Light-weight high-strength hollow glass microspheres and bamboo fiber based hybrid polypropylene composite: A strength analysis and morphological study

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ABSTRACT
Polypropylene (PP) based hybrid composites with treated hollow glass microspheres (t-HGM) as inorganic low density filler and naturally sourced bamboo fibers for strength reinforcement are prepared. The hybrid composites may fulfill the need for potential light-weight and high-strength modern engineered materials required for automotive and aerospace industry applications. The interfacial adhesion between different filler-matrix interfaces such as fiber-PP and t-HGM-PP has been enhanced by using maleic anhydride-grafted polypropylene (MA-g-PP). PP and MA-g-PP taken in a 9:1 ratio constitute the base matrix (BM), while the bamboo fiber is varied from 0 to 20 wt% keeping the HGM loading fixed at 10 wt% with respect to BM. While a density reduction of ~8.5% is achieved by addition of HGM’s, the decrease in mechanical strength has been more than compensated by the added bamboo fibers. Interestingly, for 20 wt% fiber addition the tensile, flexural and impact strengths increased by 23.5%, 38.5% and 47.9%, respectively, over and above the virgin PP values. The morphological studies via SEM showed good wetting of both fillers without any signs of aggregation and hindrance to each other’s property contribution. The work paves the way for engineering and design of components based on other promising light-weight high-strength natural fiber based composites.

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1. Introduction

The research communities worldwide have been making constant efforts for the development of industrially useful light-weight high-strength materials since ages. Light-weight components of any fuel consuming body offer good carrying capacity, better fuel efficiency and faster travel rates. Aluminum has been used in automotive industries for a long time due to its light-weight and ability to resist corrosion. Due to this, AUDI encouraged new car body concepts such as the space frame technology. In contrast to this development, proponents of steel industries introduced a light-weight car body (ULSAB) mainly based on mild and high-strength steel components [1]. There has been a great hustle of the material research groups and industries for the development of new light-weight high-strength materials. With the advent of first natural fiber polymeric composite in 1920–30s as an airplane part, to reduce its weight, motivated the use of natural fiber reinforced composites in other industries also [2].

With the recent developments in the field of polymer composites, some industries have engrossed themselves in the development of these materials that offer greater flexibility in enhancing strength and reducing weight. Polymer composites, having base matrix thermoplastics or thermosets, are reinforced by the fibers which can take good amount of stress at the time of application. Many car manufacturers and suppliers have employed polymer composites for door panels, seat backs, headliners, package trays, dashboards, and interior parts. The use of natural fibers has been proposed in many automotive and construction industries [3]. Nadir et al. [4] proposed an optimal composite panel formulation for automotive interior application which consists of coir (coconut)
fiber reinforced polypropylene (PP). James et al. [5] have presented a review of procedure of selection, preparation and property comparisons of different natural-fibers. In the study, the authors have reported major challenges such as moisture stability, fiber-polymer interaction and inconsistency in fiber properties from different sources and the potential industrial applications of natural-fiber based composites. In another study by Yi et al. [6], whole and spirit wheat straws have been incorporated in the PP webs to make light-weight composites and observed an improvement in the properties over previously prepared jute-PP composites. It is also reported that split configuration of wheat straw fiber gives better reinforcement as compared with the whole wheat straw fiber because of the increased surface area and aspect ratio of split configuration. There has been a great debate among scientists and engineers over the preference of usage of manmade fibers, such as glass, aramid and carbon fiber, or natural cellulosic fibers such as henequen, coconut, jute, flax, hemp, sisal, bamboo, wood and paper. In contrast with the traditionally used engineering fibers, e.g. glass, carbon or other mineral fibers, these lingo-cellulosic fibers impart many benefits to the composite namely relatively low density, no health hazard, negligible wear to the processing equipment during processing, low cost, easy availability and good bio-degradability. Joshi et al. [7] reviewed the potential of plant fibers over synthetic fibers for reinforcing materials. The group also stressed that the plant fibers are better for the environment than glass fibers.

