

# Preparation of Syntactic Foams made from Green Polyethylene and Glass Microspheres: Morphological and Mechanical Characterization

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Polymeric syntactic foams are composites made from the mixture of Hollow Glass Microspheres (HGM) and polymer matrices. One of their main characteristics is their low density and the production of these composites using a matrix derived from renewable sources potentiates their development without neglecting sustainability. In this paper, the properties of High Density Polyethylene (HDPE)/HGM syntactic foams containing 1% and 5% w/w HGM and 5% w/w of a compatibilizer are assessed. The composites were prepared by two processing routes: single screw extruder and twin screw extruder. The morphology and mechanical properties (tensile and impact) of the syntactic foams thus manufactured were ascertained. Morphological analysis indicated that matrix/filler adhesion was poor for all samples and that the best HGM dispersions were obtained in twin screw extruded samples. Mechanical properties were affected by the processing route adopted and by the content of hollow glass microspheres added. Elastic modulus, tensile strength and strain were reduced by 20, 10 and 23%, respectively, in systems processed in a twin screw extruder. Impact strength was the exception, with an increase of more than 300%. Higher contents of hollow glass microspheres led to reductions in mechanical strength of the syntactic foams, varying from 5% for the elastic modulus to 50% for strain.

**Keywords:** *Syntactic foams, hollow glass microspheres, green polyethylene.*

## 1. Introduction

The search for lighter materials to facilitate transport and use, has led to a growing number of studies in areas, such as science, engineering and design. Polymers and polymer composites are promising options to replace metallic and ceramic materials<sup>1</sup> in several applications as they are light in weight, have a good set of mechanical properties, are easy to process, can be molded in different shapes and can be easily colored.

Composites consist of a mixture of different materials which maintain their original properties and are separated by an interface. Composites are created in order to obtain new materials with unique properties. In general, one of their components acts as reinforcement (filler) and the other as a binder material (matrix). If the matrix is a polymer, a polymer composite is obtained. The development of composites is currently one of the fastest, simplest and cheapest techniques

to combine material properties leading to products with distinct characteristics which are not typical of the matrix. The scientific community has expanded research so that composites can be obtained with materials that, in addition to their economic advantages, are more ecologically sound, either within the production chain, applications or disposal after use<sup>2</sup>.

Fillers and matrices may be of natural or synthetic origin. Fillers can be fibrous or particulate, ranging from natural or synthetic fibers to organic or inorganic particulate materials. The partial substitution of the polymer matrix by these fillers helps to reduce the amount of synthetic polymers present in the material, which is advantageous since polymers have high production costs and are environmental pollutants when discarded. Besides, filler addition leads to improvements of different characteristics of the neat resin. Low-density composite materials are required for a multitude of applications and these materials can be prepared by incorporating a

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lightweight filler or gas in a polymer matrix<sup>3,4</sup>. In the 1950s the use of syntactic foams as a new lightweight material gained prominence<sup>5</sup>. The American Society for Testing and Materials (ASTM) defines syntactic foam as a composite material consisting of hollow microspheres dispersed in a matrix<sup>4,6</sup>. Of Greek origin, the word "syntactic" means "to arrange together"<sup>4,7,8</sup>.

Due to advances in manufacturing research for greater structural stability, Hollow Glass Microspheres (HGM) have stood out as a viable alternative since they have low density and produce composites with interesting characteristics such as dimensional quality and low mass-volume ratio<sup>9</sup>. Nowadays, new mechanisms of obtaining HGM are under development, aiming at making production more accessible, with less environmental impact and optimizing the reuse of glass waste in the production chain of these materials<sup>10</sup>.

Syntactic foams are considered as particulate filled polymer composites and they are categorized as physical foams as the matrix is not foamed chemically, but the gas-containing particles are mechanically added into the matrix<sup>4,11,12</sup>. The hollow microspheres are responsible for the syntactic foam's low density, high specific strength and low moisture absorption. Besides HGM have a burst pressure high enough to withstand the forces imposed upon them during the formulation, mixing, and dispensing processes<sup>4</sup>.

Due to the synergistic effect of the processability of the polymer and the high compressive strength of the microspheres, the syntactic foam can be processed by different routes such as extrusion, injection, compression and internal mixer, maintaining a high physical integrity index of the constituents at the end of processing<sup>13,14</sup>. Processing versatility enables HGMs to be inserted into the production environment without major changes in already established industrial plants.

