

Preparation and Characterization of Hollow Glass Microspheres- Reinforced Poly (acrylonitrile-co-butadiene-co-styrene) Composites

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In this study, poly(acrylonitrile-co-butadiene-co-styrene)/hollow glass microspheres (ABS/HGM) composites were prepared by means of a twin-screw extruder. HGM were incorporated at different loadings of 2.5, 5.0, and 7.5 wt.% at the central extruder zone with different types of ABS. The morphological, physical, thermal, rheological and mechanical properties of ABS/HGM composites were investigated. Statistical analysis reveals that high impact ABS addition is significant for improving composites' impact strength. The results also indicated that addition of 5.0 wt.% of HGM along with 5.0 wt.% of powdery ABS at the central extruder zone maintains the HGM integrity while powdery ABS contributes to better filler dispersion in the matrix resulting in light-weight composites having improved mechanical properties.

Keywords: *Hollow glass microspheres, poly (acrylonitrile-co-butadiene-co-styrene), light-weight composites.*

1. Introduction

In the last few years research communities worldwide have been making constant efforts for the development of industrially useful light-weight materials that also exhibit high mechanical performance¹⁻⁴. As a result of recent developments in the field of polymer composites, some industries have engaged in the development of materials that offer greater flexibility in enhancing strength allied with weight reduction⁴. The materials, used in marine, aerospace and automotive applications need to exhibit low density associated with high strength, stiffness and high impact strength. In addition, environmental concerns are a challenge for the automotive industries to promote vehicle weight reduction without compromising their performance⁵⁻⁶. Therefore, hollow glass microspheres are normally used as reinforcing materials in a polymer matrix to produce light-weight composites with high mechanical properties³⁻⁴.

Hollow glass microspheres (HGM) consist of outer stiff glass spheres with gas inside and exhibit some desirable properties such as lightness, low thermal conductivity and low dielectric constant. In the average, HGM have diameter of 15 to 65 μm with a very thin wall of 0.5 to 1.5 μm and density between 0.12 and 0.60 $\text{g}\cdot\text{cm}^{-3}$ ^{1,2,7}. On the other hand, poly(acrylonitrile-co-butadiene-co-styrene)(ABS) is a widely used engineering thermoplastic owing to its desirable properties, such as good dimensional and thermal stability, processability, chemical resistance, mechanical properties and fair cost⁸. However, the low ABS rigidity may lead to drawbacks during usage. Therefore, reinforcing inorganic

fillers such as HGM, calcium carbonate, talc, clay, etc, were used to improve ABS rigidity⁸.

Delogu and coworkers⁹ combined environmental and economic assessments to evaluate the usage of talc and HGM as reinforcing agents in polymer composites used as lightweight materials in automotive components. The authors observed that based both on environmental and economic assessments HGM-reinforced polymer composites are preferable to talc filler-reinforced composites. Liang¹⁰ studied the mechanical properties of three types of ABS composites reinforced with hollow glass beads of different sizes and size distributions using a twin-screw extruder. The authors observed that the composite mechanical properties increase at filler volume fraction of 5% and the effects of filler size and its distribution did not affect the mechanical properties evaluated. In our previous work¹¹, ABS was reinforced with HGM to evaluate the effect of HGM addition at two different extruder feeding zones. The results showed that HGM at a maximum of 5.0 wt.% greatly improved the properties of the composites, including thermal stability as well as mechanical and rheological properties. The addition of HGMs at the feeding zone closer to the die maintains the integrity of the hollow glass beads while promoting composites of improved mechanical properties and lower density when compared with the composites obtained by the addition of HGMs closer to the hopper. However, further efforts are needed to obtain a more accurate way of manufacturing light-weight polymer composites reinforced with HGM with high mechanical properties.

So, the present work aims at investigating the effects of incorporating HGM and powdery ABS together in a central

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extruder zone and evaluating if this addition contributes to maintain the integrity of the HGM filler during the extrusion process. The morphological, physical, mechanical, thermal and rheological properties of ABS/HGM composites were evaluated. On the other hand, the effect of the use of a high impact ABS modifier on the composite properties was also evaluated.