Natural cellulosic fibers consist of four main parts namely cellulose, hemicellulose, lignin and pectin. The crystalline cellulose part is distributed in the amorphous lignin matrix and provides the reinforcement to the so formed natural composite [3]. In recent times, these cellulosic fibers and waste cellulosic products such as shell flour, wood flour and pulp have been extensively used for the reinforcement of different thermosetting and thermoplastic resins [8–15]. Bisanda et al. [16] showed that the alkali treatment of sisal fiber greatly improved the wettablity of the fibers resulting in a 21% improvement in the compressive strength of the prepared composites. The improved wetting is believed to be due to the increased fiber surface roughness and surface tension. This translates into higher interfacial bonding through fiber-resin interpenetration and mechanical interlocking. Franco et al. [17] have studied the effect of fiber treatment on the mechanical properties of short henequen fibers reinforced polyethylene matrix. They further add that reinforcement of the matrix with silane treated or pre-impregnated fibers resulted into an improvement in the fiber-matrix adhesion leading to a significant increase in the tensile strength and flexural modulus of the composites. Chat-topadhyay et al. [18] used maleic anhydride grafted polypropylene (MA-g-PP) and alkali treatment of the short bamboo fiber fibers during the time of fiber extraction for improving fiber-matrix interface adhesion, and thereby, reinforce PP. The alkali treatment of fiber helps to remove a portion of uronic acid, a constituent of hemicellulose, and other polar groups present in it so as to reduce its moisture absorption tendency [19]. The incorporation of MA-g-PP imparts hydrophobicity to the fibers due to the esterification of the hydroxyl group present with the anhydride group offered by MA-g-PP. Thwe and Liao [20] have also supported the fact that water uptake by natural fibers reduces when MA-g-PP modified PP matrix is used. The treatment helps to improve interfacial adhesion that reduces water accumulation in the interfacial voids and prevents water from entering the fiber. Although, the silane treatment or pre-impregnation of natural fibers shows significant improvement in properties but it also increases fiber cost many-a-fold due to use of costly silanes. The alkali treatment, however, is relatively very cheap yet strong reinforcement strategy and may be employed preferably for the natural fiber treatment before incorporating them into the thermosetting or thermoplastic matrix. The use of compatibiliser for treating the fibers prior to processing or as an additive during processing results in improved mechanical properties [21,22].

Natural fiber based composites, especially bamboo fiber based ones, have drawn the huge interest due to their environmental friendly and sustainable nature. In a review by Zakikhanli et al. [23], bamboo fiber materials have been compared with the glass fiber in terms of their mechanical property, recyclability and environmental sustainability. Also, bamboo fibers are proposed to have relatively low density, low cost, low energy consumption during the time of extraction as compared to glass fibers. In contrast to glass fibers, bamboo fibers absorb good amount of CO2, can be recycled easily and are completely biodegradable. Further, bamboo is preferred over the other plant fibers due to several advantages [24–28]. Bamboo fiber is abundantly available in most of the tropical countries and considered to be the world’s best known natural engineering materials. For example, in India it has been proposed to be the neglected golden hen as it is the most under-utilized natural resource with a contributing share of ~45% of the entire world’s bamboo forests [29]. Bamboo is beneficial with being one of the fastest growing natural fiber and has its cellulosic fibers aligned along the length of the bamboo which provide it maximum tensile strength, flexural strength and rigidity in that direction [30]. It has found major applications in meeting different structural and commercial requirements. Also, there has been a recent increase in the use of bamboo fiber reinforced polymeric composite materials due to the use of advanced processing technologies [24,27,31–34].

In the quest for development of a low cost, low density and green materials of suitable strength, researchers have preferred natural fibers over glass, carbon or any other man-made fiber. However, to the best of our knowledge, researchers have not yet attempted to keep the density of their thermoplastic composite same or less than that of the base matrix, while maintaining a significant improvement in the properties and reduction of final composite cost. Keeping this objective in mind, hollow glass microspheres (HGM) commonly known as glass bubbles have been considered in this work as a useful filler to reduce the composite density. HGMs have been filled in many polymers so as to reduce weight and lower the thermal conductivity of the composites prepared [35–38]. In an article by 3M™ [39], a density reduction from 0.90 to 0.785 g cm−3 has been reported for PP based composites. But HGM incorporation affects the tensile and impact strength considerably, with the latter affected relatively more due to their inherent brittle nature. Further, an improper interfacial adhesion between the inorganic and polar filler (HGM) with the organic and non-polar matrix (PP) is expected and needs to be addressed through appropriate surface treatment. We propose that the mentioned problems of making lightweight and low-strength PP-HGM composite could be alleviated by the treatment of HGMs and reinforcement with bamboo fiber. So in this work, we have appropriately treated HGMs (referred to as t-HGM) treatment and used these in the composite at a constant loading with fiber content variation. Short bamboo fibers (SBF) have been selected in the present study to reinforce, to lower the cost and make the PP-HGM composite more environment friendly. In this work, we have taken a mixture of PP and MA-g-PP as the base matrix (BM) and a weight ratio of 9:1 is maintained for the entire study. Loading of t-HGM is maintained constant at 10 wt% with respect to the BM. The loading of SBF is increased from 0 to 20 wt% with respect to BM. The structural and mechanical properties namely density, tensile strength, tensile modulus, flexural strength, flexural modulus and impact strength have been evaluated. Morphological observations to confirm proper filler dispersion and wetting have been captured with the Scanning Electron
Microscopy (SEM). All the wt% mentioned in this article are with respect to the BM if not mentioned specifically.

