Material Properties

Biobased porous acoustical absorbers made from polyurethane and waste tire particles

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ABSTRACT

The production of flexible polyurethane foams (FPF) with good acoustical performance to control sound and noise and incorporating bio/recycled raw materials is an interesting alternative to conventional acoustic absorbent materials. In this sense, biobased polyols like glycerol (GLY) or hydroxylated methyl esters derived from tung oil (HMETO) as multifunctional polyols, and waste tire particles (WTP) as fillers of low thermal conductivity and good capability for acoustical absorption, are prospective feedstocks for FPF preparation. In this work, FPF were prepared by adding different amounts of these components to a formulation based on a commercial polyether polyol. Results of scanning electron microscopy (SEM) analysis, compression tests and normal-incidence sound absorption coefficient (α_N) measurements are presented and discussed. The addition of WTP or GLY to the commercial formulation enhanced both the modulus and yield stress of the obtained FPF in all cases. Moreover, a high recovery of the applied strain (>90%) was attained 24 h after the compression tests. On the other hand, the normal-incidence sound absorption coefficient, α_N, reached high values mostly at the highest evaluated frequencies (α_N ~0.62–0.89 at 2000 Hz and α_N ~0.70–0.91 at 5000 Hz). SEM micrographs revealed that the foams obtained present a combination of open and closed cell structure and both the modifiers and particles tend to decrease the cell size.

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1. Introduction

Noise pollution is one of the worst environmental problems and continues to get worse due to rapid developments of modern industries and transportation [1,2]. Especially, the car is a source of serious noise pollution, which consists of structural noise (sound from the engine or contact with the road) and airborne noise (sound from the engine, road noise, or wind caused at high speeds) [3,4]. One of the key solutions for reducing noise pollution is to improve sound absorption efficiency in houses and edifices by increasing damping capacity and optimizing pore structure of construction materials [1–3].

Polyurethane (PU) is one of the most versatile polymeric materials with regard to both processing methods and mechanical properties. Foams constitute more than 60% of all PU products, the

flexible ones constituting the main part of polyurethane production [5]. Flexible polyurethane foams (FPFs) offer the possibility to be used both in thermal insulation and acoustic absorption, among others interesting technological applications. FPFs are porous materials able to absorb the sound energy, making them very useful for noise control. When a porous material is exposed to incident sound waves, the air molecules at the surface and moving through the material within the pores are forced to vibrate and lose some of their original energy. This is because part of the energy of the air molecules is converted into heat due to thermal and viscous losses at the walls of the internal pores and tunnels within the material [6]. Thus, the most important characteristic of flexible polyurethane foams is to have cavities with interconnecting open pores, and its cell structure can play a crucial role in controlling not only mechanical but also acoustic properties. The cell structure in FPF synthesis is simultaneously determined by the two main chemical reactions: gelling to produce urethane groups between isocyanates and polyols, and blowing to produce urea groups between isocyanates and intermediate amines from unstable carbamic acids by

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inclusion of water [2]. The reactions are directly affected by various main ingredients used in the foam formulations. Commonly, the ingredients consist of polyols, isocyanates, chain extenders, silicon surfactants, blowing agents and catalysts [7]. In addition, the cellular structure can be modulated by controlling the relative formation rates between urethane and urea groups, and thus the relative rates can significantly influence the modulus build-up and CO_2 gas liberation during the formation of final foam morphology.

Nowadays, the production of FPF is based on petrochemical feedstocks and the use of natural raw materials and/or waste products in their formulation is a big challenge with environmental and economic advantages [8]. Therefore, to move forward towards more eco-friendly materials, the use of polyols derived from natural sources is attractive, not only due to environmental reasons but also because of the economic benefits. With the exception of castor and lesquerella oils, vegetable oils do not bear hydroxyls naturally. Thus, the chemical modification of vegetable oils is a promising alternative in the production of green polyols to be further reacted with the isocyanate component to achieve the required polyurethane [8,9]. Several methods are currently known to add hydroxyls at the unsaturated sites: hydroformylation followed by hydrogenation, epoxidation followed by oxirane opening, ozonolysis followed by hydrogenation, and microbial conversion [5].

In recent years, a number of studies have been carried out to develop new materials and technologies improving the sound absorption properties. However, studies on the soundproof properties of composite products are still limited. In this sense, the use of recycled rubber in the production of sound absorbers can help to solve the existing problems of both, waste disposal and noise pollution. Hong et al. [10] found that recycled rubber particles had some excellent sound energy absorbency properties and a composite panel made with recycled crumb rubber created good sound attenuation. Yang et al. [11] studied straw—waste tire composites and showed that straw/recycled waste tire rubber composites had similar mechanical properties to wood/recycled tire rubber composites. Moreover, the straw/waste tire composites also possessed better sound insulation. More recently, Zhao et al. [12] showed that wood-waste tire rubber composite panel (WRCP) possesses better soundproof effect than that of commercial wood particleboard and composite floorboard. However, as far as we know, no studies about the sound insulation properties of biobased FPFs reinforced with waste tire particles had been published.

In this work, hydroxylated methyl esters and glycerol were obtained, respectively, as main and by-product of the chemical modification of tung oil, following a two-step procedure. First, fatty acid methyl esters and glycerol (GLY) were obtained by means of alkaline transesterification. Then, the resultant fatty acid methyl esters were modified by hydroxylation with performic acid generated *in situ*. In this way, hydroxyl groups (-OH) were added to the carbon chain, resulting in hydroxylated methyl esters derived from tung oil (HMETO). Both (HMETO and GLY) are multi-functional polyols that would allow modifying the cross-linking density and, consequently, the morphological, physical, mechanical and acoustic properties of the FPFs [9], and thus were used to change a formulation based on a commercial polyether polyol and a polyisocyanate. Furthermore, the foams were modified by the addition of waste tire particles (WTP) as filler of poor thermal and acoustic conduction. The effects of these changes on the mechanical and acoustic properties of the resulting foams were evaluated.

