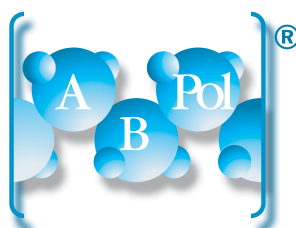


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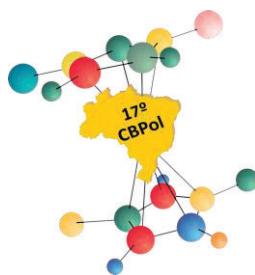
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BIMODAL EVA FOAMS REINFORCED WITH CELLULOSE NANOFIBERS

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Abstract - Cellulose nanofibers are promising materials in the development of polymeric foams, because they act as heterogeneous nucleation sites for the growth of cells during foaming. In this research, we studied the incorporation of cellulose nanoparticles in poly(ethylene-co-vinyl acetate)-EVA foams. The foams were produced with different fiber contents. The main results indicate that with the addition of only 1% of cellulose nanofibers, cell density significantly reduces when compared with the pure EVA foams. On the other hand, by increasing the cellulose content, the agglomeration of nanofibers also increases, which results in heterogeneous cell sizes and bimodal foam formation.

Keywords: foams, EVA, nucleation, cellulose, bimodal foam

Introduction

The insertion of fillers in polymeric foams is generally associated with reducing the cost of the final artifact, as well as modifying some specific property, such as, for example, increased stiffness, increased thermal stability, greater cell nucleation (smaller cells and in greater amount), facilitate the opening of pores, act as a flame retardant or change some surface characteristic in the polymeric wall, in the contour of the cells [1-2]. Currently, the fillers most used in the formulation of polymeric foams consist of inorganic materials, but, recently, the use of organic materials, such as vegetable fibers, has aroused interest due to the fact that they are less abrasive and lighter when compared to inorganic materials [2].

Cell nucleation is a term for a process that induces the formation of a bubble in the polymer matrix. Considering a polymer melt already completely saturated with a blowing agent, with a phase change, either by temperature or pressure induction, the system becomes supersaturated. Therefore, the gassed polymer solution tends to form small bubbles in order to re-establish a steady state of low energy. The theory of classical cell nucleation in polymeric materials classifies cell nucleation into two types: homogeneous nucleation and heterogeneous nucleation [3-6].

In homogeneous nucleation, with the phase change, the spontaneous formation of small air bubbles occurs randomly within the polymeric matrix, and when a bubble reaches a critical size, the other bubbles, of smaller size, tend to migrate to this region, coalescing and propagating the growth of this unit. The existence of small voids in the polymeric matrix is also attributed, which favor the migration of gas from the expanding agent to this region.

In heterogeneous nucleation, it is suggested that the gas is dispersed in a heterogeneous environment, with at least two distinct phases. Among the heterogeneous elements attributed to this theory, the use of fillers, different polymer matrices and also crystals (in the case of semi-crystalline polymers) stand out. During cell formation, the gas tends to migrate to the region of lower energy. In a heterogeneous system with charges, the lowest energy region is preferably found in the charge

interface region, that is, in the contact area of the polymer with the charge. The manipulation of this interface region, either by content or by the size of the filler, can impact the variation in the cellular morphology of the foam in formation [6,7].

Changing cell morphology has a great impact on their properties. Cell size and density directly influence the physical and mechanical properties of polymeric foams. In general, microcellular foams (cell size 1-300 μm) have superior mechanical properties (compression), greater rigidity, greater wear resistance and superior thermal and acoustic properties, while conventional foams (cell size $>300 \mu\text{m}$) have greater resilience, physical-mechanical structure with greater flexibility and greater capacity for cushioning and absorbing impacts [8].