2. Experimental

2.1 Materials

ABS SV-0165 used as polymer matrix was supplied by Samsung Starex, China, with impact strength (ASTM D256-10) of 245 J.m⁻¹. High impact ABS SD-0190H modifier was also supplied by Samsung Starex, China, with impact strength (ASTM D256-10) of 390 J.m⁻¹. HGM type S038HS with no surface treatment were supplied by 3M™, Brazil, (Glass Bubbles®). The HGM density is 0.38 g.cm⁻³ while the compression strength is 34.5 MPa. The composite density was determined using ethanol PA (purity 99.9%) supplied by Merck.

2.2 Composite preparation

ABS SV-165 and ABS SD-0190H were previously dried in a Marconi (Brazil) oven at 60 °C for 24h. Composites were prepared in a corotating and interpenetrating twin-screw extruder (MH Equipments/Brazil) with length/diameter (L/D) ratio of 32 mm and 20 mm screw with rotating speed 100 rpm and temperature profile 200-200-230-240 °C.

HGMs were incorporated into an ABS matrix at the central extruder zone at percentages of 2.5, 5.0, and 7.5 wt.% along with 5 wt.% of ABS SV-165 using a side feeder (MH Equipments/Brazil) to evaluate if the incorporation of HGM together with ABS SV-165 improves the HGM distribution into the ABS matrix, as can be seen in Figure 1(a). In addition, a high impact ABS composite was also developed. The

composite contains 45 wt.% of ABS SV-165 and 45 wt.% of high impact ABS SD-0190H added at the extruder feeding section and 5 wt.% of HGM along with 5 wt.% of ABS SV-165 incorporated at the central extruder zone using a side feeder (MH Equipments/Brazil) (Figure 1(b)). Compositions used in this study are listed in Table 1.

2.3 Composite characterization

Plates were produced by compression molding in the dimensions of 165 x 95 x 3 mm in a model 30010- 4-1 (Brazil) press, at a pressure of 60 bar for 12 minutes, at 170 °C and cooled to 60 °C. Specimens for mechanical tests were obtained from plates cut using a band saw.

Morphological characterization was performed using a Shimadzu (Japan) scanning electron microscope (SEM). The specimens were frozen under liquid nitrogen, fractured, coated with gold and observed using an accelerating voltage of 15 kV.

Density was evaluated in accordance with the ASTM D4052-95 Method by the pycnometer method.

Heat deflection temperature (HDT) analysis was carried out in a Ceast Instrument (Brazil) using a deflection load of 1.8 MPa, in accordance with the ASTM D648-07 Method.

Rheological properties were analyzed in an Anton Paar Physica MCR 101 (USA) parallel plate oscillating rheometer in accordance with the ASTM D7395-07 Method, with frequency variation of 0.01 and 100 rad.s⁻¹ and temperature from -180 to 200 °C under a nitrogen atmosphere, at a rate of 10 °C. min⁻¹, the test specimens having 20 mm diameter and 3 mm height.

Tensile strength was measured in accordance with ASTM D638-10 in an EMIC (Brazil) instrument model DL 2000, at a speed of 50 mm.min⁻¹ with test specimens of 165 x 13.3 x 3 mm dimensions.

IZOD Impact strength was measured in accordance with ASTM D256-10 in a Ceast Resil equipment (Brazil) with a 4J pendulum and 63 x 12.7 x 3 mm notch specimens. All test specimens' sides were sanded with 80 grain sand paper supplied by 3M™ do Brazil.

Statistical analysis (ANOVA) was performed using the Excel 2010 software. The parameters evaluated in the

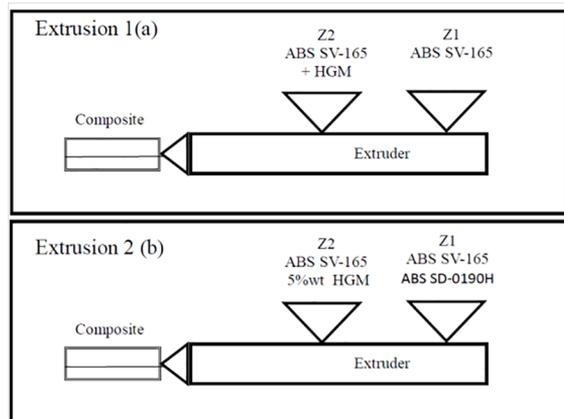


Figure 1. HGM incorporation at the central extruder zone with 5.0 wt.% of ABS (a); and incorporation of high impact ABS at the feeding zone (b).