2. Materials and methods

The FPF formulation was based on a commercial polyether polyol (JEFFOL G31-35) provided by Huntsman Polyurethanes and modified with different contents of GLY or HMETO (with respect to the mass of the commercial polyol). Both natural polyols were derived following a two-step method which has been described elsewhere [9]. Waste tire particles (WTP) with an average diameter less than 2 mm were used as filler. For FPF preparation, the following reagents were used: a pre-polymer 4,4-diphenylmethane diisocyanate (pMDI) Rubinate 5005, Hunstman Polyurethanes; distilled water as blowing agent; Tergostab B8404 as surfactant agent (Hunstman Polyurethanes); n,n-dimethylbenzyl amine (DMBA, 99.9%) and dibutyltin dilaurate (DBLE, 99.9%), both from Sigma-Aldrich, as blowing and gelling control catalysts, respectively. The formulation was based on the same total mass of components by setting an isocyanate index = 1.1. Different amounts of GLY, HMETO and WTP were added to prepare FPFs, according to Table 1. In addition, 4 wt% of water, 1.5 wt% of surfactant, 3 wt% of DMBA and 1.5 wt% of DBLE, respect to the total polyol mass were added. The polyols were dehydrated under vacuum at 70 °C before use. Polyols, WTP, water, catalysts and surfactant were previously weighed and mechanically mixed for 20 s. Then, the pMDI was added and the whole system was mixed for another 20 s. The reactive mixture was placed in an open container and allowed to free rise at room temperature. The foams were stored for a week at room temperature prior to be characterized.

2.1. Characterization techniques

Apparent density was calculated as the ratio between the mass and the volume of cylindrical samples (28 mm diameter and 30 mm height) cut from the middle of the foams; the average values of four specimens of each sample are reported.

2.1.1. Scanning electron microscopy (SEM)
The surfaces of the foams were analyzed using a scanning electron microscope (JEOL, model JSM-6460 LV). Small specimens were cut from the middle of the foams in the direction of rise. The pieces were coated with gold before being observed under the microscope.

2.1.2. Compression tests
Cylindrical specimens of 28 mm diameter and 30 mm height were cut from the foams, and tested at room temperature in an INSTRON 8501 universal testing machine. The compression force was applied in the foam rise direction. At least four specimens taken from the center of the free raised foams were tested. Samples were first compressed to 80% of the original length at a crosshead speed of 10 mm/min. The average values of compression modulus (calculated as the slope of the stress-strain curve at low deformations), compressive strength (according to ASTM D1621 it was taken as the stress reached at the compressive yield point, since it occurs for all samples before 10% deformation) and densification strain (taken as the strain at the point of intersection between the horizontal plateau stress line and the backward extended densification line, as described in a previous paper [13], were calculated from these tests.

Then, the samples were unloaded and allowed to recover for 1 minute and 24 hours. The length reached after the recovery time (l_r) was compared to the initial specimen height (l_i) and used to calculate the recovery (R_r) ratio, as indicated in equation (1):

$$R_r = \frac{l_r}{l_i} \times 100 \qquad (1)$$

Table 1
Nomenclature and composition of prepared FPFs.

Sample designation	GLY (wt.% respect to commercial polyol mass)	HMETO0 (wt.% respect to commercial polyol mass)	WTP (wt.% respect to the total mass)
0GLY-0HMETO	0	0	0
0GLY-5HMETO	0	5	0
0GLY-10HMETO	0	10	0
0GLY-0HMETO-10WTP	0	0	10
0GLY-0HMETO-20WTP	0	0	20
0GLY-0HMETO-30WTP	0	0	30
5GLY-0HMETO	5	0	0
10GLY-0HMETO	10	0	0
10GLY-0HMETO-10WTP	10	0	10
10GLY-0HMETO-20WTP	10	0	20
10GLY-0HMETO-30WTP	10	0	30
10GLY-10HMETO	10	10	0
10GLY-10HMETO-10WTP	10	10	10

2.1.3. Normal-incidence sound absorption coefficient (α_N) measurements

Acoustic tests were performed using a standing wave tube Brüel & Kjaer 4002 (Denmark) to determine the acoustic properties of the foams.

Sound absorption coefficients were measured for normal incidence sound generating pure tones matching center frequencies of thirds octave bands between 100 and 5000 Hz, divided into two ranges test: from 100 to 1600 Hz, and from 800 to 5000 Hz. Test specimens had a cylindrical shape of 100 mm in diameter for the range of frequencies between 100 and 1600 Hz, and 30 mm in diameter for the range of frequencies between 800 and 5000 Hz. In both cases, the height of the cylindrical samples was 30 mm.

The test procedure was performed according to the ASTM C384-04: Standard Test Method for Impedance and Absorption of Acoustical Materials by Impedance Tube Method. This standard does not define global acoustic parameters to simplify the comparison, therefore single numbers defined in ASTM C423-09a.a: Standard test method for sound absorption and sound absorption coefficients by the reverberation room method, were adopted. For each foam, the Noise Reduction Coefficient (NRC) and the Sound Absorption Average (SAA), were calculated.

3. Results and discussion

3.1. Effect of the modification of the foam formulation by using bio-derived polyols

The reference foam prepared with the synthetic polyol JEFFOL G 31–35 was modified by replacing part of this polyol by 5 and 10 wt% of GLY, 5 and 10 wt% of HMETO and 10 wt% GLY+ 10 wt% HMETO. These low molecular weight modifiers (in comparison with JEFFOL G31-35) act as cross-linking agents because of their high functionality (>2).

3.1.1. Density and compressive properties

Table 2 presents the densities and compressive properties of the different unfilled foams. The average density increases with increasing glycerol content, which is associated with the higher reactivity of the GLY that limits the volume expansion of the foams and increases the cross-linking density [9]. Moreover, the addition of HMETO also increases, to some extent, the foam density, which was related with the higher functionality of the HMETO, in comparison with that of the synthetic polyol, although lower than that of the GLY [9]. As expected, the foam prepared with both GLY and HMETO presents an intermediate density between that of the 10% HMETO and 10% GLY [9].

Fig. 1 shows the compression stress-strain curves for unfilled foams modified with GLY and/or HMETO. The curves show a linear elastic region, followed by a stress-plateau region [14–16], with the stress increasing again for large strains. As is known, the slope of the initial linear part of the curve is related to the compression modulus and the stress at the end of the elastic region corresponds to the compressive yield strength. After this point, the material starts to crack and the following plateau corresponds to the coexistence of collapsed and uncollapsed zones. After the plateau, the stress increases again because densification takes place. The comparison of curves presented in Fig. 1 denotes that slope and stress value at the plateau increases as GLY or HMETO content increases.

