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Micro-tomographic characterization of composite recycled glass-silicone foams for applications in civil engineering

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Abstract

Non-invasive x-ray micro-computed tomography was applied for a complete quantitative and qualitative analysis of the cellular structure of composite foams constituted by a silicone matrix and a glass production waste filler. Composite foams with different glass filler weight content in the range 0% to 80% were synthesized and characterised. The tomographic analysis was employed in order to assess the structural heterogeneities, void fraction values and bubble size distribution for all composite foams. The 3D micro-CT images analysis, performed at different cross-sections, highlighted heterogeneous cell growth or more elongated cells in the case of low and high filler content foams, respectively. Batch with 60% of glass filler was identified as a composite foam with effective void fraction values and relatively uniform spheroidal cellular structure (average sphericity 0.723 and diameter 0.107 mm).

Keywords: Polymer-matrix composites (PMCs); Microstructures; Foaming; CT analysis

1. Introduction

Micro-computed tomography (μ -CT) is a non-destructive technique based on the use of reconstruction algorithms applied to X-ray scans. This analysis method allows obtaining 3-dimensional dense clouds of information that can be displayed as 3D images and 2D sections that can be manipulated and qualitatively and quantitatively analyzed¹⁻⁴. Even if μ -CT is a precise technique, the resultant resolution depends on the scan parameters (e.g., tilt angle, number of scans, the relative distance between the sample, the X-ray source and detector) and experimental limitations such as artefacts and digital noise that are intrinsic in the reconstruction process^{5,6}.

In material science, μ -CT is used for the assessment of the morphometric^{7,8} or mechanical⁹ properties of the material, to microscopically assess the actual sample geometry and identify geometrical parameters affecting the mechanical behaviour of the samples¹⁰.

Tomographic has been proposed for the analysis of different types of cellular materials. This technique has been widely applied to evaluate the cellular structure of metal foams¹¹⁻¹⁴. In the same way, significant applicative potentials have been also experienced in polymer foams^{15 16 17}, including polyurethane¹⁸, polyethylene¹⁹, polystyrene²⁰.

A noteworthy aspect is the possibility to three-dimensionally distinguish the foam cells population by parameterizing their size, shape and spatial location, making this technique stimulating in engineering design, process optimization and quality control.

Lightweight materials are increasingly used in civil engineering for several applications spreading from lightweight filling materials to cellular cemented clays²¹ or concrete²² for large-scale structures. In recent years, significant interest has been found in the development of foamed composite materials for engineering applications with waste materials used as fillers^{23 24}.

Recycled products give a positive impact on energy consumption and also limits the opening of new quarries for the production of new aggregates. To reach an effective eco-sustainability, industries and

end-users are becoming more sensitive to new cleaner production and consider recycled materials as a resource rather than a waste material destined for landfills.

In this context, glass-based cellular materials have been developed with promising results for structural and insulating applications ^{25,26}. Life Cycle Assessment (LCA) has been effectively used to highlight and quantify the eco-efficiency of glass waste recycling chain by identifying engineering solutions for sustainability thanks to the development of new products to be used in energy buildings efficiency ^{27 28}. However, the use of recycled glass to produce lightweight cellular foams is still not yet mature to make its use cost-effective as a lightweight aggregate construction material.

The aim of this work is to evaluate the synthesis and morphologically characterize an eco-sustainable composite foams consisting of a siloxane matrix and glass waste filler as a future application in thermal insulation panels for civil engineering. The high chemical compatibility of the siloxane compounds with different fillers has allowed to assess the applicability of this composite material, with promising results, in various fields of application ²⁹⁻³¹. In this regard, the glass filler has good chemical compatibility with the silanol groups of the silicone matrix ³². The strong chemical interaction between the two components is a stimulus to identify their potential effective combination aimed to obtain a performing composite material in terms of physical-mechanical properties. For this purpose, a fundamental topic is offered by the morphology of the cellular structure of the composite foam which plays a key role in the durability and stability of the foam itself ³³. The definition and discrimination of the main morphometric parameters of the foam and how these vary according to the synthesis conditions is a relevant aspect that needs to be investigated for its optimization during the experimental research and development.