Table 1. Codification and composition of the ABS and ABS/HGM composites.

Codification	Composition
ABS/C	Z1:ABS control, 100 wt.% ABS SV-165
ABS/2.5 HGM/E1	Z1:92.5 wt.% ABS SV-165 + Z2: 5.0 wt.% ABS SV-165 and 2.5 wt.% HGM
ABS/5.0HGM/E1	Z1:90 wt.% ABS SV-165 + Z2: 5.0 wt.% ABS SV-165 and 5.0 wt.% HGM
ABS/7.5HGM/E1	Z1:87.5 wt.% ABS SV-165 + Z2: 5.0 wt.% ABS SV-165 and + 7.5 wt.% HGM
ABS/5.0HGM/E2	Z1:45 wt.% of ABS SV-165 and 45 wt.% of high impact ABS SD-0190H + Z2: 5.0 wt.% of HGM + 5.0 wt.% of ABS SV-165

statistical analysis included sum of squares (SQ), degrees of freedom (GI), and mean squares (MQ). Values of $p < 0.05$ were considered significant.

3. Results and Discussion

3.1. Morphological properties

SEM micrographs of the composites with 2.5, 5.0 and 7.5 wt.% of HGM with 5.0 wt.% of ABS SV-165 incorporated at the central extruder zone (Z2) are shown in Figure 2. It is possible to observe that some HGM were removed from the ABS matrix at the time of the fracture probably due to the low chemical affinity between reinforcement and matrix¹¹. The ABS polarity is restricted to the acrylonitrile monomer, the remaining of its structure being of a nonpolar character, while HGM presents some polarity due to the hydroxyl groups at the microsphere surface. The interaction between matrix and reinforcement, if any, could be due to intermolecular attraction forces between the matrix acrylonitrile monomer and HGM hydroxyl groups.

It also can be seen in Figure 2 that almost all the HGM appeared to have withstood the compressive forces encountered during the extrusion process after being incorporated at

the central extruder zone. The HGM are submitted to less shear forces when fed at this zone and therefore maintain their structure during the extrusion process. In our previous study¹¹, the HGM were incorporated at the extruder feeding point and the results showed that HGM were broken due to the higher residence time at the extruder associated with higher shear forces of the twin-screw extrusion process. The addition of ABS powder along with the HGM seems to promote better incorporation of the reinforcement by the polymer matrix, however, according to Figure 2(a) and Figure 2(c) the addition of 2.5 wt.% and 7.5 wt.% reinforcement promotes the agglomeration of the microspheres, while the addition of 5.0 wt.% results in better filler dispersion in the polymer matrix as can be seen in Figure 2(b). The better filler dispersion with 5.0 wt.% HGM probably occurs because the addition of the ABS SV-165 was also done in the same quantity (5.0 wt.%) at the central extruder zone, which may promote better dispersion of the filler in the matrix, while the addition of 2.5 wt.% and 7.5 wt.% of HGM generates filler agglomeration. The addition of 5.0 wt.% HGM and 5.0 wt.% of ABS powder at the same time at the central extruder zone promotes a synergistic effect in HGM dispersion, which was not observed for the 2.5 wt.% and 7.5 wt.% HGM-containing composites.