The compression modulus, compressive strength and densification strain of the unfilled foams are also presented in Table 2. The higher modulus and compressive strength with the incorporation of GLY to the formulations is related to the increase in both foam density (more compact cellular structure) and cross-linking density (higher functionality of GLY per gram in comparison with the replaced synthetic polyol).

The addition of polyols with high functionality increases the cross-linking density of the FPF matrix through urethane linkages decreasing the mobility of the chains. However, the unbalance among the hard segments originated from the addition of cross-linkers and the flexible segment matrix produced by the long chains of polyether polyol could cause unstable brittle foam structure, as discussed later. On the other hand, the foams modified with HMETO do not have noticeably modified their compressive behavior with respect to the reference PU foam. HMETO has a long carbon chain (mainly C18) with a lower hydroxyl value (163.2 mg KOH/g) in comparison with GLY (1829.2 mg KOH/g). Consequently, less reactive sites in HMETO promotes a slower exothermic cross-linking reaction than GLY, leading to more stable flexible foam structure with less cross-linking points. Moreover, unlike GLY, which is a triol of low molecular weight (92.09 g/mol) with one secondary and two terminal OH groups, HMETO has secondary hydroxyl groups in the middle of the carbon chain and higher molecular weight than GLY. Therefore, HMETO has higher steric hindrance for further cross-linking reactions than GLY, and thus it was expected that the addition of the former polyol would not greatly modify the flexibility of the reference foam.

The differences in the kinetic of reaction according the polyols chemical structure derived from vegetable oils have been described

Table 2
Density and compression properties of the unfilled foams.

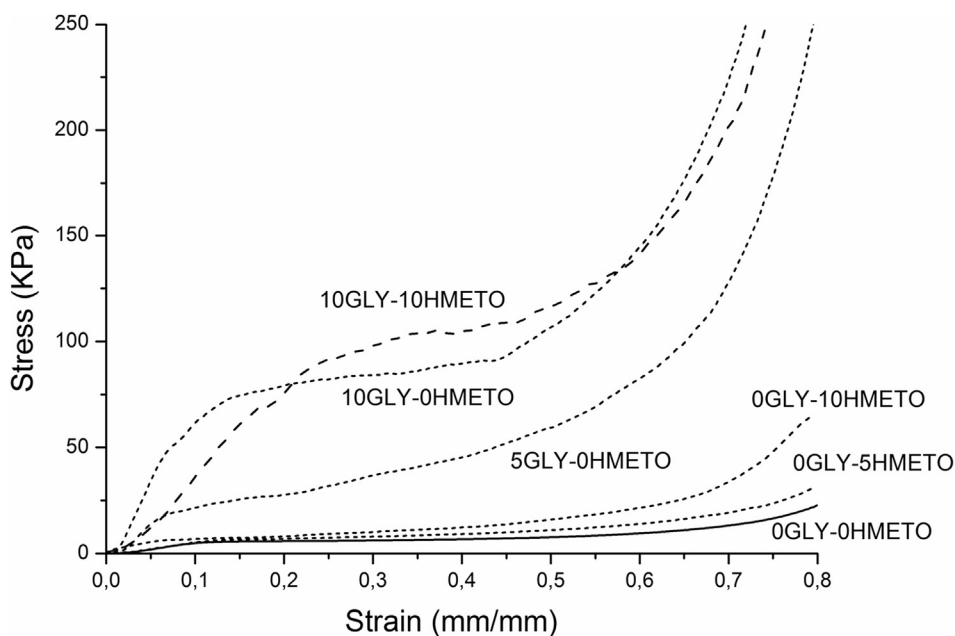| Sample	Density (kg/m³)	Compression modulus (kPa)	Compressive strength (kPa)	Densification strain (mm/mm)
0GLY-0HMETO	31.9 ± 2.3	69.1 ± 14.2	5.9 ± 1.4	0.68 ± 0.04
5GLY-0HMETO	52.1 ± 1.8	819.9 ± 123.2	39.7 ± 12.0	0.67 ± 0.02
10GLY-0HMETO	65.4 ± 3.0	845.9 ± 182.6	67.3 ± 5.5	0.69 ± 0.02
0GLY-5HMETO	32.2 ± 2.6	71.3 ± 16.3	5.2 ± 1.4	0.68 ± 0.03
0GLY-10HMETO	36.6 ± 4.7	90.7 ± 26.6	5.6 ± 2.0	0.67 ± 0.04
10GLY-10HMETO	62.8 ± 10.3	530.1 ± 39.4	93.9 ± 15.3	0.57 ± 0.00

Fig. 1. Compression stress-strain curves of FPF modified with GLY and HMETO.

by Narine et al. [17]. These authors prepared rigid PU foams by using a canola oil derived polyol synthesized following ozonolysis/hydrogenation pathway. They compared their physical and thermal properties with those of rigid foams prepared from commercial soybean and castor oil based polyols, and attributed the differences mainly to the position of the hydroxyl group within the dangling chains.

The effect of GLY on the modification of PU foams was studied in previous works. Mosiewicki et al. (2014) showed that the addition of GLY in the reactive mixture increases the modulus (rigidity) and yield stress of the obtained foams, but also the fragility of the foam cells. Calvo-Correas et al. [18] used GLY as modifier in a rigid polyurethane foam formulation based on a linseed oil-polyol, obtaining a PU matrix with higher cross-linking density and compression properties. Also in this case, higher densities were obtained as GLY content increased due to the decrease of chain length between cross-linking points, leading to higher rigidity and fragility of the PU matrix.

Densification strain values were not significantly affected by changes in the composition of the unfilled foams, which is not surprising since it indicates the deformation at which collapsed cell edges come into contact with each other, causing the material behavior to approach that of the bulk polymer. Unlike foam properties that are drastically affected by the size, shape and amount of cells (related to apparent and cross-linking densities), the bulk polymer behavior is similar for all the formulations tested since their composition was not greatly modified. The exception is the 10GLY-10HMETO sample, which showed the lowest densification strain since the largest amount of commercial polyol (20 wt%) was replaced.

