Journal of Research Updates in Polymer Science, 2022, 11, 31-35

The Influence of Density on the Mechanical Response of Reinforced High-Density Polyurethane Foams: A Statistical Approach

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Abstract: In this work, rigid polyurethane foams (RPUF) reinforced by micro fibrillated cellulose (MFC) were manufactured using the free rising method and also under confinement inside a closed mould, aiming to increase apparent density and improve mechanical response. Neat RPUF were also manufactured for comparison. The mechanical response, evaluated by compression (following ASTM D1621 standard) tests were correlated with the final composite apparent density (evaluated following ASTM D1622 standard). Simple linear regression statistical models, based on F-test, were developed using stat graphics software, aiming to understand and correlate the increment in density and its influence on the improvement in mechanical response. Different models were developed to describe the foam behavior. The main results show a more significant influence of the density on strength than stiffness for the neat RPUF, unlike the MFC-reinforced RPUF, which presented an opposite response. These effects could be caused by the lower content of voids when the foams were produced under confinement, and by the greater crosslink density, when MFC was added.

Keywords: Rigid polyurethane foams, high-density foams, micro fibrillated cellulose, cellular composites.

1. INTRODUCTION

Cellular composites are a new class of polymeric materials destinated for specific or advanced applications. An improvement in performance is generally reported for foams when a second phase is used with the polymer. Thermal, combustion, photo response sensibility are some examples of improvements, when fillers are used into polyurethane foams [1,2]. Rigid polyurethane foams (RPUF) are the most consumed cellular polymer worldwide and Micro or nano-fibrillated cellulose (MFC or NFC) are suitable bio-fillers to enhance the mechanical response of such foams [3].

The final density of the foam also plays an important role in the improvement of RPUF performance and some techniques, such as the expansion into closed molds or reactive injection are largely employed in industry, aiming to regulate the density by a simple methodology or increase the mass production of products with high surface quality. Some examples include the reactive injection molding technique (RIM), used to produce components with high complexity with low cost and high productivity [4].

Despite the advantages in use a closed cavity, in laboratorial scale, the use of robust equipment for the production of parts in large scale is not necessary. Then, techniques that may produce components in small scale is necessary. In previous report, the expansion of filled RPUF into a closed mold was reported. Significant differences were reported on cell size, distribution as well as on the final foams' density and, consequently, mechanical, thermal and viscoelastic response [5-7]. Two different expansion degree were evaluated and these characteristics were related with the degree of a called mechanism confinement.

Despite the gains reported in previous reports, no relations on cell size/distribution were made as well as relations regarding the gains in density and its influence in gains in compressive or tensile response of such foams.

Indeed, there is some analytical models that correlates the differences in morphological aspects with mechanical response [8], however, for the best of our knowledge, there is no reports using statistical models, such as linear regression for the prediction of properties over a specific range of density or cell size. Then, this paper aims to present a statistical method to predict the properties of foams, depending on the density. Linear regression was applied and a deep

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E-ISSN: 1929-5995/22

discussion is made, relating the final property with the morphological difference.

2. METHODOLOGY

Data of previous reports was used to predict and preform the models [3,6]. The foams manufacturing also followed a previous report [1-6]. Briefly, bio-based RPUF were prepared into a closed stainless-steel mould, using different “confinement” degrees. A blend of castor oil and glycerine was used as polyol and Methylene diphenyl diisocyanate (MDI) was used as a polymeric diisocyanate. Furthermore, other chemicals, such as commercial amine-based catalyst, silicon oil surfactant and water (blowing agent) were also incorporated for the foams’ production [1-6].

In this specific study, the final RPUF’s confinement degrees of 50 and 30 were related to the free rised RPUF (or 0% of confinement). To obtain RPUF with the desired confinement degrees, reaction mixture amounts, equivalent to 142.8% or 200% of the total mould volume, was inserted into a metallic mould, which was closed to produce 70% and 50% of confinement effect, respectively [3]. The mass of reagents was adjusted to obtain RPUF with apparent densities between 40 and 120 kg.m^{-3} and MFC (at 0.4wt. % related to the total RPUF mass) was used as reinforcements. Compression mechanical test (evaluated following ASTM D1621 standard) was performed, and correlated with the final composite apparent density (evaluated following ASTM D1622 standard).