For this class of materials, μ -CT is able to discriminate the porosities of the composite matrix providing reliable information about the cell structure and morphometric parameters by performing specific software data analysis ³⁴⁻³⁶. However, due to the intrinsic features of the technique, attention must be paid for correct identification of cell walls, cellular segmentation by using suitable threshold

values on the histogram of the intensity of a grayscale image) avoiding software inaccuracy in the reconstruction^{37–39}.

In such a context, μ -CT was used to evaluate the influence of the amount of filler on the foaming dynamic in glass-silicon composite foams. The X-ray micro-tomographic imaging was assessed as a suitable technique to give valuable and accurate information concerning the cellular structure of the composite foam in order to acquire more in-depth insights on changes in cell morphology induced by different filler content in the foam formulation. 3D tomography images were applied to acquire a better knowledge of cell coalescence and cell collapse phenomena occurring during the foaming and their effect on cellular structure. Furthermore, thorough morphometric characteristics, among all the composite foams, including porosity, dimension, distribution and shape of the cells were discussed.

2. Materials and Methods

2.1 Glass particles

The glass filler was obtained as secondary raw material from the manufacturing process (i.e., sawing dust) of glass plates. The material received from the manufacturing plant was properly washed in distilled water and dried at 120 °C for 24 h to eliminate the residual moisture through a vacuum oven. The resulting glass dust was sieved to obtain a homogenous distribution of the dimensions of the particles (i.e., between 53 and 125 μm).

2.2 Foam Synthesis

Recycled glass filled silicone foams were prepared by using an open to air mould foaming technique. As a matrix, a couple of siloxane compounds, trimethylsilyl terminated methylhydrosiloxane dimethylsiloxane copolymer (molecular weight 1,400-1,800) and a silanol terminated polydimethylsiloxane (molecular weight 18,000), supplied by Gelest Inc., Morrisville, USA, coded as PMHS and PDMS, respectively, were used. Furthermore, Tin(II) 2-ethylhexanoate (Sn(II)) compound was used as catalyst. The foam preparation was performed, at first dispersing glass filler,

under agitation for about 60 s, in polydimethylsiloxane (PDMS) compound. Ethanol and water were added as solvent in order to improve the workability (reducing its viscosity) and easily obtain a homogenous slurry. Afterwards, the polymethylhydrosiloxane (PMHS) was added to the mixture (PDMS/PMHS ratio 1:2) and vigorously mixed for 15s. Eventually, the tin catalyst was added, still under vigorous mixing, for about 15s. The so obtained slurry was poured into an open cylinder-shaped mould (diameter about 25 mm). The foaming process was favoured by heating at 60 °C for 24 h in order to complete the siloxane crosslinking according to the following reaction ⁴⁰:

The blowing process is due to the formation, during the reaction between hydride and hydroxyl groups of siloxane compounds, of the gaseous hydrogen product. The applied curing was verified in a previous paper ⁴¹ as suitable in order to allow an effective crosslinking of the chemicals and the whole solvent removal of solvent. Foams with different weight amount of glass filler, in the range 20-80 wt.% of siloxane matrix (PDMS+PMHS), were made. A list of all compound amounts and glass filler content are reported in Table 1. As a reference, an unfilled silicone foam was considered (GF-0). The glass/foam ratio was defined as filler/(filler+PDMS+PMHS). For each batch, three replicas were applied.