Another important feature in the formation and application of syntactic foams is the compatibility between the hollow glass microspheres and the polymer matrix. The level of interaction between the filler and the array will determine the load transfer efficiency along the interface between the components<sup>15,16</sup>. Compatibilizing agents are used to promote adhesion between the HGM and the polymer matrix, thus improving composite mechanical properties under tensile<sup>17</sup> and flexural stress<sup>18</sup>. The most commonly used compatibilizers to serve as a bridge between the matrix and the filler are those made from Maleic Anhydride, Dicumyl Maleate and Silane Agents<sup>19-21</sup>. The works of PATANKAR and KRANOV<sup>9</sup>, PATANKAR<sup>20</sup> and ÇELEBI<sup>22</sup> point out the efficiency of compatibilizing agents in the formation of syntactic foams.

There are several reports in the literature indicating that particle size, filler content, particle-matrix interaction, dispersion and filler distribution have major influences on the properties of polymer composites filled with hollow glass microspheres<sup>23-25</sup>. Considering that processing conditions have major effects on particle dispersion and distribution,

in this paper, the effects of the processing conditions using single screw and twin screw extruder on the morphology and mechanical properties of the syntactic foams made from HDPE/HGM with maleic anhydride grafted PE (PE-g-MA) as a compatibilizer, are investigated.

## 2. Methodology

### 2.1 Materials

The polymer matrix used in this paper was HDPE (SHA7260 grade, Braskem), and density was the control property (0.955g.cm<sup>-3</sup>). The hollow glass microsphere (iM16K) (3M<sup>TM</sup>) used as an inorganic filler and had the following specifications: density of 0.46g.cm<sup>-3</sup>, average diameter of 20 µm and crushing strength of 16000 Psi. The polar compatibilizer employed was maleic anhydride-functionalized polyethylene (PE-g-MA), marketed under the name Orevac<sup>®</sup> 18507 (Arkema), with density of 0.954g.cm<sup>-3</sup>, melt flow index (190°C/2.16kg) of 5g.10min<sup>-1</sup> and melting point of 128°C. The choice compatibilizer was based on the work of Patankar and Kranov (2009)<sup>9</sup>.

### 2.2 Processing

The syntactic foams were prepared by two different processing routes: single screw extruder and twin screw extruder. In each process the HGM level varied between 1 and 5% while maintaining PE-g-MA at a constant level (5%), as show in Table 1.

#### 2.2.1 Single Screw Extruder

The foams were processed in a bench top single screw extruder model AX-16 (AX Plásticos) under the following operating conditions: screw rotation speed of 50 rpm, temperature profile from the feeding zone to the matrix of 140°C to 150°C.

#### 2.2.2 Twin Screw Extruder

The composites were prepared in a modular co-rotating twin screw extruder (NZ, model SJ-20), diameter of 22 mm, L/D = 38, and a shape factor of 1.48 with screw configuration with two kneading block sections of intensive shear. The temperature profile employed from the feeding zone to the matrix was 170°C to 190 °C and screw speed was 300 rpm.

The choice of the processing parameters was determined by the work in the literature with different inorganic loads, allowing comparisons between their effects, and considering the limitations imposed by the equipment with respect to feed and screw speed of rotation.

### 2.3 Production of test specimens

After being processed in the extruders, the composites were pelletized and compression molded in a hydraulic press MH-08-MN (MH Equipamentos Ltda) operating at 180°C

**Table 1.** Composite formulation

Legend	HDPE (wt%)	PE-g-MA (wt%)	HGM (wt%)	Processing
SS1	94	5	1	Single screw extruder
SS5	90	5	5	Single screw extruder
TS1	94	5	1	Twin screw extruder
TS5	90	5	5	Twin screw extruder

with 2 minutes of pre-pressing at 1 ton of applied load, 1 minute without load and then 3 minutes under a load of 3 tons. These conditions were necessary to generate good test specimens for mechanical testing (tensile and impact).

## 2.4 Characterizations

### 2.4.1 Morphological analysis - Scanning Electron Microscopy

Scanning electron microscopy of the gold coated fractured surfaces of tensile tested specimens was performed on a Shimadzu SSX-550 apparatus operating in the 6-15 kV range. Adhesion between the polymer matrix and the HGM, as a function of the processing route adopted, was then ascertained.

