Industrial Crops and Products 89 (2016) 339–349

Contents lists available at ScienceDirect

Industrial Crops and Products

journal homepage: www.elsevier.com/locate/indcrop

Influence of the irradiation dose in the cellular structure of natural rubber foams cross-linked by electron beam irradiation

L.O. Salmazo[a,*], A. Lopez-Gil[a,b], Z.M. Ariff[d], A.E. Job[c], M.A. Rodriguez-Perez[a]

[a] Cellular Materials Laboratory (CellMat), Condensed Matter Physics Department, University of Valladolid, Paseo de Belén 7, 47011, Valladolid, Spain
[b] CellMat Technologies S.L. Paseo de Belén 9-A, 47011 Valladolid, Spain
[c] Faculdade de Ciências e Tecnologia, UNESP—Universidade Estadual Paulista, Rua Roberto Simonsen, 305, CEP 19060-900, Presidente Prudente, SP, Brazil
[d] School of Materials and Mineral Resources Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Pulau Pinang, Malaysia

ARTICLE INFO

Article history:
Received 8 February 2016
Received in revised form 6 May 2016
Accepted 11 May 2016
Available online 1 June 2016

Keywords:
Biopolymer
Dry natural rubber
Electron beam irradiation
Foams
Cellular structure

ABSTRACT

This work focused on the production of natural rubber foams by cross-linking the polymer matrix using high energy electron beam at different irradiation doses (from 50 to 150 kGy) and foaming it with a chemical blowing agent. The aim was to study how the irradiation dose influenced the cellular structure morphology of the produced foams. This was accomplished by quantifying the evolution of cellular structure parameters, such as cell size and cell density, with respect to foaming time and irradiation dose. The results showed that the foams irradiated at the lowest dose are more prone to suffer cellular structure degeneration, resulting in the formation of bimodal cellular structures, while foams irradiated with the highest dose, exhibited more uniform cellular structure. In the latter case, the nucleation density clearly increased resulting in the formation of foams with homogeneous cellular structures and smaller cell sizes (≈20 μm).

1. Introduction

Natural rubber (NR) is a bioderived elastomeric polymer which is extensively used for the production of tires, gloves and gaskets (Rippel and Bragança, 2009; Kohjiya and Ikeda, 2014). It is harvested from the *Hevea Brasiliensis* tree as a liquid suspension called latex in which the presence of other substances such as proteins, fatty acids, carbohydrates to name a few, make its properties highly variable. Moreover, latex requires to be chemically stabilized with ammonia prior to being processed because its properties can be environmentally affected during storage. On the contrary, the dried form of NR (i.e. dry natural rubber) which is obtained after a centrifugation process and subsequent drying of latex, present more uniform properties and stability with time (Najib et al., 2011). As a foamed material, NR finds numerous applications especially in household comfort elements such as mattresses, cushions and pillows. However, for these productions, the liquid suspension, latex, is employed as the main raw material (Eaves, 2004). The dried version of NR has not found many application niches as a foamed material so far. In addition, there are few works in literature dealing with the production of NR foams using the dried version of NR (Ariff et al., 2008; Joon-Hyung et al., 2006; Joon-Hyung et al., 2007; Najib et al., 2009; Najib et al., 2011).

NR has to be cross-linked during processing in order to have the desired properties not only for being applied as a solid material but also as a foam. For instance, the production of mattresses and pillows (latex foams) is based on the established *Talalay* and *Dunlop* processes, which require the cross-linking of the polymer chains (Eaves, 2004). The same is required with the production of automotive tires in which the well-known vulcanization process is used to cross-link the polymer chains (Mark et al., 2005). The NR polymer matrix can be cross-linked either by chemical reagents (peroxides or sulphur) (Banik and Bhowmick, 2000; Manaila et al., 2014) or by irradiation with high energy electron beam. The irradiation process has two clear advantages over the conventional chemical processes: firstly, the final foamed material does not present chemical residues. Secondly, the cross-linking degree can be controlled throughout the applied irradiation dose (ID) before the foaming process. The process has found tremendous interest in the scientific community and there are plenty of articles in the literature regarding the effect of high energy electron radiation not only on the properties of NR, modified NR and their blends (Ahmad et al., 2005; Almaslow et al., 2013; Banik and Bhowmick, 2000; Chirinos et al., 2003; Craciun et al., 2014; Hassan et al., 2007; Jing et al., 2013; Khalid et al., 2010; Manshaie et al., 2011; Mitra et al., 2008; Nabil and Ismail, 2014; Ratnam and Zaman, 1999;

* Corresponding author.
E-mail address: lesalmazo@yahoo.com.br (L.O. Salmazo).

http://dx.doi.org/10.1016/j.indcrop.2016.05.023
0926-6690/

Ratnam et al., 2000; Sharif et al., 2005; Stelescu et al., 2014) but also on the properties of polyolefins such as low-density polyethylene (LDPE), high-density polyethylene (HDPE) and ethylene-vinyl acetate (EVA) (Eaves, 1988; Gheysari et al., 2001; Gheysari and Behjat, 2001; Khonakdara et al., 2006; Mateev et al., 1996; Mateev and Karageorgiev, 1996).