Fig. 2 shows the recovery values (R) after 1 minute and 24 hours of the compressive tests (release of the load). The recovery is slower in the foams modified with GLY, as denoted in the lower values reached at 1 minute (in comparison with the values reached by the other samples). When compressed, air needs time to leave and reenter to the cell structure delaying the compression as well as the re-expansion of the foam [19,20]. Hence, it is expected that foams with higher density require a longer time to recover the original geometry after compression [19,21]. Moreover, after 24 hours the

recovery values were about 90%, while the rest of the foams (without GLY) recover almost all their original shape. This behavior could be associated with its unstable brittle foam structure, as mentioned previously, and it is also a clear indication that the compression may rupture some of the cells, causing permanent damage in the foam structure, and thus preventing its full recovery. Additionally, and as was previously pointed out, foams obtained by using HMETO regained almost their original geometry after 80% compression in height, highlighting their amazing elastic behavior. Vegetable oil based polyols with only internal hydroxyl groups are widely used for flexible foam applications [22,23] due to the less tightened cross-link network formed by the internal OH polyols and facilitated by the presence of dangling chains.

3.1.2. Acoustic properties

Generally, sound waves lead to vibration of the cell walls and air inside cavities, and the sound energy is dissipated through vibration damping of the cavity walls and air [2,24,25]. In addition, sound absorption performance can be improved by sound damping which can be increased with increasing stiffness of cell walls [2,26,27]. Additionally, interconnectivity as well as number, size and type of pores are important factors. These should be considered while studying sound absorption mechanisms in porous materials since the acoustic wave penetration is controlled inside the porous frame, and thus dissipates the acoustic energy from visco-thermal couplings [2,28]. Decrease of the cavity size in open pore structure generally leads to increasing airflow resistance and sound absorption performance [2,29,30]. In addition, the increment of interconnectivity in porous medium may provide irregular transmission routes for sound waves. In this sense, large size porous cells or interconnected cells favor the lower frequencies sound absorption.

Fig. 3 shows the normal-incidence sound absorption coefficient versus frequency for the unfilled foams. The results denote that the replacement of the synthetic polyol by GLY and/or HMETO does not change the general pattern of absorption coefficient variation as a function of the frequency. Modified foams, especially those containing GLY, present higher apparent densities and compression moduli than the reference foams, which is directly associated with
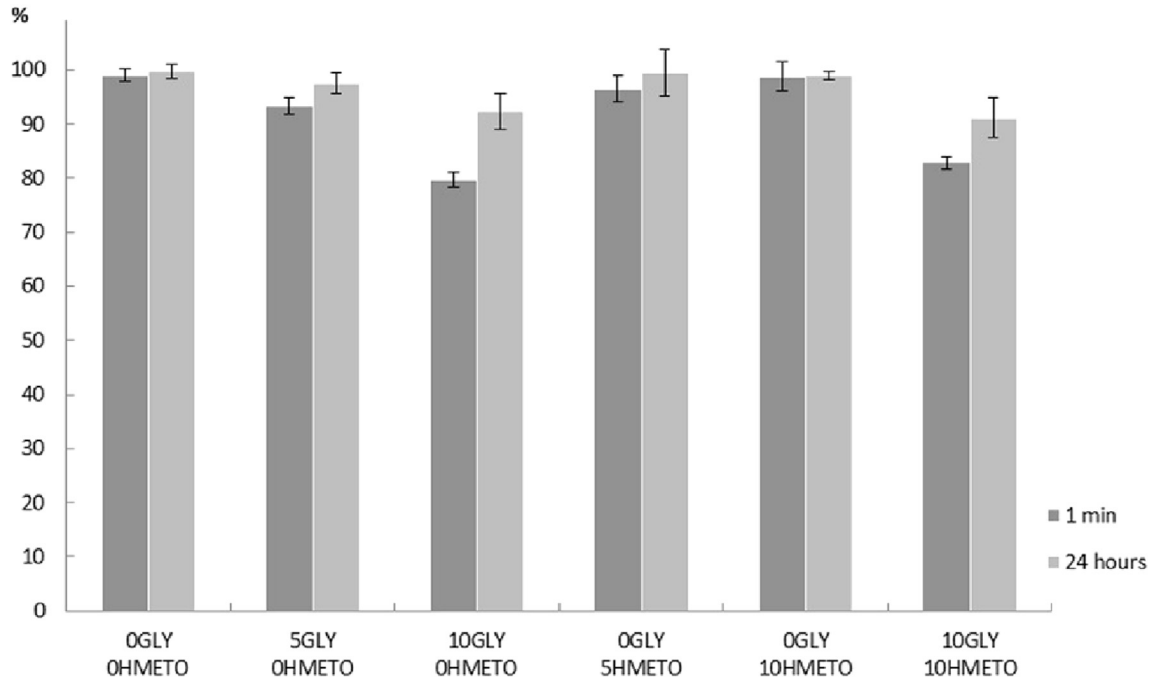
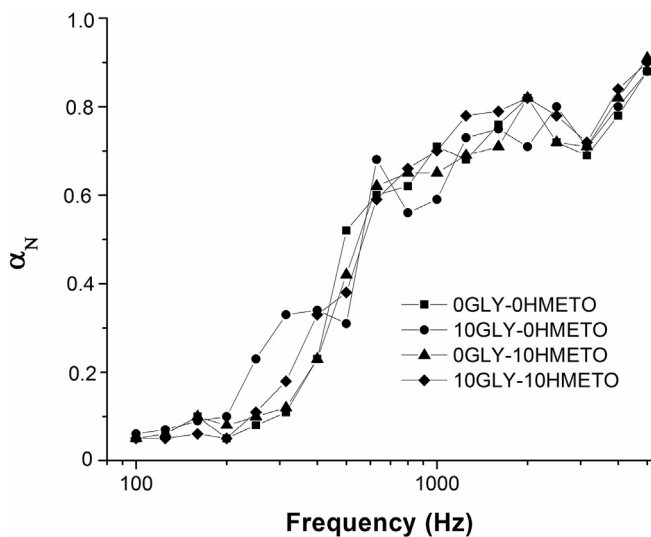**Fig. 2.** Recovery of unfilled foams after compression tests.