Table 1 - Siloxane solution compositions for different glass content

<i>Compound</i>		<i>GF-0</i>	<i>GF-20</i>	<i>GF-40</i>	<i>GF-50</i>	<i>GF-60</i>	<i>GF-70</i>	<i>GF-80</i>
PDMS [%]	Siloxane	42.6	36.8	29.7	26.0	21.7	17.2	12.0
PMHS [%]	Siloxane	21.3	18.6	14.9	13.0	10.9	8.6	5.8
Ethanol [%]	Solvent	14.9	12.6	10.3	9.0	7.7	6.1	4.5
Water [%]	Solvent	10.6	9.0	7.4	6.5	5.4	4.3	3.2
Sn(II) [%]	Catalyst	10.6	9.0	7.4	6.5	5.4	4.3	3.2
Glass [%]	Filler	0.0	14.0	30.3	39.0	48.9	59.5	71.3
Glass/Foam [%]		0.0	20.0	40.0	50.0	60.0	70.0	80.0

Figure 1 – Sem image of a fracture surface on 70 wt% filled composite foam

In order to assess the filler matrix interaction scanning electron microscopy (SEM) was performed by using a focused ion dual-beam/scanning electron microscope (FIB-SEM ZEISS Crossbeam 540, ZEISS, Obwerkochen, Germany).

Figure 1 shows as a reference, the fracture surface of 70 wt.% filled composite foam. Sample fracture was obtained under nitrogen liquid in order to avoid plastic deformation of the matrix. By evaluating the micrograph, that shows a detail of the composite foam cross-section wall, it is possible to evidence that the glass particles are homogeneously dispersed in the silicone matrix. Furthermore, good interfacial contact between filler and matrix can be identified.

2.3 X-ray tomography

μ -CT was chosen as a technique to assess the morphological properties of the analysed composites glass-silicon foams. A high-resolution micro-CT, SKYSCAN 1272 by Bruker (United States) was used to make X-ray scans. Taking into account the good rotational symmetry of the sample, to obtain acceptable data, the rotation step angle was set equal 0.4° up to a total rotation of 180° . The accelerating voltage and the current flow were set to 60 kV and 100 μ A. A 0.11 mm copper filter was

used to enhance the image contrast. The acquired scans were post-processed to obtain a 3D image. The resulting images resolution is equal to 21.73 $\mu\text{m}/\text{pixel}$.

2.4 3D Image processing

The acquired data and the reconstructed images were processed by applying digital filters to enhance the image quality and reduce the intrinsic noise that is peculiar for this technique. In particular, misalignment compensation, beam hardening correction, smoothing and ring artefact reductions algorithm were applied by the use of the software NRecon by Bruker (United States).

The so obtained dataset was then post-processed by the use of the software CTAn by Bruker (United States) to obtain quantitative data by performing both 2D and 3D analyses. In this phase, further digital filters were used to reduce image noise by taking into account the real preview morphology of the samples (i.e., the images were de-speckled by eliminating pixel agglomerates smaller than 15 pixels). In particular, in order to characterize the cell foam structure and to obtain the cell foam features, the following procedure was applied: median filtering of grey-scale images, segmentation by a threshold, border killing (removal of the pores touching the borders of the image and, finally, calculation of cell features.

3. Results and Discussion

3.1 Foam morphology

Figure 2 – Example of a 3D Reconstruction (glass foam loaded with 20% of filler)

The 3D tomography structure of a reference composite recycled glass foams with 20 wt.% of filler content, as obtained after image post-processing, is reported in Figure 2. In order to better visually evaluate the foam morphology, the 3D image was obtained generating a virtual cut along the foaming axis of the sample. The sample is characterized by a relevant poly-dispersion, indicating that several phenomena occurring during the foaming stage.

The glass-filled silicone foam is characterized by non-regular circular-shaped structures with a mixed open/closed cell morphology. Some small and narrow openings (cell windows) were identified ensuring an interconnection among cells. The cell walls (struts) are dense and compact and the overall structure seems to be without defects.