After mechanical tests, linear regression was performed for the properties, using Statgraphic® software (Spanish version), aiming to verify the correlation between density increment and improvements in mechanical response. Models were created through linear regression to evaluate the effect of the increase in density on the mechanical properties in compression. All of them follow the assumptions of simple analysis of variance (ANOVA) regression, being normality, linearity and independence of residues and equality of variances and used significance of 95%. Being those created in this work the most relevant for properties of interest of RPUF.

Scanning electron microscopy (SEM) was carried out for the neat RPUF and MFC filled one in a Phenom microscope, model ProX$^{®}$ desktop, at 5 kV. The samples were carefully cut in thin slices and the top surface was sputter-coated with gold.

3. RESULTS AND DISCUSSIONS

3.1. Morphological Aspects

Figure **1** shows the SEM images for the studied RPUFs. A homogeneous cell structure for neat and reinforced foams with MFC is observed with a thinner cellular structure for the MFC 0.4 wt.%. Besides, there

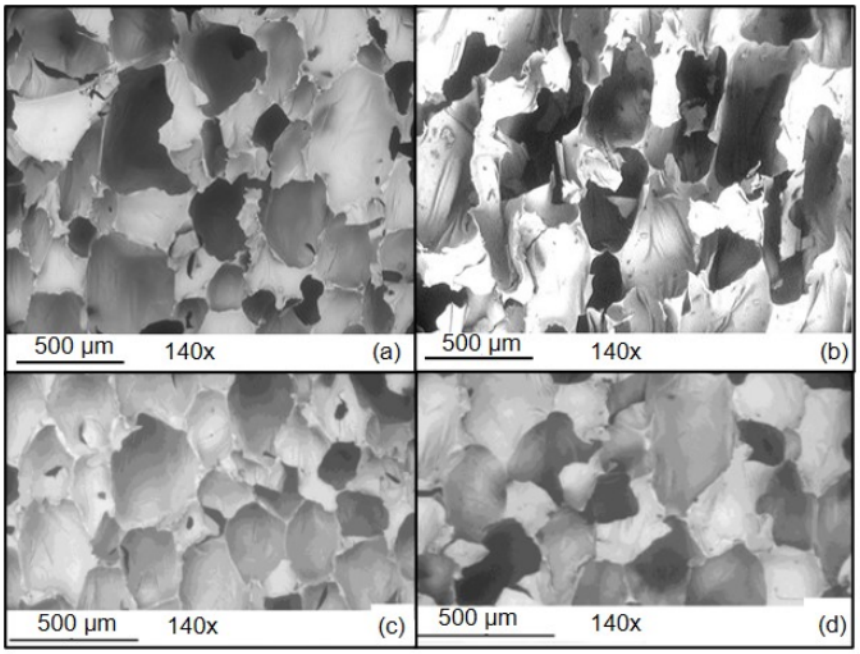

Figure 1: Linear regression models created to evaluate the influence of density (x axis, kg.m^{-3}) increments on the compressive modulus (Ec) (A) and maximum resistance in compression (Sc) (B) for the foams without reinforcements.

is no aggregate formed, despite the expansion into the closed cavity. This aspect may be related to the low percentage of reinforcement employed, not reaching the saturation limit into the PU matrix [3].

According previous report, a significant increase in the cells' anisotropy was obtained for the freely expanded RPUF incorporated with MFC (0.39±0.032), compared with unfilled one (0.28±0.015). These differences are related to the higher system reactivity (from 130 to 60 s for the neat freely expanded RPUF and MFC freely expanded RPUF, respectively). Moreover, there were a small difference in complex viscosities comparing the unfilled bio-based polyols (900 mPa.s) with those with MFC (1500 mPa.s), which means that the filler does not influence on the overall system reactivity.

3.2. Neat Foams

Figure **1** presents the models created to fit the results of compressive modulus (Ec) and strength (Sc), for the studied RPUF. The model created to evaluate the influence of the increase in density on the modulus in compression follows the equation "$E_C = 1/(-0.210243+26.7054/\rho)$". Interpolating the results, there is a trend towards a more significant increase in foam stiffness from 73 kg/m^3, which can be seen in the scatter plot. That is, the modulus will increase much more significantly with not-so-relevant increments in bulk density. This effect may be related to the greater uniformity of the cells from that point onwards, which promotes less dispersion in size and elongation, as previous reported on the micrographs [8].