Fig. 3. Normal-incidence sound absorption coefficients as a function of the frequency of the unfilled foams.

smaller pore sizes and increased stiffness of cell wall, respectively. In this case, these two contrary effects may compensate, resulting in normal-incidence sound absorption coefficients that do not differ significantly with different foam formulation, and are mainly affected by the frequency of the test. This behavior is also supported by the NRC and SAA values measured for the unfilled foams (Table 3), which are all around 0.5.

3.2. Effect of the addition of WTP

3.2.1. Density and compressive properties

Selected formulations were reinforced with waste tire particles. The attempts at preparing filled samples by using formulations with 5 or 10% HMETO and no glycerol were unsuccessful, leading to very heterogeneous reinforced foams that collapsed in about one day, and thus they were discarded as polymeric matrices. Table 4 presents the densities and compressive properties of the stable foams subsequently modified by the addition of WTP as structural filler.

The addition of WTP to the reference polyurethane (prepared with the synthetic polyol) clearly leads to an increase in the foam density, mainly evidenced in the foams with 20 and 30 wt% of particles, which can be associated with the increase of viscosity of the reactive mixture containing WTP that delay the expansion of the foam during curing. On the other hand, the effect of the WTP in the foams modified with 10 wt% of GLY is less significant, probably because the high reactivity of the reactive modifier masks or compensates the WTP effect in terms of decreasing the growth rate of the foam. The same result is observed in the foam modified with GLY and HMETO when WTP are added. In fact, the differences in the density values of these foams are not statistically significant.

Regarding the compressive properties of filled foams, it can be seen from Table 4 and Fig. 4a that modulus and strength of the reference foam show significant increases with the addition of 10 wt% of WTP. However, larger filler contents (20 and 30 wt%) do not lead to further changes in these properties. Moreover, the compression properties of the composite foams vary appreciably among samples, as can be seen by the large error bars in the measurements. In general, there were two ways to improve the mechanical strength of the foam, the first is to increase density, the latter is to reinforce the skeleton structure of the cell strut and cell wall [31]. In this study, this increase was attributed to the higher density, because the reinforcement of the cell struts was not significant since the added filler is not stiff but rubbery. On the other hand, the fluctuating compression properties observed in the reinforced samples can be attributed to the varying densities and cellular structures [15,32], which are greatly affected by the incorporation of WTP and thus dominate over the reinforcing effects of the filler.

In contrast, the addition of WTP to the polyurethane system

Table 3
Sound absorption coefficients (fraction) NRC and SAA of the unfilled foams.

Frequency (Hz)	0GLY 0HMETO	5GLY-0HMETO	10GLY-0HMETO	0GLY-5HMETO	0GLY-10HMETO	10GLY- 10HMETO
NRC	0.53	0.47	0.46	0.38	0.50	0.50
SAA	0.49	0.48	0.51	0.37	0.48	0.51

Table 4
Density and compression properties of the foams filled with WTP.

Sample	Density (kg/m^3)	Compression modulus (kPa)	Compressive strength (kPa)	Densification strain (mm/mm)
0GLY-0HMETO	31.9 ± 2.3	69.1 ± 14.2	5.9 ± 1.4	0.68 ± 0.04
0GLY-0HMETO-10WTP	39.3 ± 1.3	180.4 ± 43.0	21.7 ± 1.6	0.59 ± 0.01
0GLY-0HMETO-20WTP	59.2 ± 3.4	178.9 ± 36.5	16.2 ± 1.9	0.57 ± 0.04
0GLY-0HMETO-30WTP	50.4 ± 6.3	174.4 ± 51.6	20.3 ± 3.0	0.56 ± 0.03
10GLY-0HMETO	65.4 ± 3.0	845.9 ± 182.6	67.3 ± 5.5	0.69 ± 0.02
10GLY-0HMETO-10WTP	52.9 ± 6.6	656.0 ± 139.4	74.9 ± 9.8	0.54 ± 0.01
10GLY-0HMETO-20WTP	68.4 ± 3.6	623.7 ± 88.0	61.9 ± 9.2	0.56 ± 0.02
10GLY-0HMETO-30WTP	66.0 ± 8.6	564.8 ± 90.4	58.0 ± 12.9	0.55 ± 0.01
10GLY-10HMETO	62.8 ± 10.3	530.1 ± 39.4	93.9 ± 15.3	0.57 ± 0.00
10GLY-10HMETO-10WTP	62.1 ± 5.3	565.1 ± 110.1	68.1 ± 4.9	0.56 ± 0.03