Figure 3 – Transaxial (lower left images) , sagittal (right images) and coronal (top images) sections for increasing glass content: (a) 0 wt.%; (b) 20 wt.%; (c) 40 wt.%; (d) 50 wt.%; (e) 60 wt.%; (f) 70 wt.%; (g) 80 wt.%

In order to better highlight the effect of the filler addition on the cellular microstructure of the foam, 2D slices in the reference planes of all foams with increasing glass content are shown Figure 3. By increasing filler content, a progressive reduction of bubble dimension is qualitatively visible.

In all composite foams, a well-structured morphology without macroscopic defects can be identified. Only for samples at higher glass filler content (GF-70 and GF-80), some randomly internal cracks are shown. These are probably related to a large amount of filler in the structure that favours the filler/matrix adhesion reduction. All the samples evidenced a quite regular cell geometry both in longitudinal and transversal directions. The cell size distribution is almost homogeneous mainly at low filler content foams. However, some heterogeneities on composite foams are shown by increasing the filler content (i.e., local large size bubbles or voids in the structure, indicating a possible bimodal distribution of the cells) ⁴².

From a structural point of view, at low waste glass content, each cell appears to be well interconnected with the adjacent ones pointing out the presence of possible structured three-dimensional pathways. The cell walls are thin and compact. As previously discussed, these foams are characterized by an open/closed cells structure with narrow opening windows that guarantee the connection among neighbouring cells. Due to the large bubble interconnection, the bubble shapes appear not regular or spheroidal ^{25, 42}.

The bubble growth process in the silicone matrix occurs because of the nucleation of gas bubbles in the siloxane compounds during the condensation process, according to Eq. 1. Then, the bubbles, during the foaming stage, grow up, interact and coalesce each other inducing a wider dispersion in the cell size ⁴³.

These composite foams are characterized by a relevant foaming ratio (defined as initial to final foam volume ratio or roughly can be related to the bubble volume fraction identifiable in the cross-section images) with large and homogeneously distributed bubbles in the whole sections. The large foaming ratio can be probably related to coalescence phenomena occurring among bubbles that produces large volume bubbles. Furthermore, the bubble size increase could be due to the gas phase expansion in the

silicone foam considering that the pressure decreases along the flow direction. During the foaming, due to friction losses, the pressure along the flow direction is lower than the previous condition. This exerts lower pressure acting on the gas bubbles wall, favouring the expansion of the bubbles ⁴⁴. However, at increasing glass filler content the workability of the synthesis slurry progressively increases (empirically identifiable by the increase of the viscosity of the slurry) heavily limiting coalescence phenomena. The bubbles do not grow up and the obtained composite foam is mainly constituted by small, regular and spheroidal bubbles well distributed in the filled foam structures (GF-50 and GF-60).

Homogeneous and regular distribution of the bubbles, for the foams characterized by intermediate filler content, indicates that the foaming process is still effective. However, the coalescence phenomenon of the bubbles is progressively regressing due to the gradual increase in viscosity of the slurry which has also a limiting action on the ratio of foaming ²⁵. At the same time, the agglomeration of the glass fillers, that becomes relevant for high filler content, should influence the bubble coalescence affecting pore size, pore shape and porosity.

For very high composite foams (GF-70 and GF-80) this phenomenon becomes significant due to the very low workability of the composite synthesis slurry. This promotes the bubble break-up caused by the increased viscous force acting on the growing bubbles and also hinder the coalescence phenomena due to drainage of the film at the interface that requires more time ⁴⁵. Furthermore, during the foaming evolution, the glass-siloxane slurry progressively becomes denser due to the occurring crosslinking reaction that favours gas cells shrinkage ⁴⁶. Moreover, the presence of glass powder in the siloxane-based slurry could influence the foaming kinetics due to chemical interaction between constituents. The glass filler is constituted by surface hydroxyl groups that are able to interact with the hydroxyl-terminated and hydrated groups of the siloxane compounds, similarly to dehydrogenative coupling reaction between siloxanes molecules ⁴¹. Therefore, an increase in the kinetic reaction can be identified coupled with a higher hydrogen evolution (as a reaction product of glass-siloxane coupling). Eventually, the foaming ratio appears to be very low, e.g. for GF-80 samples, the foaming