### 2.4.2 Mechanical tests

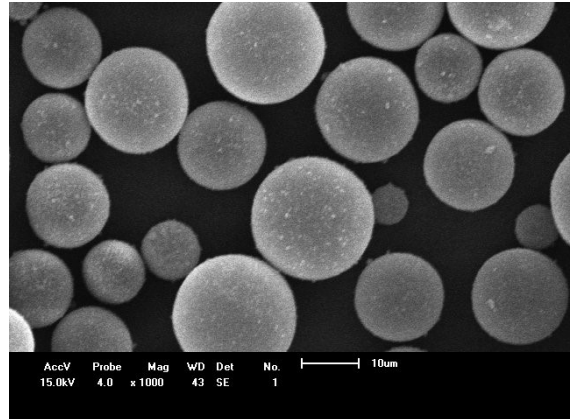
Tensile testing was performed in an EMIC DL 30000 Universal Testing Machine operating at 50mm/min with a load cell of 50 kN, according to ASTM D638 at room temperature. Izod impact tests were performed according to ASTM D256 on a CEAST Resil 5.5 equipment, operating with a 2.75J hammer. The specimens were notched (notch depth = 2.5mm) before impact. All results reported are a mean of 5 specimens.

## 3. Results and Discussion

### 3.1 Morphological analysis

Scanning electron microscopy (SEM) photomicrographs images of the fracture regions of tensile tested specimens before (iM16K) and after processing by the two routes adopted here are shown in Figures 1-3. The aim was to observe the interactions of the syntactic foams constituents and to visualize the damage caused to the filler at the end of each processing and to correlate it with the properties of the systems.

The photomicrographs show although there were few agglomerations of the microspheres and no complete wettability of the filler by the polymer matrix, HGM adhesion to the matrix (indicated by the blue arrows) were observed for for both SS1 and SS5 systems. Although some of the hollow glass microspheres (HGM) were damaged at some point during processing, in general, a high HGM integrity index was observed for both systems.

**Figure 1.** iM16K-type HGM particles

The high integrity of the glass microspheres after processing is in agreement to what was observed by BARBOZA and DE PAOLI (2002)<sup>26</sup> for PP/HGM and by Kumar et al. (2016)<sup>27</sup> for HDPE/HGM syntactic foams. The authors attributed this behavior to poor HGM adhesion to the polymer matrix, making the stress to which the foams were subjected during tensile test not to be shared with the spherical structures, resulting in the maintenance of their physical integrity. However, as for the presence of glass sediments (indicated by the red arrows) inside the systems, several authors (BARBOZA and DE PAOLI, 2002; YALCIN et al., 2015)<sup>26,32</sup> reported that the processing of the components through the knife mill was the cause of most of the stresses necessary for damaging the structure of microspheres.

Figure 3 shows the photomicrographs of the syntactic foams processed in a co-rotating twin screw extruder, Figures 3a and b correspond to the TS1 system, and Figures 3c and d correspond to the TS5 system.

The photomicrographs of the TS1 and TS5 foams reveal a morphological aspect similar to those of the syntactic foams processed in single screw equipment, but there was higher matrix/filler contact. These aspects range from poor adhesion to the existence of hollow spaces and the presence of damaged microspheres.

As for the presence of damaged microspheres, photomicrographs revealed that the TS1 and TS5 systems showed the most pronounced existence of glass sediments originating from HGMs, increasing the matrix contact surface as reported by Hu et al. (2013)<sup>28</sup>. Such behavior regarding the physical integrity of the microspheres was already expected,