containing 10% of GLY as replacement of the synthetic polyol leads to a decrease in the modulus, as shown in Table 4 and Fig. 4b, without affecting significantly the compression strength. Higher values of compression strength indicate that foam is sturdier, which depends on both higher cross-linking density and greater apparent density [33]. However, the disruption of the foam cell walls due to the addition of particles is also significant and, in this case, is responsible for the decrease in the mechanical properties. As reported for similar systems [33], the density and the compression force values cannot always be directly correlated because the structure of the foam could be less regular: thinner cell walls and larger foam cells could cause decrease of compressive strength,
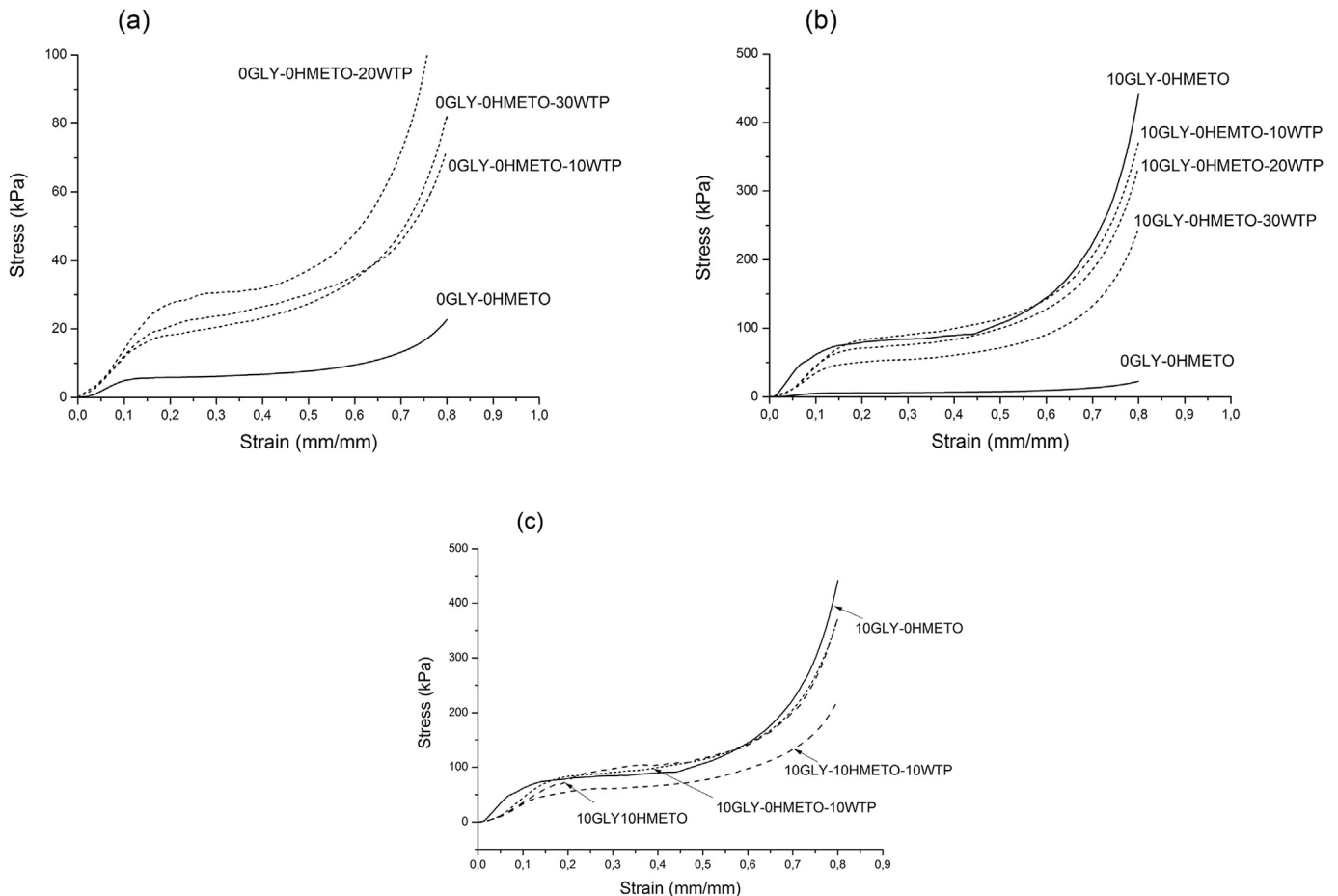

Fig. 4. Compression stress-strain curves of FPF modified with WTP, GLY and HMTO. **a)** composite foams based on reference formulation. **b)** Composite foams based on foams modified with glycerol. **c)** Filled and unfilled foams modified with 10% biobased polyols.
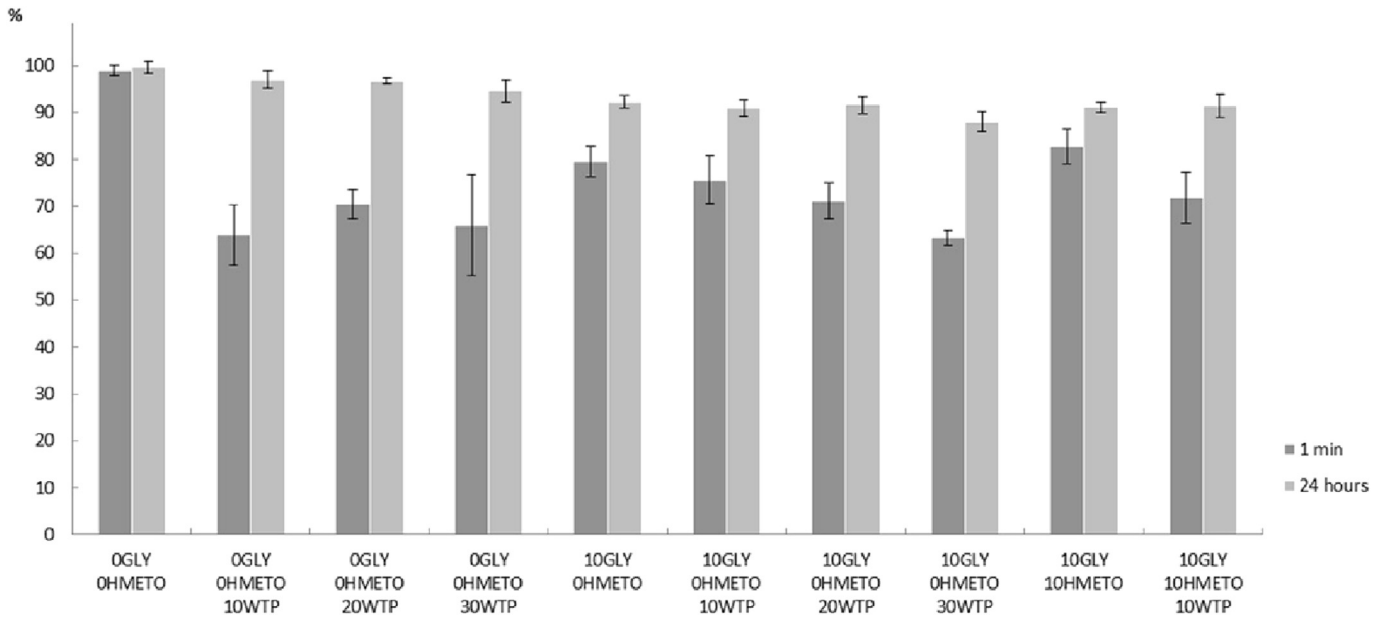
Fig. 5. Recovery of filled FPU foams after compression tests.

even if the apparent density was high.