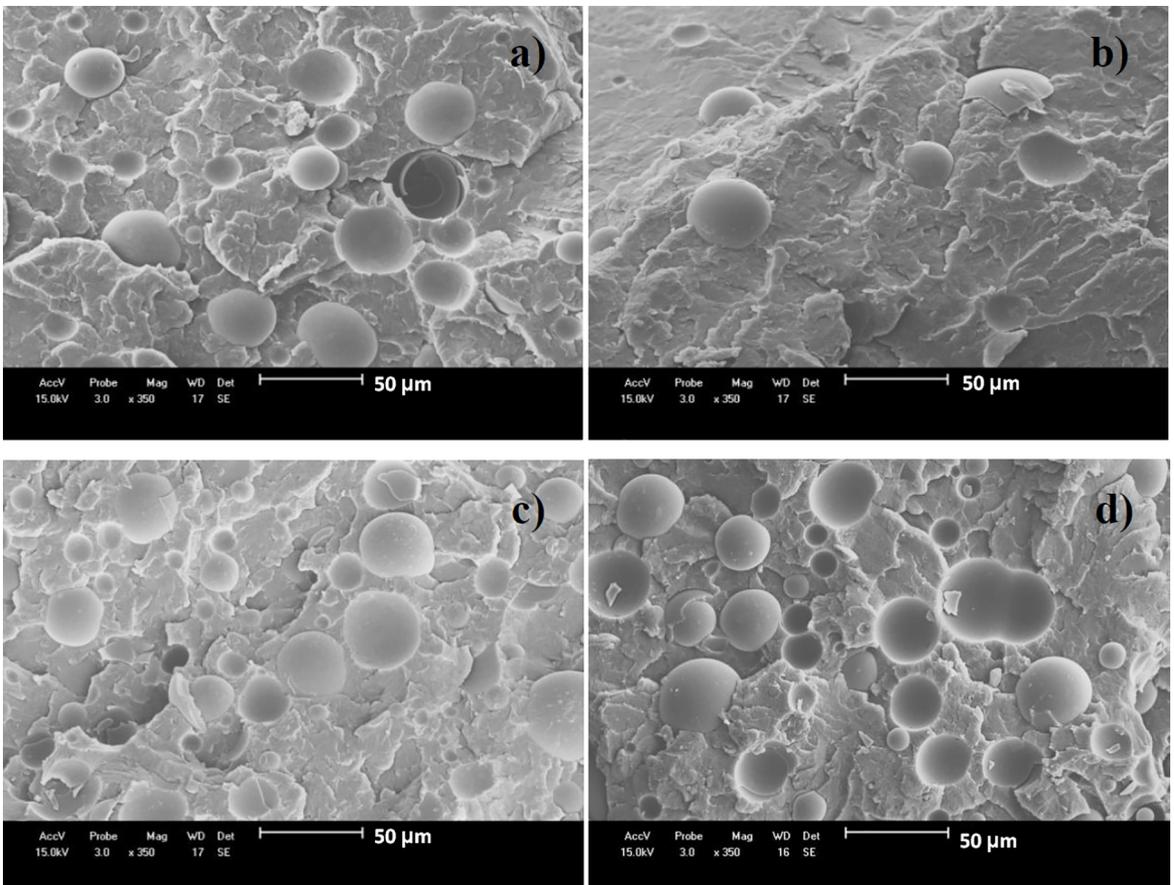


Figure 2. SEM micrographs of the composites with ABS/2.5 HGM/E1 (a), ABS/5.0 HGM/E1 (b), ABS/7.5 HGM/E1 (c) and ABS/5.0 HGM/E2 (d).

The SEM micrograph of the composite with 5.0 wt.% of HGM and 45 wt.% of high impact ABS is shown in Figure 2(d). HGMs were also removed from the ABS matrix due to the lower chemical affinity between matrix and reinforcement, as explained above. An agglomeration of the microspheres can also be seen in Figure 2(d).

3.2 Density and HDT values

Reduction a materials density, therefore its weight, without reducing its mechanical properties is one the main challenges of the automotive industries^{3,11}. The density and HDT values of the composites studied are presented in Table 2. The addition of HGM reduced the density of all samples studied. It may be observed that the addition of 5.0 wt.% of HGM promotes a decrease of 12.5% in density, when compared with the matrix. This is first attributed to the added light-weight HGM which possess a density of 0.98 g.cm⁻³. Adding the microspheres along with the ABS powder at the central extruder zone (Z2) also contributes to preserving the HGM integrity during compounding probably due to the better incorporation of the microspheres into the polymer matrix, however, no statistical differences were observed as can be seen in Table 2.

The composites presented an increase in HDT with the addition of HGM when compared with the ABS matrix. The composite with 7.5 wt.% of HGM showed the best result with an increase of 8% in HDT value, when compared with the ABS/C. According to Scaffaro *et al.*¹² the increase in HDT values is attributed to the increase in composite

stiffness, due to the presence of HGM, which therefore requires more energy for molecular mobility. On the other hand, the composite with high impact ABS exhibits a HDT value like the ABS matrix. This result may indicate that the higher quantity of butadiene present in the composite matrix with the addition of high impact ABS might have rendered the composite more ductile.