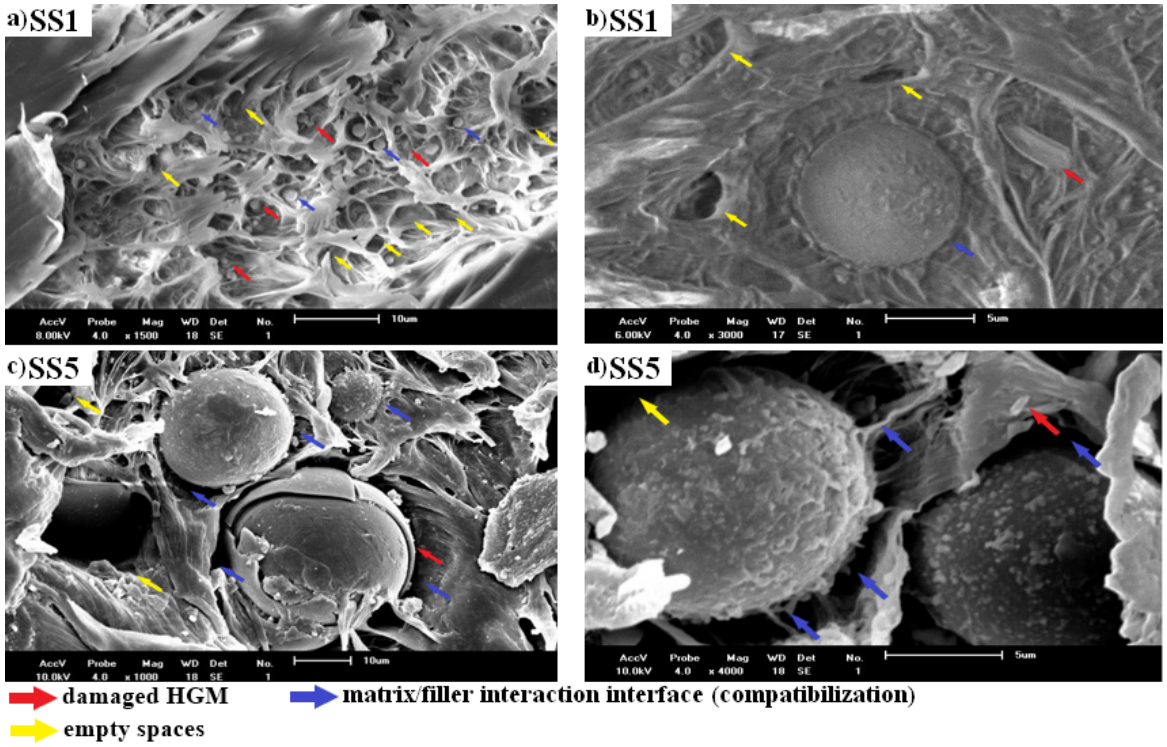


Figure 2. Photomicrographs of single screw extruded systems (SS) with 1 (SS1) and 5% (SS5) HGM.

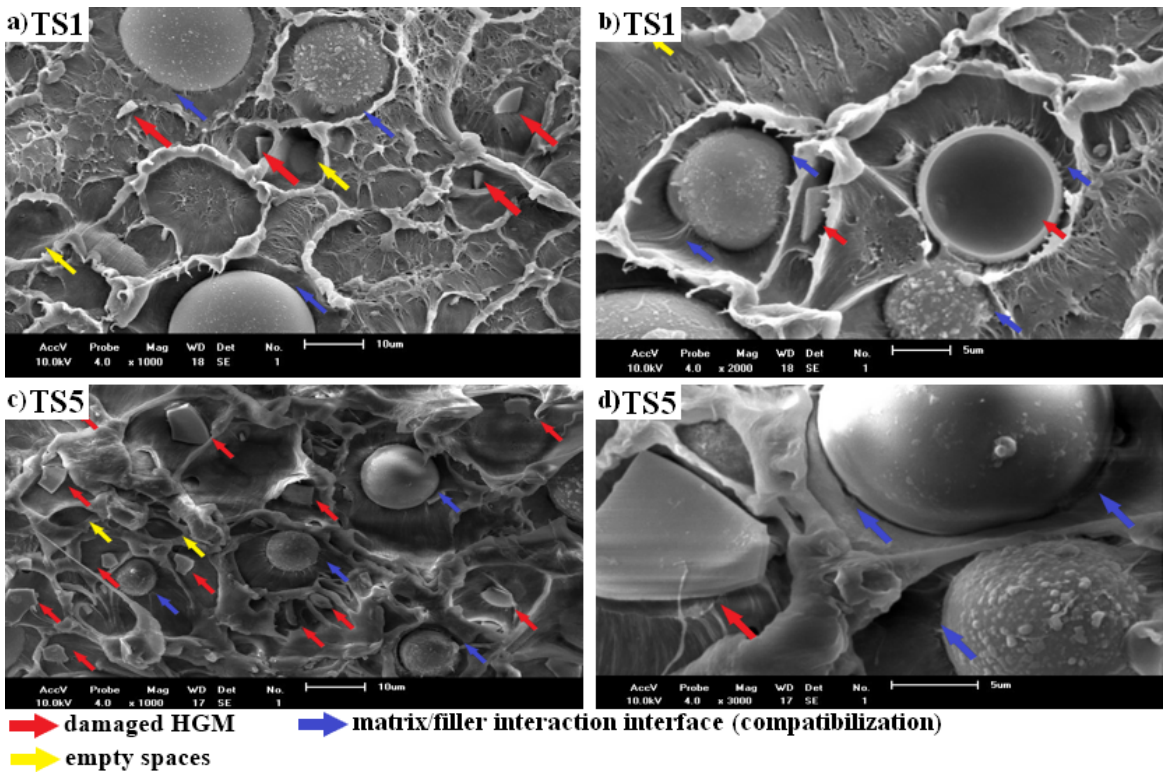


Figure 3. Photomicrographs of the systems via twin screw extruder (TS)

since in addition to the pelletizing of the extruded yarn, this processing through screw configuration offers more severity for the shear stresses, which is the region with the highest concentration of kneading elements<sup>33</sup>.