process is not stable and an average foaming ratio of about 25% was achieved. The cellular foam structure is very dense and compact although several internal macro- and micro-porosity can be identified. The bubbles are characterized by a depressed ellipsoidal shape (due to their collapse during the foaming stage because the high slurry viscosity) and they are not interconnected each other indicating that this foam structure is unstable and with low cohesion strength.

3.2 Morphometric parameters

Starting from digital analysis on 3D tomographic images a statistical and morphometric parameters discrimination for each sample was carried out to better investigate the influence of the glass filler addition on the morphological properties of the composite foams. Some statistical parameters are reported in Table 2. Table 2 was populated according to the method described in §2.4.

Table 2 - Statistical parameters of bubble size distribution at a varying glass filler content

	Average Diameter [mm]	SD [mm]	CoV	Sphericity	Degree of Anisotropy	Void volume fraction [%]	Foam Density [g/cm ³]
GF-0	0.17	0.23	1.31	0.667	0.251	66.61	0.28
GF-20	0.13	0.1	0.75	0.669	0.458	66.50	0.53
GF-40	0.10	0.07	0.73	0.691	0.410	62.43	0.65
GF-50	0.11	0.08	0.75	0.695	0.210	60.15	0.71
GF-60	0.11	0.07	0.68	0.723	0.163	56.68	0.82
GF-70	0.08	0.04	0.51	0.715	0.308	40.54	1.03
GF-80	0.07	0.04	0.64	0.683	0.315	9.97	1.26

Standard deviation (SD) was used to measure of the dataset dispersion from its mean. However, considering that datasets are characterized by different means, coefficient of variance (CoV) was also used as a statistical parameter to evaluate the variability of the spread of data. It is defined as the standard deviation σ to the mean value μ percentage ratio. The sphericity index is the ratio between the surface area of a sphere with the same volume of the bubble and the real surface area of the bubble. By definition, a sphere has sphericity equal to unity. Analyzing the statistical parameters, it is possible to evidence that increasing glass filler content a gradual reduction of composite foaming taken place as highlighted by the progressive reduction of average diameter of bubbles and total void volume

fraction. A transition from low density to compact composite foams occurred at about 60-70 wt.% of glass content. This aspect was confirmed by the evolution of CoV at increasing glass amount. Lower CoV values are observed at for GF-70 sample. For the composite foam with low glass content, the coalescence phenomenon plays an important role in bubble growth thus inducing a high COV. Instead, at intermediate glass content, the coalescence is significantly inhibited and a homogenous distribution of bubbles can be identified (low CoV). Finally, for high glass content, the cellular structure of the foam is structurally limited, the low adhesion and cohesion induces a heterogeneous distribution of small size bubbles with subsequent slightly higher CoV. These heterogeneities are mainly attributed to a not effective interaction of filler with the matrix and also to the formation of waste glass agglomerates inside the polymer matrix that significantly influences the foam morphology ⁴⁷. This implies a greater variability of the statistical data associated with the geometry and morphometry of the bubbles.

No trend on the degree of anisotropy can be identified at increasing filler content. Conversely, a progressive reduction of void volume fraction at increasing waste glass content can be identified. This behaviour can be ascribed to a reduced foaming ratio for high filler content composite foam formulation. GF-80 sample showed a void fraction lower than 10%. Instead of composite foams with waste glass content up to 50% evidenced an almost stable void content (about 60%) indicating that the addition of the waste glass filler did not heavily influence the foaming process.