2. Experimental

2.1. Materials

Injection grade PP (Repol, H110MA), with a density of 0.908 g cm\(^{-3}\) and melt flow index of 11 g/10 min (measured at 230 °C, 2.16 kg) has been supplied by Reliance Industries Ltd., India. MA-g-PP (OPTIM® P-425 grade) with a density of 0.908 g cm\(^{-3}\) and melt flow index of 110 g/10 min (measured at 190 °C, 2.16 kg) has been supplied by Pluss Advanced Technologies Pvt. Ltd., India. Glass bubbles iM16K, with a true density of 0.46 g cm\(^{-3}\) and significant crush strength of 16,000 psi, have been obtained from 3M India Ltd. Locally grown bamboo culm is converted into bamboo chips and then cut into appropriately sized fibers to be finally used for making composites. (3-Aminopropyl)triethoxysilane (APTES) has been obtained from TCI Chemicals, India, and synthesis grade \(n\)-propylamine for catalyzing silane treatment from Loba Chemie Pvt. Ltd. Sodium hydroxide pellets, for alkali treatment of fibers and hydroxylation of HGMs, have been purchased from Sisco Research Laboratories Pvt. Ltd., India.

2.2. Treatment of hollow glass microspheres

A complete treatment of HGMs involves 2 steps namely hydroxylation followed by silane treatment. The method employed for the treatment is less toxic as compared to the other treatment methods used for HGM. The benefits of this screened procedure are supported in a previous article by Mutua et al. [40].

2.2.1. Hydroxylation

For the hydroxylation of inorganic oxides on HGM surface, 10 g of HGM’s are added to NaOH (0.5 mol/l) aqueous solution (400 ml). This solution is stirred for 1 h at 90 °C to create hydroxyl groups on the surface of HGM’s. The solution is then cooled which is followed by its filtration, performed using Whatman® ashless (grade 42) filter paper to separate HGM’s. The filtered HGM’s are then washed with distilled water until the pH of residue water reaches neutrality. This is followed by vacuum drying at 70 °C for 8 h to eliminate any residual water present on HGM surface.

2.2.2. Silane treatment

10 g of dried hydroxylated HGMs are reacted with 1 g APTES in 200 ml ethanol solution and 0.2 g \(n\)-propylamine catalyst. This reaction is performed with reflux for 1 h at 60 °C. After the treated HGM’s containing solution cools, it is filtered off using Whatman® ashless (grade 42) filter paper and washed once with ethanol followed by three times washing with distilled water. The retentate is then dried under vacuum at 80 °C for 24 h. The treatment of HGM surface is found to be appropriate as confirmed from morphological studies through SEM images of untreated and treated HGMs illustrated in Fig. 1(a) and (b), wherein its surface is seen to be nicely and sufficiently treated.

2.3. Extraction of short bamboo fiber (SBF)

Fibers have been extracted in a very cost effective way involving a 2 step process detailed below:

2.3.1. Mechanical process

To extract fibers from bamboo culm, firstly the diaphragm and node are removed to obtain an inner hollow portion used for processing [23]. These hollow portions are then cut into smaller pieces which are heated at 80 °C for 24 h to reduce their moisture content and to make their grinding easier and better. Fiber is acquired by grinding lignin in the middle lamellae. These fibers possessed wide ranging lengths and aspect ratio. Hence, in order to get fibers of desired length (3–6 mm), these fibers are sieved by 2 different sieves differing in sieve opening size (0.47 mm and 1.4 mm), that help to separate too big and too small fibers. The fibers obtained had an average length of 3.97 ± 1.03 mm and diameter that varied from ~290 to 720 μm.