Regardless of the processing route, the effect of PE-g-MA addition was observed through the improved adhesion of hollow microspheres in the polymer matrix. Similar behavior was observed by ÇELEBİ (2017)<sup>22</sup> for PP/HGM syntactic foams with the addition of a silane agent. LU et al. (2015)<sup>29</sup> prepared syntactic foams based on polyurethane and HGMs and observed that the interaction between filler and matrix was promoted by hydroxyl groups - OH on the surface of the microsphere and carbonyl groups (C = O).

Many authors have studied the influence of compatibilizers on the adhesion between the polymer matrix and HGM processed under different conditions and have shown that its absence causes poor matrix/HGM adhesion<sup>9,19,21</sup>.

### 3.2 Mechanical tests

#### 3.2.1 Tensile strength

Figure 4 shows the elastic moduli of the syntactic foams processed by single and twin screw extrusion. The mean values and the respective standard deviations of each system were illustrated according to the filler content with microspheres (1% and 5%), followed by assessment of the performance of foams compared to the matrix.

Results indicate that the processing route affects the mechanical behavior of the syntactic foams. Single screw extrusion led to materials with similar or slightly higher modulus than that of the neat matrix, particularly that with 5% HGM. This behavior can be explained by the restriction of the mobility of the polymer chains at higher HGM contents<sup>30-32</sup>. On the other hand, the foams obtained via a twin screw extruder showed a 20% reduction in the elastic modulus, which can be attributed to the lower integrity of the hollow microspheres during processing in the twin screw extruder. Microspheres breakage leads to the formation of rigid microparticles, with little or no adhesion to the polymer matrix, causing the stress concentration and reduced mechanical performance of the syntactic foams. This behavior is in agreement with the systems morphology observed by SEM.

At lower HGM contents, the propagation of microcracks, generated at during load application, is more difficult. However, at higher HGM contents, crack propagation becomes relatively easy due to the presence of multiple possible paths through adjacently located HGMs<sup>24</sup>. This representation is illustrated in Figure 5.

The higher modulus value for foams processed in the single screw extruder are in agreement with other literature studies, such as in the study in which the authors produced Polybutylene Succinate (PBS)/HGM<sup>2</sup> and HDPE/HGM foams

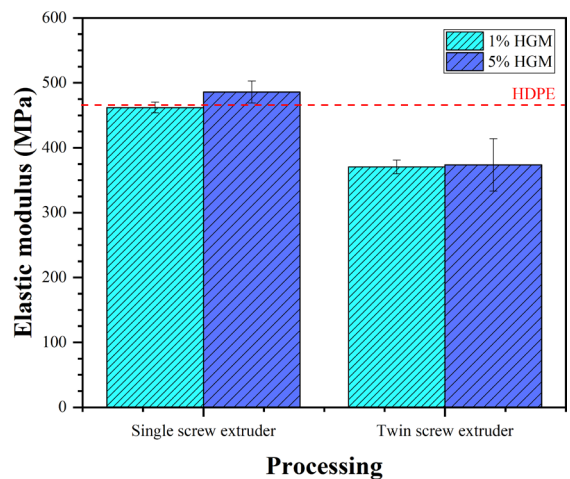


Figure 4. Elastic modulus x Processing

in the presence of a compatibilizer<sup>27</sup>, which indicated that such processing contributed effectively to the distribution of the filler in the matrix, however, it was inefficient in its dispersion.

Crack propagation along the matrix/HGM interface, is shown in Figure 5 (c). The two components are weakly bound by hydroxyl groups present on the surface of the glass microsphere and the polymer matrix.