When compared with pure ABS, the density of all composites studied decreased while the thermal stability increased. These two properties are important for the automotive industry since ABS is one the most widely used polymers in this industry⁸.

3.3 Rheological properties

Dynamic rheological analysis can provide information on the evolution of the polymeric materials in the melt state, which can be used to anticipate the internal structures and processing properties of polymeric materials^{11,13}. Storage modulus (G') represents the elastic response of a material, which relates to the potential energy stored by the material during deformation. Hence, the value of G' can be used as a comparative estimative of the stiffness of the material^{13,14}. Figure 3 represents the frequency dependence of the storage modulus (G') for the ABS and ABS/HGM composites. It is apparent that the G' of the composites increases with the increase in HGM content. This result may be associated with the reinforced effect caused by the incorporation of the rigid HGM¹⁴. Furthermore, this result indicates that large-scale polymer relaxations are restrained by the presence of HGM

Table 2. Density and HDT of the composites as a function of HGM content with statistical analysis of the samples studied.

Samples	Density		HDT				
	(g.cm ⁻³)		(°C)				
ABS/C	1.04 ± 0.001		83.3 ± 0.4				
ABS/2.5HGM/E1	0.99 ± 0.001		87.2 ± 0.2				
ABS/5.0HGM/E1	0.91 ± 0.001		86.6 ± 0.7				
ABS/7.5HGM/E1	1.02 ± 0.001		89.7 ± 0.8				
ABS/5.0HGM/E2	0.95 ± 0.010		84.9 ± 0.4				
ANOVA – Density							
Source of variation	SQ	gl	MQ	F	P Value	F critical	Significant
ABS SV-165 in Z2	0.007	5	0.001	0.0085	0.931	7.709	No
HGM wt.% 2.5 / 5.0 / 7.5	0.007	53	0.000015	0.7530	0.543	9.552	No
Addition of ABSSD-0190H	0.009	3	0.00053	0.1259	0.757	18.513	No
ANOVA – HDT							
Source of variation	SQ	gl	MQ	F	P Value	F critical	Significant
ABS SV-165 in Z2	31.892	5	17.6470	4.9554	0.090	7.709	No
HGM wt.% 2.5 / 5.0 / 7.5	31.892	5	1.5930	0.1660	0.854	9.552	No
Addition of ABSSD-0190H	6.655	5	0.8816	0.6108	0.478	7.709	No

Sum of squares (SQ), degrees of freedom (Gl), and mean squares (MQ)

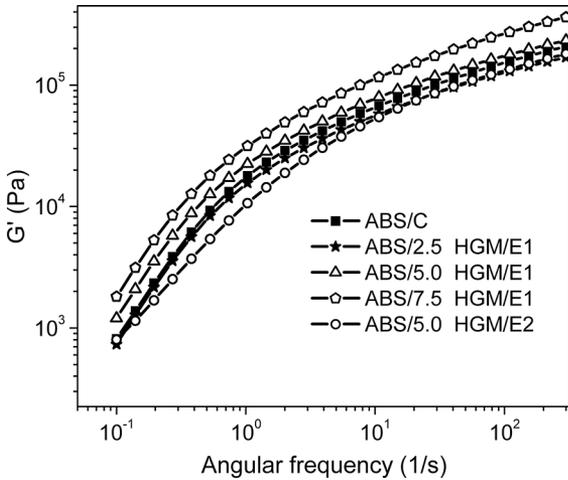


Figure 3. Storage modulus (G') versus angular frequency for composites with 2.5, 5.0 and 7.5 wt.% of HGM and composite with high impact ABS.

effectively, which agrees with the HDT results. In addition, the incorporation of HGM improves the stiffness of ABS, which is consistent with the results obtained in other studies^{11,13,14}. The storage modulus of the composite with high impact ABS was lower than that of the ABS/C polymer. This behavior can be attributed to the higher quantity of butadiene that can lead to a more ductile composite material.