As far as foaming is concerned, the cross-linking process promotes increment in viscosity and melt strength of the polymer, which provide more stability to the cell wall during cell growth stage of foaming thus giving higher expansion capability with less tendency of cell collapse. It has been reported that the irradiation process is industrially used for the production of flexible closed-cell polyolefin foams (Rodríguez-Pérez, 2005). Moreover, a lot of scientific works have been published in the recent years dealing with the subject (Dias and Silva, 2007; I-Chun et al., 2004; Rezaeiana et al., 2009; Wang et al., 2013; Xing et al., 2008; Youssef et al., 2007) and most of them focused on studying the ID influence towards the obtained cellular structures. In the work of *Wang* et al. several irradiation doses (25, 50, 75 and 100 kGy) were employed for the production of foams based on blends of LDPE/EVA by a physical foaming process where CO_2 was used as the blowing agent. Although there were no significant differences between the produced foams in terms of cellular structure, the sample irradiated with 100 kGy showed the lowest average cell size (≈20 μm). In the work of *Youssef* et al., a similar study was carried out on LDPE foams with and without blending with EVA. The range of IDs employed was the same (i.e. 25–100 kGy) but in this case, a chemical foaming process was employed in which azodicarbonamide was used as the blowing agent. In this case, there was a drastic reduction of the expansion ratio when the ID was increased. The work of *Xing* et al. studied the effect of ID (in the same range of the previous works) and the foaming temperature on the expansion ratio and the cellular structure of LDPE foams produced from a gas dissolution foaming process with CO_2 as the blowing agent. They discovered that the foaming temperature had more influence in the determination of the final cellular structures than the ID. The only clear trend obtained was that the increment of the ID yielded a reduction of the expansion ratio regardless of the foaming temperature. As far as the authors' knowledge, the only work related to the production of NR foams is the one conducted by *Ghazali* et al. in which blends of NR/EVA were foamed by a chemical foaming process with different blowing agent contents (Ghazali et al., 1999). These blends were irradiated before foaming with a broader range of IDs than in the previously mentioned works (20–200 kGy). The foams were obtained in a range of densities between 0.3 and 0.5 g/cm^3. The researchers claimed that the increment of the ID restricted the expansion of the polymer. However, the cellular structures were not conveyed and analyzed.

The above review on the existing literature related to the subject has revealed that the control of the cellular structure in terms of cell size and homogeneity by the irradiation process is still a challenge. This work attempted to go further into the subject by analyzing accurately the evolution of cellular structure parameters such as cell size and cell density with respect to the electron beam exposure. The monitoring and evaluation of these parameters will be performed on the produced NR foams after being irradiated with high energy electrons at different doses and foamed via chemical foaming process at different foaming times.

2. Materials

Dry natural rubber (NR) of the Crepe Brazilian Clear (CCB) type was employed as the polymer matrix for the production of cross-linked natural rubber foams. Azodicarbonamide (ADC) was used as the blowing agent. It was provided by *Lanxess* in the form of yellow powders with an average particle size of 3.9 μm and with a decomposition temperature of 210 °C (data obtained from the technical data sheet). Moreover, Zinc Oxide (ZnO), which was supplied by *Silox*, was added to the formulations with the aim of catalyzing the thermal decomposition reaction of the blowing agent. The formulation employed in this study is summarized in Table 1.

Table 1
Characteristics of the reagents and formulations employed.

Raw material	Chemical formula	Phr[a]	Density (kg/m^3)	Purity (%)
Dry natural rubber (NR)	$(C_5H_8)_n$	100	930	–
Zinc Oxide	ZnO	0.25	300	94
Azodicarbonamide	$C_2H_4O_2N_4$	10	1600	99

[a] Parts per hundred of natural rubber.

3. Production process

The production process consisted of four steps: blending, thermoforming, cross-linking and foaming. First, the formulation described in Table 1, was compounded in a Haake internal mixer model *Rheodrive 5000*. The temperature and the screw speed were set to 60 °C and 60 rpm respectively. For the second step, the compound was thermoformed in a hot-plate press at a temperature of 80 °C and by applying a pressure of 10 MPa for 5 min. In this way, solid sheets with 2 mm in thickness were obtained. In the third step, the obtained solid sheets were subjected to electron beam irradiation in the facilities of MEVION TECHNOLOGY with the aim of cross-linking the polymer matrix. The energy employed was 10 MeV, the power of 40 kW, 4 mA intensity and the frequency of 500 Hz. Five solid sheets with different IDs: 50, 75, 100, 125 and 150 kGy, were obtained. Finally, small samples (20 × 20 mm^2) extracted from the irradiated natural rubber sheets were foamed by immersing them in a silicon oil bath heated at high temperature (231 °C). Several foams were produced at different times for each irradiation dose: 30, 37, 45, 53, 60, 75 and 90 s. All these foams were denominated accordingly throughout the work with the acronym NRF (natural rubber foam) followed by the applied ID. For instance, the natural rubber foam irradiated with 50 kGy was denominated as NRF50. In addition, solid natural rubber sheets were also produced (i.e. without ADC and ZnO) following the same production route. They were subjected to the same IDs previously specified with the aim of evaluating the degree of alteration induced to the virgin polymer matrix by the irradiation process (cross-linking). These samples will be denominated with the acronym NRS (solid natural rubber) followed by the applied ID. NRS50 referred to the sample produced without ADC and irradiated with 50 kGy.

4. Characterization techniques

4.1. Density, expansion ratio and porosity measurements

Density measurements of the foamed samples (ρ_f) were performed by the geometric method; that is by dividing the weight of each specimen between its corresponding volume (*ASTM standard D1622-08*). The relative density of the foams (ρ_r) was in turn calculated as the ratio between the density of the foam (ρ_f) and that of the corresponding solid (ρ_s) as shown in Eq. (1).

$$\rho_r = \frac{\rho_f}{\rho_s} \quad (1)$$

The volumetric expansion ratio (*ER*) of the foams was calculated inversely, that is, as the ratio between the solid density and the foam density (Eq. (2)).

$$ER = \frac{\rho_s}{\rho_f} \quad (2)$$