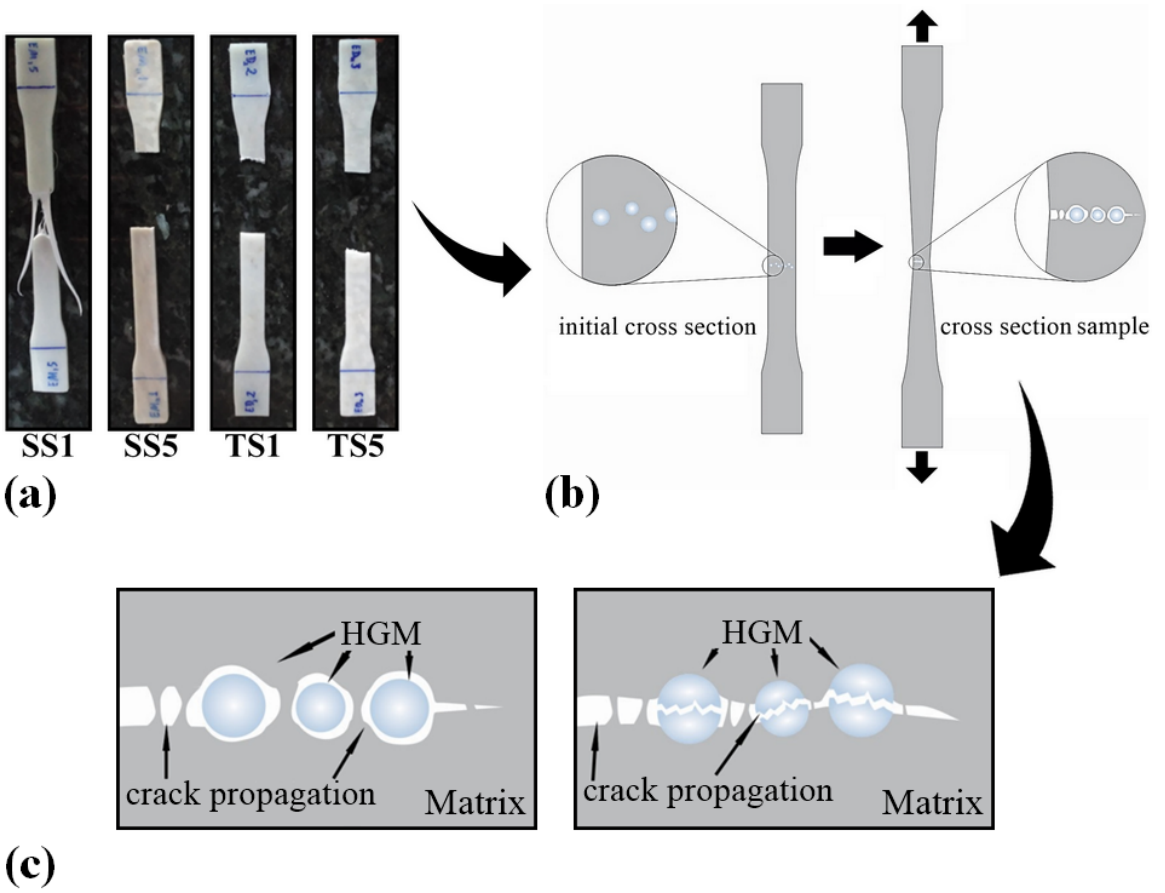
Figure 6 illustrates the maximum tensile strengths of syntactic foams obtained by the two different processing routes. Results indicate this property to decrease with HGM addition to HDPE.

These figures show that (single screw and twin screw extruder) processings produced systems with a 1% HGM and better performance for LMS than foams containing 5% of microspheres.

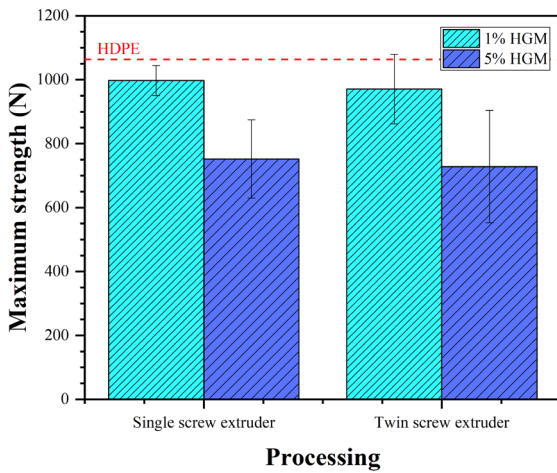
The data indicates that the syntactic foams obtained by both single and twin screw extruder, the increased HGM content and consequently the increased glass sediments resulting from the damage to the microspheres due to the processing route did not benefit the behavior regarding the limit of maximum strength. KUMAR et al., (2016)<sup>27</sup> observed similar behavior in extruded compatibilized HDPE/HGM foams. Despite their good interface interaction, increased HGM contents led to lower tensile strengths of HDPE/HGM syntactic foams.