In this way, the manipulation of the shape and size of the cells, in order to combine microcellular and conventional cells in a foam, with a bimodal cellular structure, has been a great challenge from the technological point of view. According to Qiu et al., (2020) [9] it is more difficult to produce and stabilize the morphology of foams with a bimodal cell structure when compared to foams with a uniform cell structure. The use of a bimodal structure of cells allows the combination of superior mechanical properties, high resistance to abrasion with impact cushioning capacity, an ideal condition for use in footwear.

Experimental

Materials

The EVA copolymer (trade name EVATENO 3019 PE) was provided by Braskem S.A. It contains 19% vinyl acetate and a density of 0.940 g/cm^3 , a MFR ($190 \text{ }^\circ\text{C}/2.16 \text{ Kg}$) of $2.5 \text{ g}/10 \text{ min}$ and a melting temperature of $86 \text{ }^\circ\text{C}$. The chemical blowing agent azodicarbonamide (ACA), activated with zinc oxide (ZnO), was supplied by Inbra Industria Química Ltda. Dicumyl peroxide, grade DCP 40 SAP, was supplied by Retilox Química Especial Ltda. The vegetal oil-based lubricant (trade name OLVEX 51) was supplied by SGS Polímeros. The silicon-based surfactant (trade name NIAX L-595) was supplied by Momentive Performance Materials, Inc. The microcrystalline cellulose (MC) grade Sigmacell type 20 mm (cod. S3504) was supplied by Sigma Aldrich S.A.

Methods

Production of Nanocellulose by Mechanical Grinding. Ultrafine grinding of MC was performed using a Masscolloider Masuko Sangyo, model MKCA6 – 2J wheel mill. Milling was performed in a suspension containing water and 3% MC. The equipment was coupled to a recirculating pump and the milling time was 4 h at a speed of 2000 rpm. After grinding, the cellulose suspension was centrifuged using a centrifuge Novatecnica, NT820 model, at a speed of 5000 rpm for 30 min. The phases were separated and the solid/water relation was measured and stabilized at a solids ratio for all samples of approximately 20% cellulose.

Preparation of Foams

The incorporation of the suspensions 20% of cellulose nanofibers (CN) in the EVA was carried out in a mixing chamber (torque rheometer) at a temperature of $120 \text{ }^\circ\text{C}$ with a rotor speed of 100 rpm during 600s. The cellulose was added to the EVA at concentrations of 1%, 2% and 3%. Dispersant additives were added to the cellulose suspension with high solids content, 1 g oil (Olvex 51), 1 g of n-heptane and 1 g of surfactant (Niax Silicone L-595) to facilitate dispersion during the incorporation of nanocellulose. The content of the additives was kept constant regardless of the cellulose content added to the polymer and the cellulose suspension was added dropwise during the processing period. Thereafter, the material was pressed into a 1 mm plate using a thermal press SCHULZ at $120 \text{ }^\circ\text{C}$ for 2 min. The plates were placed in a thermal oven with vacuum at $60 \text{ }^\circ\text{C}$ for 24 h to promote the oil migration to the composite surface.

Additives to produce the EVA foams were added to the composite in the same torque rheometer at $120 \text{ }^\circ\text{C}$, with 100 rpm during 250s. The content of the additives was kept constant for

all formulations: azodicarbonamide (3 parts hundred resin – phr); dicumyl peroxide (2 phr) and zinc oxide (0.5 phr). After the mixing, the material was molded into a preform, by using a heat press at 120 °C for 2 min. The expansion of EVA foams was carried out in a thermal press at 170 °C at constant pressure, by using a method in which the sample is compressed by a period of 10 min with 7.000 kgf of closing force, and the expansion of the foam occurs when the mold is opened.