Analyzing the void volume fraction and foam density it is possible to identify a significant modification of these parameters for glass filler content above 60%. The foam density or bubbles volume fraction are parameters related to competing for foaming phenomena occurring during the dehydrogenative coupling reaction of the silicone foam. According to ²⁵ and ⁴², a usual threshold filler content can be identified above which a significant modification on bubble size and distribution occurs. The integration of this information may allow deducing the threshold filler content that can be used to obtain a suitable and reliable heat-insulating material in the civil engineering field. Certainly, specific studies, integrated with the morphometric evaluation, which can be acquired by

tomography technology, could provide additional information in terms of experimentation and design of a functional composite foam for the intended application.

The average bubble size diameter decreases at increasing glass filler amount in the composite foam. In fact, after 40% of glass content addition, a reduction of about 60% of bubble size diameter has been observed. Afterwards, a slight stabilization at intermediate filler content (40-60 wt.% of glass filler) can be identified. In this range, the average cell diameter was about 0.1 mm. Afterwards, at very large filler content a progressive and significant reduction of bubble diameter occurred reaching a minimum for GF-80 sample (bubble diameter 0.065 mm). Concerning the sphericity parameter, a maximum at a filler content of 60% can be observed. The agglomeration of the glass fillers, sensitive at varying filler content, could play a role on bubble morphology (i.e. pore size, pore shape and porosity).

The observed trend of the sphericity parameter can be explained by considering that at first at low glass content foam bubbles can start the coalescence process. Thus, when the siloxane matrix completed the crosslinking process interconnected voids with complex geometry (therefore, low sphericity) can be highlighted. Conversely, at increasing glass content in the composite foams, the coalescence phenomenon is triggered. When the foam solidification is completed a very large amount of bubbles not interacted each other inducing a lower interconnected structure and therefore small bubbles of spheroidal shape were predominant. With very high glass powder, content few bubbles are able to coalesce due to the high viscosity of the formulation. At the same time, the bubbles start to collapse under the foam generating ellipsoidal shaped bubbles with long axis orthogonal to the gravity direction. Eventually, small size with low sphericity bubbles was mainly observed.

Figure 4 – Frequency distribution of cell size diameters for four reference composite foams at varying glass content.

Figure 4 shows the frequency distribution of cell size diameters for three reference composite foams at varying glass content. The Y-axis is the percentage fraction of bubble counts with a specific diameter cell size (determined on 3D volume analysis), within a particular bubble size range denoted by X-axis. At increasing filler content, a progressive increase in the number of small-sized pores can be observed. Unfilled foam showed a broad cell size distribution (about 0.2-1.8 mm). A significant variation in cell size distribution can be identified for unfilled foam, where the non-homogenous cellular morphology was previously qualitatively highlighted from the 3D images. On the other hand, the presence of glass powder in the foam implies an evident thinning of the bubble size range in the foam microstructure. In particular, all foams loaded with glass showed a maximum bubble diameter of about 1.0 mm.

The volumetric porosity can be defined as the ratio of the volume of the bubbles (voids) with the apparent volume. Consequently, it is possible to divide this contribution into sub-classes based on bubble size diameters, according to the following relation:

$$V_i(\%) = \bar{V}_i \cdot n_i / V_B \quad \text{Eq. 2}$$

Where $\bar{V}_i$ is the average volume of a particle with a diameter d_i , n_i is the number of bubbles classified with this diameter. V_B is the total volume of bubbles. $V_i(\%)$ is the volume percentage of bubbles with i -class diameter.

Figure 5 – Frequency plot of volume bubble ($V_i(\%)$) at varying diameter for four reference composite foams at varying glass content

$V_i(\%)$ index represents a reliable parameter to evaluate if a given class of diameters affects the total foam porosity. A high index for the i -th class identifies a high incidence of this bubble size diameter range. Figure 5 summarizes the volume bubble fractions at increasing diameter range for some reference composite foams. Analyzing the distribution variation for different filler contents some considerations can be extrapolated. The distribution of the frequency in terms of the diameter size of an unfilled sample is characterized by wide and less pronounced multi-peak shape. Vice versa, increasing glass content, the distribution curve evolves toward high and narrow shape, with a skewness effect more and more concentrated for smaller diameters. In particular, in the case of the GF-0 batch, a bimodal distribution can be observed. A first peak occurs in the size range 0.6-0.8 mm. Furthermore, a second relevant peak above 1.6 mm diameter was identified. This second peak can be associated with the coalescence of and interconnection phenomena of different bubbles originated

during the foaming stage. Aggregation is facilitated by the low viscosity of the slurry due to the absence of filler.