Figure 7 shows the strains at break of each system when under investigation. As expected, regardless of the processing route chosen, HGM addition led to syntactic foams with decreased strains at break compared to neat HDPE and this decrease was more severe with higher HGM contents.

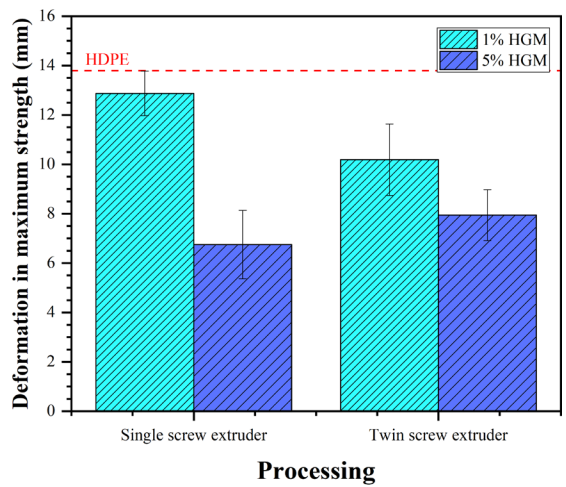
Results also indicate that this decrease was more severe for the twin extruded systems as for the single screw extruded samples strain reduction on compared to the matrix was 6.06% and 50.73% for SS1 and SS5, respectively, and



**Figure 5.** Illustration of the mechanism of crack propagation in syntactic foams: (a) Behavior of samples after tensile testing; (b) microspheres poorly adhered to the matrix and (c) microspheres adhered to the matrix.



**Figure 6.** Maximum strength x Processing



**Figure 7.** Deformation in maximum strength x Processing

for those produced by twin screw extrusion reductions of 25.62% and 42.04% for TS1 and TS5, respectively, were observed. This behavior was expected as rigid fillers do not undergo significant deformations and hinder polymer chain mobility and this decrease is more severe the higher the amount of HGM in the system<sup>3,25</sup>. Similar behavior was obtained by DOUMBIA et. al. (2015)<sup>30</sup> for polypropylene matrix syntactic foams.

The higher reduction in strain at break observed for twin screw extruded samples is attributed to the higher amount of glass sediments arising from the filler damage as seen in the micrographs. The presence of HGM in the syntactic foams reduces the continuous area of the matrix, and the tensile stresses reduce the cross section of the test specimens, which, together with a not very efficient anchorage, leads to foam disruption<sup>9,34,35</sup>.

Summarizing, the tensile properties of twin screw extruded syntactic foams are lower than those of the matrix and, in general, lower than single screw extruded systems, which is probably due to the higher HGM filler breakage. As for the percentage of microspheres, lower contents allowed to obtain more rigid syntactic foams.

### 3.2.2 Impact strength

Impact strength values for all systems investigated are shown in Figure 8.

Results indicate that an expressive increase in the impact strength, when compared to the HDPE matrix was observed for twin screw extruded systems, especially for the composite with 1% HGM (315.13%). Although an increase in filler content to 5% HGM reduced the amount of energy absorbed from the TS5 composite, impact strength still remained more pronounced (215.35%) than that of the matrix. The higher volumetric fraction of these particles within the matrix due to their low density generated more stress around the particle interface during impact overload and resulted in less impact resistance. Regarding processing via single screw extruder, the performance of the SS1 foam decreased approximately 12.17% compared to the matrix, and that of the SS5 foam was not assessed due to the equipment limitations.

The behavior of the foams shown in Figure 8 revealed that the addition of HGM was more effective in raising the impact strength in the systems processed in the twin screw extruder, since this processing requires more intense shear forces for the blend of the components when compared to the single screw extrusion, which resulted in a better distribution and dispersion of the filler in the matrix.

These behaviors showed that the addition of microspheres was more effective for the increase of impact strength in the processing routes using the twin screw extruder, since these processing require higher shear forces for the blend of the components when compared to the single screw extruder, which results in a better distribution and dispersion of the