The complex viscosity (η^*) of ABS/C and ABS/HGM composites (ABS/2.5 HGM/E1, ABS/5.0 HGM/E1, ABS/7.5 HGM/E1 and ABS/5.0 HGM/E2) as a function of angular frequency (ω) is shown in Figure 4. In the shear rate range studied, the complex viscosity of pure ABS and all the composites shows a shear thinning effect, which is ascribed to the reduction in entanglement density of ABS chains under the influence of high shear stress. Furthermore, the composites exhibit increased viscosity with the increase in HGM content. This phenomenon can be attributed to the interactions established between the polymer melt and the microscopically rough surface of the HGM surface.

Complex viscosity values indicate that the incorporation of HGM does not change the shear thinning behavior but affects the index of viscosity at a given shear rate. Similar results are found in other reports involving polymer based/HGM composites^{13,14}.

3.4 Mechanical properties

Table 3 presents the tensile strength and modulus of ABS/C and composites as a function of HGM content. Addition of 2.5 wt.% HGM causes a slight decrease in the tensile strength value when compared with the polymer matrix, while the addition of 7.5 wt.% results in a more accentuated decrease in the composite tensile strength value. This behavior may be ascribed to HGM agglomeration previously observed in SEM analysis, which decreases the effectiveness of reinforcement. The 5.0 wt.% HGM composite had the

highest tensile strength value, which might be associated with improved HGM dispersion into the polymer matrix, as observed in Figure 5. However, no statistically significant difference was observed in tensile strength as a function of HGM content. According to the literature, when the HGM are homogeneously dispersed in the polymer matrix they effectively act as reinforcement^{11,15-17}. On the other hand, the composite with high impact ABS and 5.0 wt.% HGM (ABS/5.0 HGM/E2) presents a decrease of 16% in tensile strength when compared with ABS/C. The ductile behavior promoted by the higher amounts of ABS butadiene associated with microspheres' agglomeration observed in Figure 2(d) may contribute to the decrease in tensile strength in this sample. In general, the modulus increases continuously with filler addition. The increase in modulus is also caused by the presence of the microspheres, which improves the stiffness of the composite¹⁸⁻²⁰. Modulus enhancement with HGM loading corresponds well with the afore-mentioned storage modulus observed in dynamic rheological measurements.

Impact strength of the ABS and ABS/HGM composites was also determined, as presented in Table 3. The composites exhibit lower impact strength than neat ABS, which may be attributed to the fact that the HGM content brings brittleness to the formulations studied^{11,21}. However, when the HGM content is equal to 5.0 wt.% the impact strengths of the ABS/HGM composites is higher than those of any other composite formulations (2.5 wt.% and 7.5 wt.% of HGM). Thus, an increase in impact strength does not depend only on the improved interface adhesion between ABS and HGM but may depend on a complete stress transfer path that may be associated with better dispersion of the microspheres in the polymer matrix, which can promote better stress transfer to the matrix from the reinforcement microspheres. A similar result was also found in a report involving polymer-based/HGM composites¹³. The composite containing high impact ABS shows the highest impact strength. The higher quantity

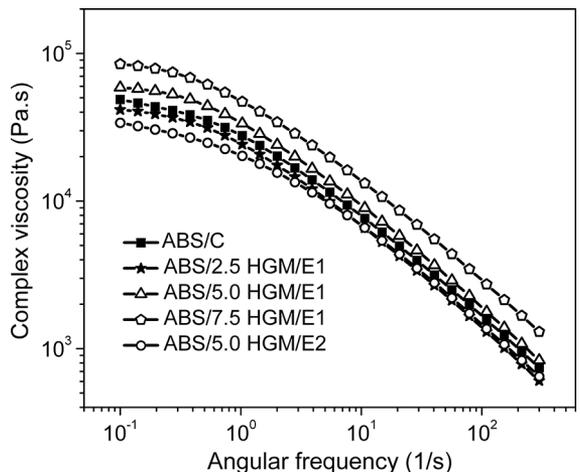


Figure 4. Complex viscosity (η^*) versus angular frequency for composites with 2.5, 5.0 and 7.5 wt.% of HGM and composite with high impact ABS.

Table 3. Mechanical properties of the composites as a function of HGM content with statistical analysis of the samples studied.