The proposed model for the evaluation on the increment in maximum compressive strength follows the same pattern as for the one evaluated in elastic modulus, with the equation: "$S_C = 1/(-0.00161731+0.333638/\rho)$". In this case, by adjusting the linear regression coefficients, it is observed that the maximum compressive strength suffers greater influence, when compared to the elastic modulus, for higher densities. That is, for pure foams, the increase in density is more related to increases in strength than in stiffness. These effects can be caused by the lower content of voids in the material with higher density, measurements previous reported [3]. Furthermore, the lower anisotropy can influence this

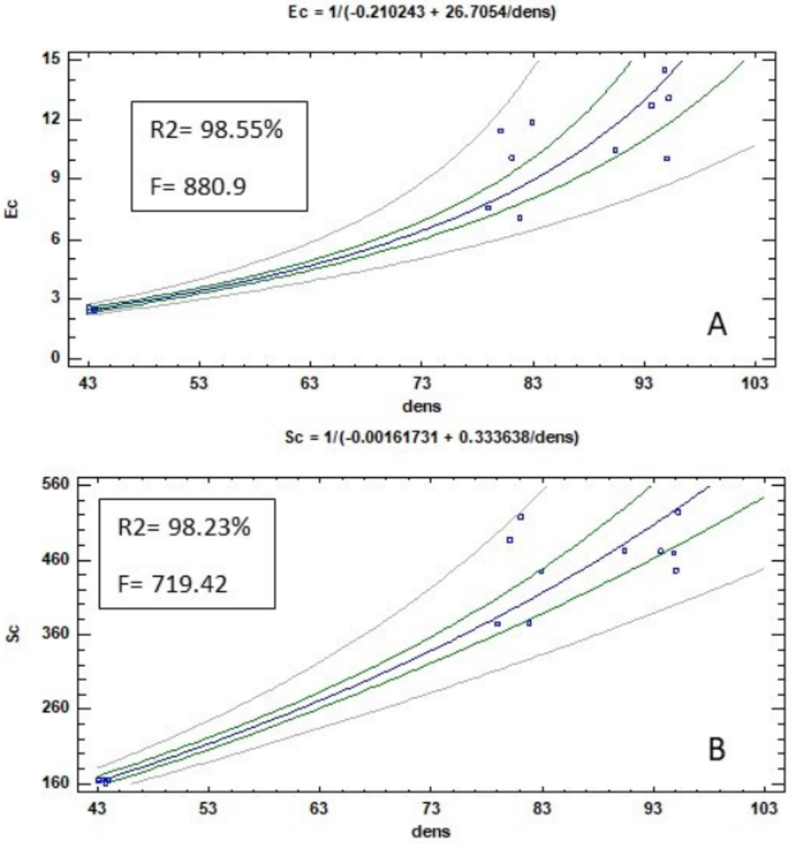

Figure 2: Linear regression models created to evaluate the influence of density increments (x axis, kg.m^{-3}) on the compressive modulus (Ec) (**A**) and maximum resistance in compression (Sc) (**B**) for the foams with MFC as reinforcement.

