directionally dependent. The latex foams used in mattresses and pillows are obtained by industrial processes such as Talalay and

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Dunlop in which the expansion of the polymer is also isotropic (Eaves, 2004).

The production of natural rubber foams with anisotropic cellular structures could be important for applications in which for instance, different mechanical properties depending on the load direction are required. This is because the cells are elongated. Shape anisotropy in cells can be defined as the ratio between the maximum and the minimum length of the cell. Polymer foams usually present anisotropy ratios of about 1.3 (Gibson and Ashby, 1997). In literature there are several models that attempt to describe the elastic response of polymeric foams under a compressive load (Christensen, 1986; Gibson and Ashby, 1997; Zhu et al., 1997; Warren and Kraynik, 1987) such as the cubic cell model of Gibson and Ashby (1997). Nevertheless, in most of them anisotropic cells are not taken into account. Huber and Gibson (1988) later modified the model of the cubic cell with the aim of describing the behavior of anisotropic foams. They assumed a rectangular open cell instead of a cubic open cell and introduced the anisotropy ratio in the equation of the model. These models simulate the mechanical behavior of foams with very simple cell geometries such as cubes and rectangular prisms, which on many occasions do not represent the real morphology of the cells. A more complicated cell geometry is the tetrakaidecahedron, which is known as the Kelvin cell model (Thomson, 1887). It is assumed to be the only polyhedron that packs to fill space and minimize the surface area per unit volume. Several authors employed elongated tetrakaidecahedron with the aim of analyzing non-isotropic foams (Gong et al., 2005a,b). Sullivan et al. (2008) (Sullivan and Ghosn, 2009) defined a more general model than the previous authors based on the elongated tetrakaidecahedron by specifying three independent dimensions and introducing an additional shape parameter called *Q*. In these works of Sullivan et al., the stiffness and strength ratios of several flexible and rigid foams with anisotropy ratios between 1 and 1.8 are compared with the results obtained with the modified Kelvin model. Moreover, in the work of Hamilton et al. (2013) low-density reinforced polyurethane foams with anisotropy ratios between 1 and 2 were evaluated by the rectangular cell model and the modified Kelvin model.

For these reasons, the objectives of this work are firstly, the development of a new foaming route which allows elastomeric foams to be obtained from dry natural rubber and with different anisotropy ratios at a given density. Secondly, the study of the relationship between process, structure and properties of the foams produced. This study is mainly focused on their anisotropic morphology. The last objective is to evaluate if models generally used for low density foams such as the rectangular and Kelvin cell models are suitable for flexible foams of medium density and with anisotropy ratios higher than 2 such as the natural rubber foams developed in this work.

2. Materials and production process

2.1. Materials

Dry natural rubber of the type Crepe Brazilian Clear (CCB) was employed as the polymer matrix. The vulcanizing agents were zinc oxide supplied by Silox, stearic acid from Renichem, 2-mercaptobenzothiazole provided by Sigma–Aldrich and finally sulfur, which was supplied by Panreac. The blowing agent employed was azodicarbonamide Porofor MC-1 provided by Lanxess with an average particle size of 3.9 μm and with a decomposition temperature of 210 °C (data obtained from the technical data sheet of this material).

The formulation employed for the production of the vulcanized natural rubber foams is summarized in Table 1.

Table 1
Formulation.

Raw material	Chemical formula	Phr[a]
Dry natural rubber	$(C_5H_8)_n$	100
Zinc oxide	ZnO	4.25
Stearic acid	$CH_3(CH_2)_{16}COOH$	3
Sulfur	S_8	2
2-Mercaptobenzothiazole	$S_2NC_7H_7$	1
Azodicarbonamide	$C_2H_4O_2N_4$	5

[a] Parts per hundred of natural rubber.

2.2. Production process

Three kinds of natural rubber foams with the same density but with different anisotropy ratios were produced in this work. The terminology employed for the different foams produced is NRFA (natural rubber foam of high Anisotropy), NRFM (natural rubber foam of Medium anisotropy) and NRFI (Isotropic natural rubber foam).

The production process of these foams consisted of 3 steps. In the first step, the raw materials were mixed in a Haake internal mixer model Rheodrive 5000. The temperature was set to 60 °C and the screw speed to 60 rpm. The temperature was low enough to avoid premature crosslinking and decomposition of the blowing agent.

Secondly, the blends produced were thermoformed in a hot-plates press to obtain solid precursors. The temperature employed was 85 °C and the blends were pressed during 5 min. Three kinds of cylindrical solid precursors of the same weight (7 g) but with different shape and dimensions were produced with the aim of obtaining the previously mentioned foams. The dimensions of the NRFA solid precursor were 10 mm in height and 31 mm in diameter. The NRFM solid precursor was 17.8 mm in height and 23.2 mm in diameter and finally, the NRFI solid precursor was 24.7 mm in height and 19.7 mm in diameter. These dimensions can be seen in Fig. 1 where 3D representations of both, the foaming mold and the solid precursors employed are shown.

Finally, the solid precursors obtained were placed in a cylindrical stainless-steel mold such as the one shown in Fig. 1 in order to carry out the final foaming step in which crosslinking and foaming took place simultaneously. A hot plates press supplied the heat required for both processes. The mold was placed between the plates of the press and the temperature was set to 160 °C. The plates of the press were just in contact with the upper and lower surfaces of the mold. After 25 min the mold was removed from the press and cooled down with water.

The height of the mold cavity was 32 mm as was its diameter. Therefore, the volume of the mold cavity was 25.7 cm^3. The expected density for the natural rubber foams produced is 0.27 g/cm^3, which was calculated by dividing the mass of the solid precursors employed (7 g) by the volume of the mold cavity. The correspondent relative density is 0.29. In Fig. 1 the terminology which has been used throughout the article is also shown with the aim of identifying the expansion direction (D_1) and the directions perpendicular to it (D_2 and D_3). Due to the cylindrical shape of the mold, directions D_2 and D_3 are equivalent and for that reason all the analyses were focused in one of these directions (D_2).

3. Experimental

3.1. Density and volumetric expansion ratio

Density measurements of the foamed and solid samples were performed by the geometric method; that is by dividing the weight of each specimen between its corresponding volume (ASTM