Characterizations

Cellulose was evaluated by transmission electron microscopy (TEM) using a Jeol Jem 2010 equipment. Uranyl acetate was used as contrast and the analysis was applied at a voltage of 120 kV. The morphology of the fractured surface of the foams was evaluated by scanning electron microscopy (SEM) using a Tescan Mira3 equipment. All samples were previously coated with Au. The observation area in all foams was analyzed in cross section (horizontal direction) of the expanded sample. The software used to measure the cell size was ImageJ. The cell population density per unit volume of the foamed composites (N_f) was determined from the SEM micrographs using eqs. (1) and (2).

$$V_f = 1 - \frac{\rho_f}{\rho_p} \quad (1)$$

$$N_f = \left(\frac{nM^2}{A} \right)^{3/2} \cdot \left(\frac{1}{1-V_f} \right) \quad (2)$$

Where V_f is the void fraction (%), ρ_f is the density of the foam (g cm^{-3}), ρ_p is the unfoamed polymer density (g cm^{-3}), N_f is the cell density (cell cm^{-3}), A is the area of the micrograph (cm^2), M is the magnification factor for micrograph, n is the number of bubbles in the SEM micrograph (cells). The cell size was measured by the Ferret diameter

Results and Discussion

Figure 1 shows the TEM micrographs after the mechanical defibrillation of nanocellulose. NC presented dimensions of approximately 50 nm referring to the nanoscale thickness after the mechanical defibrillation.

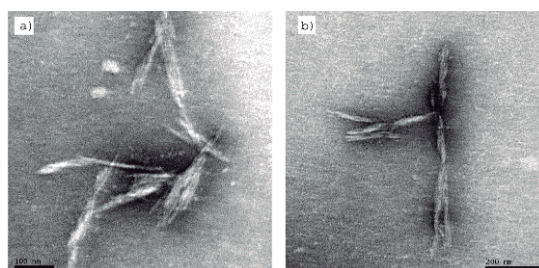


Figure 1. TEM micrograph of CN.

Figure 2 show the SEM images of the cross-sections and the cells size distribution graphs of the EVA foams and reinforced EVA foams with different contents of NC. All foams exhibited predominantly closed-cell morphologies. With the insertion of nanocellulose, all samples decreased in cell size and increased in cell density when compared with non-reinforced EVA foams, mostly because nanocellulose acts as a nucleating agent.

Doroudiani and Kortschot [10] and Lee et al.[11] relate that different cell morphologies can be obtained depending on the type, size, shape, distribution and concentration of the nucleating agent used in the composition of polymeric foams. In addition, depending on the obtained morphology, different properties can be attributed to the foams. The cell density (number of cells per unit area) is affected by the content and by the size/diameter of the filler. In general, fillers act as nucleation sites for the formation of cells. However, the existence of micropores or voids in the polymer-filler interface cause the migration of gas generated from the blowing agent to these

regions, and consequently cells spread and grow. With the reduction in fiber size, there is an increase in the contact area of fibers with the polymeric matrix, which can lead to the formation of a larger amount of nucleation sites for the formation of cells, considering an equal filler content. According to Chen et al.,[12] larger particles contain more trapped air (greater contact area considering a single fiber) and promote the formation of larger cells. By decreasing the particle size and keeping the content constant, there is a greater concentration of smaller fibers, resulting in the formation of a larger number of cells, and thus an increase in cell density.

However, considering the data shown in Figure 2, by increasing the CN content, the presence of large cells increases, and on the contour of these large cells the presence of a large amount of small cells is observed. Foams with the presence of two different groups of cells, that is, of two sizes, is discussed by Duan et al.[12] and are defined as bimodal foams.

As previously discussed, cellulose nanofibers act as nucleating agents for the formation of cells. However, during the incorporation of the fibers into the polymeric matrix, the agglomeration and aggregation of these cellulose fibers can occur, and this phenomenon can promote the formation of larger cells. A larger interface (contact area between the fiber and polymeric matrix) favors the formation of large cells, since the gas from the blowing agent tends to migrate to the least resistant region and propagate their growth from this point. Thus, with the dimorphism on the size between nanometric and micrometric agglomerated particles, the formation of a bimodal foam is favored. By increasing the cellulose fiber content, the probability of obtaining agglomerated particles is higher, as well as the probability of obtaining a bimodal foam.