Samples	Tensile strength (MPa)	Tensile strain (%)	Tensile modulus (MPa)	Impact strength (J/m)
ABS/C	22.73 ± 0.96	37.60 ± 13.97	509.90 ± 36.18	53.77 ± 2.47
ABS/2.5HGM/E1	21.51 ± 0.40	34.00 ± 7.13	491.40 ± 18.10	39.88 ± 2.78
ABS/5.0HGM/E1	22.90 ± 0.70	27.96 ± 6.00	498.40 ± 20.10	43.84 ± 5.04
ABS/7.5HGM/E1	17.39 ± 0.80	8.04 ± 2.94	555.70 ± 21.39	19.54 ± 1.54
ABS/5.0HGM/E2	19.01 ± 0.78	24.61 ± 3.18	554.80 ± 42.73	59.84 ± 5.50

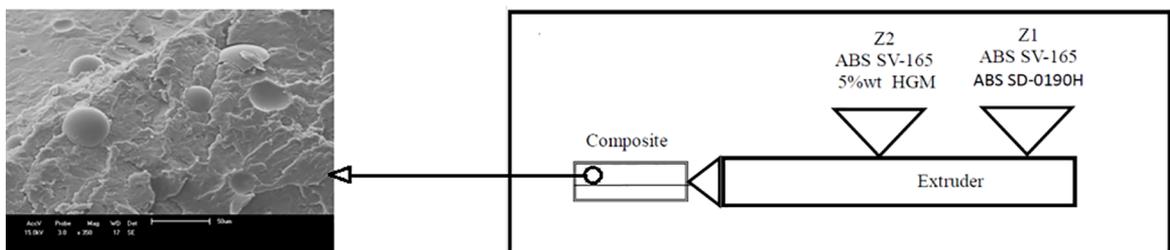
ANOVA - Tensile strength

Source of variation	SQ	gl	MQ	F	P Value	F critical	Significant
ABS SV-165 in Z2	29.995	5	4.369	0.682	0.455	7.709	No
HGM wt.% 2.5/5.0/7.5	29.995	5	8.193	1.806	0.306	9.552	No
Addition of ABS SD-0190H	20.882	3	3.297	0.380	0.602	18.513	No

ANOVA - Impact strength

Source of variation	SQ	gl	MQ	F	P Value	F critical	Significant
ABS SV-165 in Z2	517.986	5	14.372	0.114	0.752	7.709	No
HGM wt.% 2.5/5.0/7.5	517.986	5	159.642	2.410	0.238	9.552	No
Addition of ABS SD-0190H	518.800	3	271.600	18.510	0.027	2.197	Yes

Sum of squares (SQ), degrees of freedom (Gl), and mean squares (MQ)

**Figure 5.** SEM micrograph of the composite with 5.0 wt.% ABS SV-165 (Z2) and ABS SV-165 + ABS SD-0190H(Z1). *Graphical Abstract.*

of butadiene on the ABS SD-0190H contributes to improve the composite impact strength. The impact strength of the high impact ABS composite is 11% higher than the polymer matrix. Statistical analysis reveals that the addition of high impact ABS is significant to improve the composite impact strength. In addition, the impact strength of the high impact ABS composite is 43% higher than the composite with 5.0 wt.% HGM, which indicates that the high impact ABS added to the matrix contributes to the absorption of more energy during the impact test.

4. Conclusion

In this study, HGM-reinforced ABS composites have been prepared with the aid of a twin-screw extruder. Testing of morphological, physical, thermal, rheological and mechanical properties reveal that HGM plays an important role as

reinforcement for improving the ABS stiffness and thermal properties. Moreover, the addition of HGM significantly reduced the composite density, with is desirable for industrial applications. The storage modulus, viscosity and HDT values of the composites were enhanced with the increase in HGM content. When the most important properties for composite applications are considered, such as density and mechanical properties, it was observed that adding HGM (5.0 wt.%) at the central extruder zone together with 5.0 wt.% of powdery ABS showed the best results, probably because the integrity of the HGM was maintained and powdery ABS contributes to better filler dispersion into the matrix. This study shows that the properties of HGM-filled ABS matrix composites can be effectively controlled by adjusting the HGM/ABS powder feeding zone, ABS grade, and HGM content to develop light composites with higher mechanical performance that are potentially useful in the automotive industry.

5. Acknowledgments

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