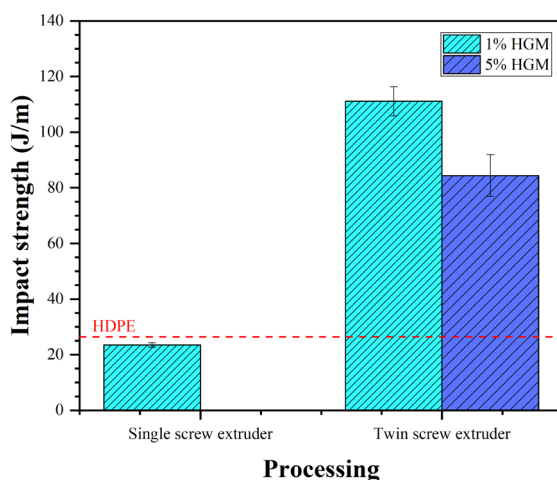


Figure 8. Impact strength of Syntactic Foams

filler in the matrix. As for the elevation of HGM content, OZKUTLU; DILEK & BAYRAM (2018)<sup>21</sup> observed in their studies on syntactic PMMA/HGM foams that the higher fraction of volume of microspheres inside the matrix generated higher stresses around the interface of the particles during the impact, resulting in lower strength due to the fragile characteristic of the microspheres. In addition, the higher number of damaged fillers in the foams with higher HGM content boosts the decrease in impact strength because the glass sediments intensify the internal stresses and decrease foam toughness. This same behavior of decrease in impact strength with the addition of microspheres is observed for syntactic foams with polypropylene matrices<sup>36</sup>, high-impact polypropylene<sup>30</sup>, and epoxy resin<sup>37</sup>.

In the study the breaking of particles from the processing possibly increased the energy during the impact due to the larger volume of microsphere fractions and to syntactic foams produced from HDPE and HGM was observed increased toughness with the addition of maleic anhydride to the systems<sup>9</sup>, and this result has also been observed in many composites and polymer blends<sup>38</sup>. Such behavior is observed in foams even when an increase in toughness compared to the matrix is not achieved, since the foams have advantages in this respect in the presence of a compatibilizing material<sup>21</sup>.

In the study on syntactic HDPE/HGM foams, PATANKAR; DAS & KRANOV (2009)<sup>9</sup> observed increased composite toughness when maleic anhydride was added to the systems, evidencing the elevation of such property for treated foams in comparison with foams without a compatibilizer. In many composites and polymer blends the addition of compatibilizer has denoted the increase of toughness in these materials<sup>38</sup>. This behavior is observed in syntactic foams even when an increase in toughness compared to the polymer matrix is not achieved, since the foams have advantages in this respect in the presence of a compatibilizing material over those with no treatment<sup>21</sup>.

There are few studies that show an increase in the energy absorbed by syntactic foams during the impact in comparison with the matrix, most of which are related to the use of thermoset resins<sup>39,40</sup>. The literature shows that the increased impact strength is strictly related to the path and the transfer of tension in the crack propagation<sup>2</sup>. The crack originated from the impact stress propagates in the matrix and is prevented from continuing this initial path when it encounters a particle of greater rigidity. At this point the crack splits into other fronts by bending over the spherical surface of filler (crack pinning-bowing mechanism). The tensile intensity in the matrix is reduced by splitting the crack around the microspheres, while the reinforcement phase produces an increase in tensile intensity because the crack fronts store more elastic energy than the original crack. Therefore, more energy is required to continue its propagation, and the tensile intensity increases until fracture at the reinforcement phase, thus continuing to propagate<sup>41-45</sup>.

This mechanism of crack propagation evidences the importance of distribution and dispersion of filler so that it occurs more efficiently in the increase of foam toughness. In addition, the intensity in the matrix/HGM interaction influences the mechanical performance of impact strength, which is best achieved by using twin screw extruder.

The mechanisms of toughening polymers with energy absorbing mechanisms with solid fillers are: microcracking (small, discontinuous cracks that are formed ahead of the main crack), shear yielding (local regions of plastically deformed matrix ahead of the crack tip near the fillers)<sup>46</sup>, and crack bowing<sup>11,37,43</sup>. So long as the microballoons remain intact, they would exhibit these same toughening mechanisms<sup>16</sup>.

## 4. Conclusions

The morphological analysis by MEV showed a poor adhesion between the matrix and the filler as a consequence of the processing routes used in this study, presenting a low wettability of HGMs by the HDPE. The mechanical results showed a reduction of the elastic modulus, and even the syntactic foams showing the highest values (SS1 and SS5) were not superior to pure matrix. The maximum strength and elongation under maximum strength were reduced for all composites. It was observed that both extrusion processings generated fractured specimens with fragile characteristics. Regarding the impact strength, the composite SS1 showed a decrease of 12.17%, and the processing using a twin screw extruder increased the strength of foams. While the composite TS1 had an increase of 315.13%, TS5 revealed an increase of 215.35%, showing a decrease in such property with the increase of HGM content.

## 5. Acknowledgements

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