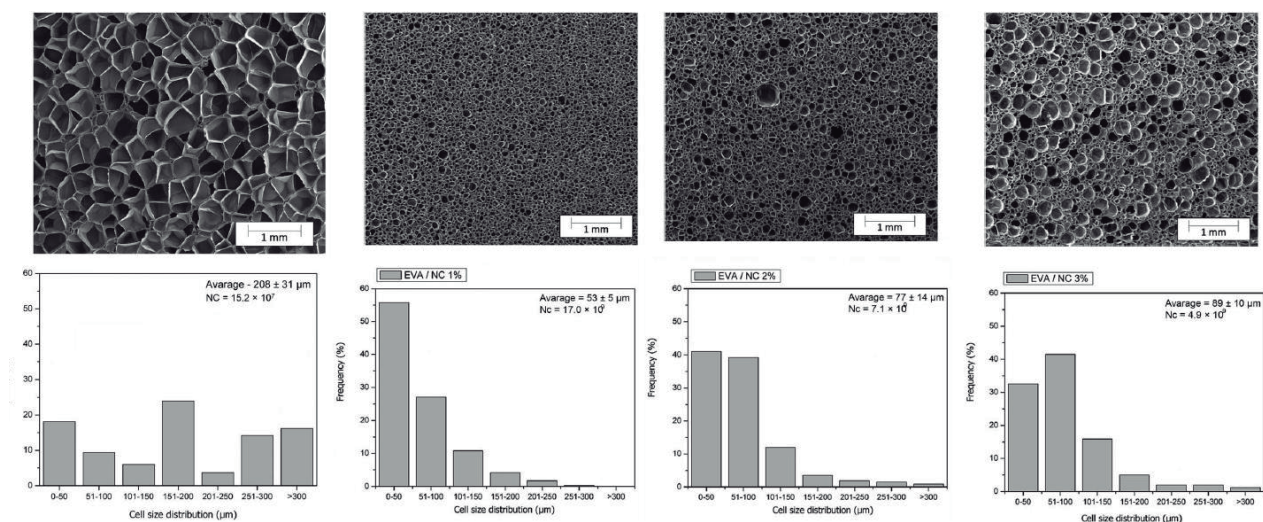


Figure 2: SEM micrographs of EVA foams and EVA foam reinforced with NC.

Figure 3 shows the variation of the arrangement of the CN in the EVA foams. An individualized nanofiber is observed in Figure 3(a), and agglomerated fibers are shown in Figure 3(b).

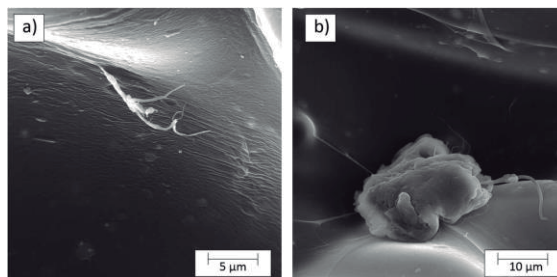


Figure 3: SEM micrograph of an EVA reinforced foam, with (a) an individualized fiber and (b) an agglomerated fiber.

Conclusions

The incorporation of cellulose nanofibers in EVA foams modifies the morphology of cells during the foam expansion process, because the fillers act as nucleating agents. The gas from the blowing agent, during the decomposition, tends to migrate to the lowest possible energy region located at the fiber polymer interface. The most efficient nucleation, observed by the cell size uniformity, was observed with 1% of NC. By increasing the content of NC, nanofibers agglomerate, affecting in the formation of heterogeneous cell sizes, with the presence of bimodal cell foams. Morphologically, compared with the EVA foams without NC, all reinforced foams showed a lower cell size and a higher cell density, that is, the number of cells per unit area.

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