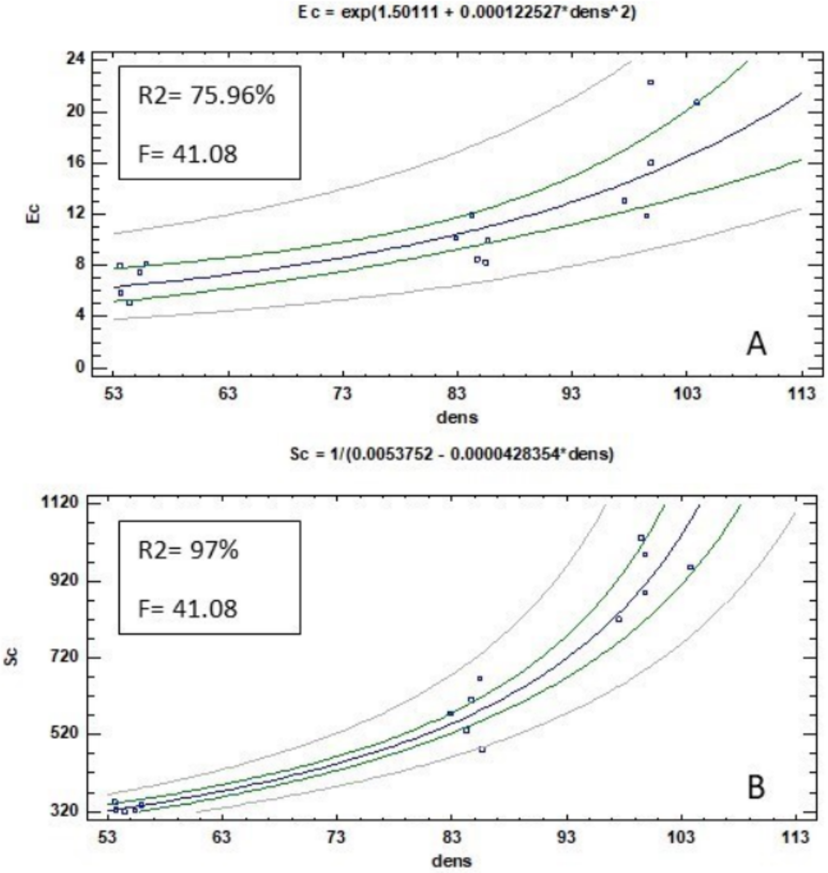

Figure 3: SEM images for the studied RPUF (**a**) Neat freely expanded RPUF, (**b**) freely expanded RPUF with 0.4 wt.% of MFC, (**c**) Neat RPUF expanded into a closed mould and (**d**) RPUF with MFC expanded into a closed mould.

result, since cells with lower elongation present lower cell diameter, as evidenced on SEM images (see Figure **1**).

3.3. Foams Reinforced with Micro Fibrillated Cellulose

For RPUF with MFC (Figure **2**), the model that best fits is the one that follows the equation "$E_C = e^{(1.50111+0.00012257\times p^2)}$" Unlike the neat foams, the increase in stiffness now follows an exponential pattern to the increase in density. The curves' format also shows that the increase in density promotes a less significant influence on the increase in stiffness, when compared to the neat RPUF, due to the insertion of the MFC.

In fact, the increase in the cross-linking content, promoted by cellulose, promoted more significant increments than the increase in density. Furthermore, according to the model stipulated for maximum compressive strength, whose equation follows "$S_C = 1/0.00553752 - 0.0000428354\times\rho)$" a behaviour similar to the neat RPUF is observed, but with much lower angular coefficient, compared to those mentioned. In this case, the confinement provided, in addition to an increase in density, a better interaction between the MFC and the PU matrix, probably caused by the greater proximity of the filler and the NCO of the isocyanate, further increasing the crosslinking of the material [6].

4. CONCLUSIONS

Rigid polyurethane foams were fabricated successfully using a simple methodology that aims to variate the final RPUF bult density in a specific range. The foams presented no apparent aggregates formed, when a micro fibrillated cellulose was used as reinforcement. The foams produced under the closed mould cavity presented lower anisotropy due to the high pressure into the cavity which can also decrease the cell size and distribution. Linear regression models were created successfully, being all of them following the ANOVA assumptions.

All models created presented a low relative error, related to the models' fitting, although those foams with MFC presented a low R² (75.9%), which may be related to the non-uniformity of cellular structure and cell stiffness, due to the reinforcement insertion. There was a correlation between cells' stiffness and strength for those neat foams, in compressive tests, according the models. On the other hand, it was not observed for the foams with MFC.

DECLARATION OF COMPETING INTEREST

The authors declare no conflict of interest.

ACKNOWLEDGEMENTS

This work was supported by Coordination for the Improvement of Higher Education - CAPES (code 001) and Euvaldo Lodi Institute (Project code: BS-2118).

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Received on 06-09-2022 Accepted on 07-10-2022 Published on 14-10-2022

https://doi.org/10.6000/1929-5995.2022.11.05