Fig. 4c shows the effect of the addition of HMETO to the reactive system in order to compare the compression behavior with that of the foams modified with glycerol and WTP. In this case, a negative effect on the elastic modulus and densification strain was observed. Even when the methyl ester/glycerol blend lead to stable porous matrix structure, the addition of soft fillers in a highly cross-linked matrix could tear the foam cell walls, decreasing the mechanical properties, as previously indicated.

With reference to densification strain, composite foams show lower values than unfilled samples indicating that the former can sustain slightly lower deformation without collapsing, probably due to the detrimental changes induced by the filler, both in the liquid reactive mixture (increased viscosity) as well as in disrupting the foam morphology, leading to less homogeneous foam structure.

Fig. 5 shows the effect of the addition of WTP on the recovery values after compression tests. It is clear that filler has a significant and detrimental effect. The recovery is slower for the reinforced foams in comparison with the unfilled ones, as denoted by the low values reached at 1 minute. This effect is, again, in part related to
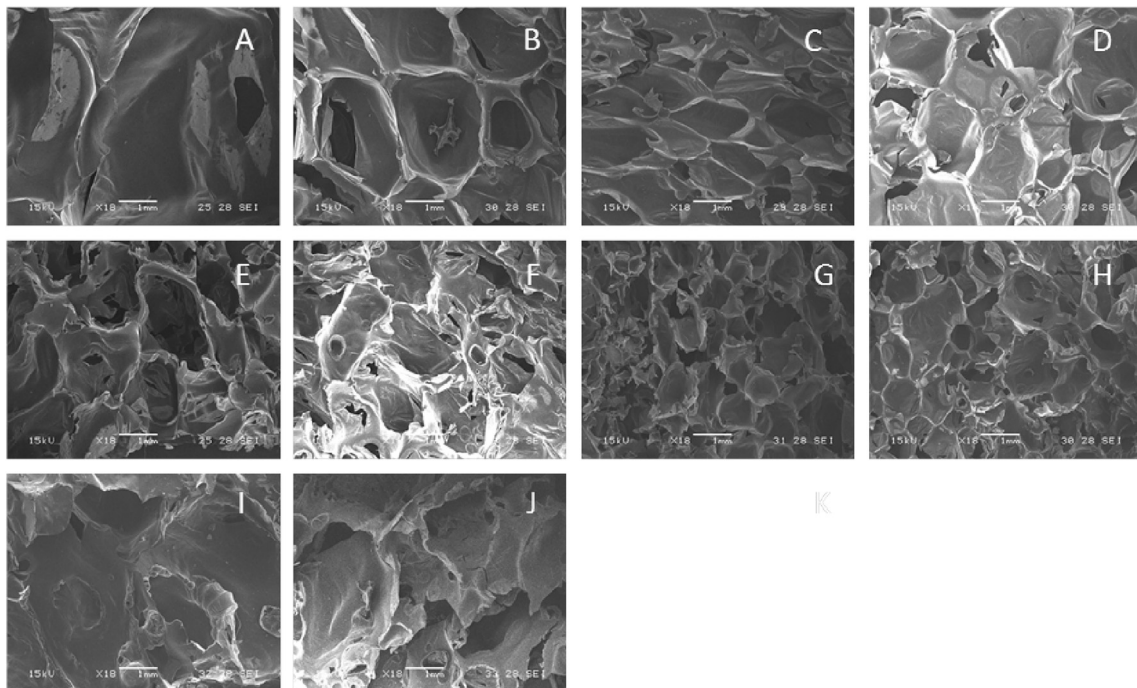

Fig. 6. SEM micrographs of selected foams (x18 magnification). A) Reference (0GLY-0HMETO); B) Reference, 10% WTP; C) Reference, 20% WTP; D) Reference, 30% WTP; E) 10% GLY; F) 10% GLY, 10 WTP; G) 10% GLY, 20 WTP; H) 10% GLY, 30% WTP; I) 10% GLY, 10% HMETO; J) 10% GLY, 10% HMETO, 10% WTP.

the high density of the reinforced foams. However, the structure of the filled foams, which is less regular than the corresponding unfilled counterparts, also may play a role, since the relationship among density and recovery is not linear. In this sense, it was unexpected to find that, in general, the lowest recovery values at 1 minute are exhibited by the filled reference foam samples, while their corresponding unfilled counterpart exhibit a nearly instantaneous and complete recovery. On the other hand, it can be seen that, with enough time (24 hours), reinforced reference samples were able to recover at least 95% of the imposed deformation, while filled modified samples reached around 90% recovery. Again, this behavior indicates that the foam structures had permanent damage, but the extent is higher for the samples modified with GLY.

3.2.2. Morphological analysis

Fig. 6 shows the micrographs obtained by SEM of unfilled and WTP filled foams. All the foams exhibit a mix between close and open cellular structure. The images confirm that the addition of both GLY and WTP leads to reduced cell sizes. Additionally,

increasing amounts of WTP leads to cells that become smaller as filler content increases. This is in agreement with their higher densities (in comparison with that of the reference neat foam), which is associated with the restricted expansion of the foams during curing. During the development of the foam, the particles act as nucleation sites, promoting the formation of a larger quantity of bubbles, which tends to increase with filler content. At the same time, growth of the cells is hindered by the increase in viscosity of the polyurethane matrix, as was also noted by other researchers [34]. However, there are some differences according to the polymer formulation: a narrow distribution of cell sizes is observed in the foams prepared with just the synthetic polyol, while cell sizes vary noticeably for the foams based on GLY. Moreover, the foams prepared with 10 wt% GLY plus 10 wt% HMETO present a more distorted cell structure than those based only on GLY as green modifier.