By increasing the glass filler content there is a progressive shift of such peaks towards smaller diameters. In particular, for the GF-60 foam, the porosity distribution in the composite foam is still clearly bimodal, although the diameters associated with the two peaks are strongly lower (0.2 and 0.4 mm for the first and second peak, respectively) than unfilled foam. This aspect is related to the progressive reduction of coalescence phenomena for composite foams at higher glass content. In fact, the peak magnitude observed at large diameter size in GF-0 sample decrease down to disappears for GF-80 samples, where coalescence phenomena are heavily limited.

Figure 6 – Trend of the first and secondary peak of volume bubble frequency at a varying diameter

These considerations are summarized in Figure 6, where the trend of first and secondary peaks observed in Figure 5 for all the composite foams at varying glass filler content is reported. It is clearly evident that the secondary peak decreases significantly at increasing filler content. Instead, a progressive increase in magnitude toward lower diameter can be highlighted for the first peak. This behaviour is associated with the significant tendency of composite foams with low filler content to

coalesce leading to the formation of a strongly interconnected porous structure with a high quantity of large bubbles. Instead, composite foams with a high filler content strongly limit the coalescence phenomena between the bubbles, therefore progressively in the cellular structure of the foam, the contribution linked to small bubbles (first peak) becomes more relevant.

Figure 7 – Evolution of cumulative volume percentage trend versus diameter

Figure 7 shows the evolution of the cumulative volume distribution trend versus diameter at increasing glass filler content in the composite foams. The addition of glass powder in the siloxane foam induces a significant translation of curves toward smaller diameters. Glass filled foams (GF-40, GF-60 and GF-80) showed a quite similar trend. For these samples, the cumulative area curve starts lower cell size dimension than GF-0 batch.

The unfilled foam trend is characterized by three linear sections. The initial section of the curve is mainly related to small size bubbles (where coalescence not occurred). Its incidence reaches about 40% of the cumulative area beyond a plateau. Bubble size in the range 0.9-1.4 does not give a contribution to the cumulative volume. This indicates that no bubbles with this dimension were observed. Afterwards, the region with a cumulative volume in the 40% -100% range is associated with a bubble size of about 1.5-1.7 mm. As previously discussed, this stage can be ascribed to the

coalescence phenomena among bubbles clusters generating interconnected local structures. Further useful information can be acquired by analyzing the evolution of the cumulative volume for GF-80 sample. The curve shows a linear trend up to a diameter of about 0.3 mm. Afterwards, a progressive deflection of the curve at increasing bubble size diameter was observed. The slope reduction found at large cell size indicates that the bubbles with a large size give a lower contribution in the cumulative volume. This trend is confirmed by the stabilization of the curve for diameters above 0.8, indicating that that coalescence is inhibited.

It is worth stating that foams with intermediate filler content, (GF-40) evidenced a cumulative volume trend identifiable, qualitatively, as a combination between GF-0 and GF-80 foams. A slight plateau at about 0.4 mm indicates a threshold value that separates the two bimodal colonies of bubbles: the first cluster of bubbles with size in the range 0.1-0.35 mm and a second cluster characterized by bubbles with large size (diameter in the range 0.55-0.8 mm).

The morphometric parameters comparison among all the composite foams (including porosity, dimension, distribution and shape of the cells) allowed to gain effective and valuable information on the cellular structure of the composite foam acquiring more in-depth insights on changes in cell morphology induced by different filler content in the foam formulation. The performed micro-computed tomography analysis carried out to evaluate the effect of glass filler content on the achievable porous structure of the composite foam allowed to identify threshold conditions for coalescence phenomena in foamed structure. These outcomes, coupled with the evaluation of morphological 3D images, can give a better understanding of the relationship between foam synthesis and porous structure in order to find an effective solution for the optimization of the formulation.

Figure 8 evolution of a) structure separation and structure thickness b) for all composite foams

Plots of the structure separation and thickness are reported in Figure 8. The structure thickness is defined as the diameter of the sphere inscribed within a region encompassing the voxels lying in the medial axis of a structure. If it is calculated for a certain phase of the structure (i.e., the polymeric foam structure) it can be related to the volumetric distribution of the structure size. On the other hand, if the same calculation is done for a non-object phase (i.e., the pores), the structure separation is obtained giving a volumetric distribution of the spacing between two individual pores (i.e., the distance between the centre of two spheres inscribed within an empty region).

The narrow peak showed in Figure 8(a) related to the G80 sample indicates a more homogeneous distribution of the bubble size. On the other hand, the broader distribution related to the structure thickness indicates that the G80 has a more irregular distribution of the cell wall. This effect is mainly due to the collapse of the bubbles creating a more dense structure with small bubbles. Moreover, if the results presented above are considered (i.e., the collapse of the bubbles was observed even in the case of G70 and G60), It is possible to conclude that G50 is the most homogeneous both if the structure thickness and separation are considered.

Conclusions

In this paper, silicone foam-based cellular composites filled with waste glass powder at different weight content (in the range 0 wt.%-80 wt.% of waste glass) were produced by a dehydrogenative

coupling reaction between PDMS and PMHS siloxane compounds. The resulting foaming was assessed by 3D image analysis performed by using X-ray Micro-Tomography. The outcomes can be summarized as follow:

- The micro-tomography was performed to qualitatively evaluate foam homogeneity and compactness. Defects and local internal voids were easily identified;
- The 3D digital image analysis was able to identify void fraction and volume and cell size distribution with very high sensitivity;
- Bubble size distribution analysis evidenced bimodal cell structures for composite foams with low filler content (GF-0 and GF-20). These class of foams showed the widest cell distribution. Otherwise, the foams with very high filler content (GF-80), characterised by some heterogeneities, show a unimodal bubble size distribution. A homogeneous bubble size distribution with spheroidal shaped cells was identified for intermediate composite foams (GF-60 and GF-70);
- Cell population density variations with filler content were also assessed. The results indicate that, among all the characterised foams, GF-60 can be considered a good compromise between a relatively uniform cellular structure with spherical-like cells and good volume void fraction;

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Figure Caption

Figure 1 – Sem image of a fracture surface on 70 wt% filled composite foam

Figure 2 – Example of a 3D Reconstruction (glass foam loaded with 20% of filler)

Figure 3 – Transaxial (lower left images) , sagittal (right images) and coronal (top images) sections for increasing glass content: (a) 0 wt.%; (b) 20 wt.%; (c) 40 wt.%; (d) 50 wt.%; (e) 60 wt.%; (f) 70 wt.%; (g) 80 wt.%

Figure 4 – Frequency distribution of cell size diameters for four reference composite foams at varying glass content.

Figure 5 – Frequency plot of volume bubble ($v_v(\%)$) at varying diameter for four reference composite foams at varying glass content

Figure 6 – Trend of the first and secondary peak of volume bubble frequency at a varying diameter

Figure 7 – Evolution of cumulative volume percentage trend versus diameter

Figure 9 evolution of a) structure separation and structure thickness b) for all composite foams

Table Caption

Table 1 - Siloxane solution compositions for different glass content

Table 2 - Statistical parameters of bubble size distribution at a varying glass filler content