3.2.3. Acoustic properties

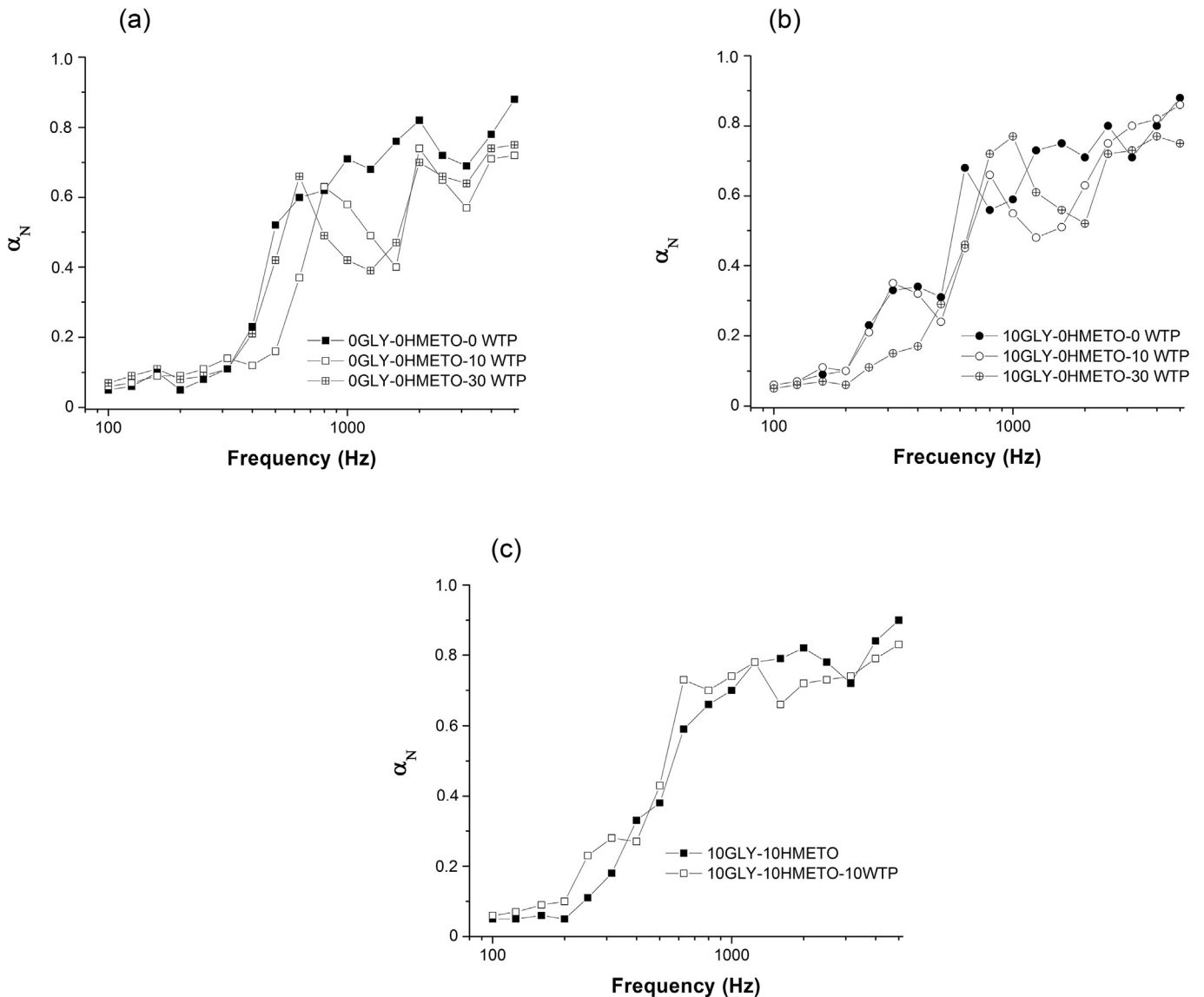Fig. 7 shows the normal-incidence sound absorption coefficient

Fig. 7. **Normal-incidence** Sound absorption coefficients of the filled foams based on the reference polyurethane (a), modified with 10% of GLY (b) and with 10% of GLY and 10% of HMETO (c).

Table 5
Sound absorption coefficients (fraction) NRC and SAA of the filled foams.

Freq. (Hz)	0GLY-0HMETO	0GLY-0HMETO-10WTP	0GLY-0HMETO-30WTP	10GLY-0HMETO	10GLY-0HMETO-10WTP	10GLY-0HMETO-30WTP	10GLY-10HMETO	10GLY-10HMETO-10WTP
NRC	0.53	0.40	0.41	0.46	0.41	0.42	0.50	0.53
SAA	0.49	0.37	0.39	0.51	0.43	0.43	0.51	0.53

versus frequency for the WTP filled foams. The results indicate that the incorporation of WTP shifts the absorption coefficient to lower values for the system based on the synthetic polyol. According to Hong et al. [10], recycled rubber particles had some excellent sound energy absorbency property; thus, it was expected that their addition improved the acoustic damping of the PU foams. However, the increase in the composite foam density as WTP is added appears to be the most important effect affecting the α_N values, since a high apparent density in a foam means less empty spaces to dissipate sound as thermal energy.

On the contrary, the foams modified with 10% GLY (including 10GLY-10HMTO samples) present a slight increase in the sound absorption with WTP content in the 500–1000 Hz zone. In this case, recycled rubber particles can be considered as advantageous fillers to be used in polymeric systems applied as sound absorbers in the low-frequency region [10]. More interconnected cells in the reinforced foams with 10% of GLY (associated with their compact and distorted structure) reduce the size and volume fraction of air voids and make the air passages more tortuous and much narrower. Therefore, in a compact structure the sound wave travels a longer distance and this leads to a reduction of the sound energy [35]. On the other hand, NRC and SAA coefficients of the filled samples are lower than the corresponding to the neat counterparts, except for the 10GLY-10HMTO foams that displays the opposite behavior (Table 5).

4. Conclusions

The present work presented a route for the production of more environmentally friendly filled flexible PU foams through the replacement of part of the synthetic polyol by biobased ones, and by the addition of waste tire particles. Promising acoustic absorption properties were observed in a wide range of frequencies. The addition of HMETO and GLY as biobased polyols to the commercial formulation leads to flexible polyurethane foams with higher densities and compression properties, with a morphology based on smaller cells than those achieved in the reference foam, which was related to increased cross-linking density of the polyurethane network. The addition of WTP leads to increased foam density and decreased cell size, with compression properties affected in different ways depending on the base formulation and sound absorption features similar to those of the unfilled formulations. Nevertheless, the obtained FPUs presented α_N values near and above 0.5, denoting good performance as acoustic absorbers from 500 Hz (medium and high audible frequencies).

Acknowledgments

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