2.3.2. Chemical treatment

The fibers obtained from mechanical sizing are treated with 1N aqueous NaOH solution for 24 h [41]. Aqueous NaOH dissolves the

![Fig. 1. SEM image of (a) untreated and (b) treated HGMs.](image-url)
non-cellulosic and amorphous parts of fibers namely lignin, hemicellulose, pectin etc. This is done because the inherent high crystalline cellulose content possesses higher strength than the non-cellulosic parts. After this, the fibers are washed with water until a pH of 7 is attained, and then later dried in a vacuum oven at 80 °C for 48 h. It has been reported previously that flexural strength can be improved substantially by modifying the topography of the fiber with an alkali aqueous solution treatment [17]. This has been explained to be due to the improvement in interfacial bonding or surface adhesion of composites as compared with other methods [23].

2.4. Design of experiment and sample preparation

Table 1 represents the sample code scheme that refers to various explanations given in later sections in the manuscript. As part of sample preparations, t-HGM content is kept constant and the SBF content changed to 5% (BM-H10-B5), 10% (BM-H10-B10), 15% (BM-H10-B15) and 20% (BM-H10-B20) to assess the impact of increase in fiber content on properties. Two additional batches, BM-H10 and BM-B10, with 10% t-HGM and 10% SBF loading separately, are prepared so as to explore any possible synergistic effect of SBF and t-HGM on properties of BM-H10-B10 composite. The density of the composite BM-B10 is also employed in reverse calculation so as to find the density of SBF in the polymer matrix.

SBF, t-HGM, PP and MA-g-PP are pre-dried at 80 °C for 24 h before initiating the composite preparation. All the materials in pre-calculated amounts are first physically mixed and then melt mixed in a temperature range of 190–210 °C in HAAKE® MiniCTW micro-conical twin screw compounder. After the melt mixing, the melt is transferred from the compounder to the injection cylinder of HAAKE® MiniJet II, which is then injected into the molds maintained at 70 °C to make specimens. Different molds are used for making specifically shaped and sized samples for tensile, flexural and impact property measurements. The injection cylinder temperature is taken 10 °C more than the mixing temperature so as to ease its flow into the injection cylinder. Injection and post-injection pressures are set at 520 and 250 bars, respectively.

Densitometer DH-600 of Dahometer is used for the density measurement with a specific gravity resolution of ±0.001 g cm⁻³ at 23 ± 2 °C. The samples are prepared in accordance with ASTM D792. 5 test specimens (80 × 10 × 4 mm³) for each composition are used for the density measurement.

2.5. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of MA-g-PP, BM-H10, BM-B10 and BM-H10-B10 have been recorded using PerkinElmer FT-IR C91158 spectrophotometer and compared in this study. The powdered samples of mentioned composites are dried and a small amount of each is compressed with KBr to form suitable pellets for spectral analysis. The FTIR spectra are obtained with a resolution of 4 cm⁻¹ within the range of 400–4000 cm⁻¹.

2.6. Mechanical properties

The estimation of tensile, flexural and impact properties has been done as per pertinent ASTM and ISO standards, the details of which are shared in the following sub-sections.

2.6.1. Tensile testing

Dumbbell shaped specimens, with a thickness of 2 mm and gauge length of 25 mm, of each batch as listed in Table 1 are prepared and tested in accordance with the ISO 527-2 (Specimen Type 1B). The testing is done on Universal Testing Machine (UTM) INSTRON® make (Model 3365), at a crosshead speed of 10 mm/min. The tensile strength at yield and modulus with their standard deviations have been reported in this paper.

2.6.2. Flexural testing

Two cuboidal shaped specimens of dimensions 80 × 10 × 4 mm³ for each batch are prepared and tested in accordance with ISO 178. Three point bending technique is employed in UTM with a test speed of 2 mm/min. The span length is set at 16 mm in accordance with the mentioned ISO standard which states that the span length should be 16 times the sample thickness (4 mm).

2.6.3. Impact testing

Notched Charpy impact strength is evaluated using the ISO 179-1/1eA standard using edgewise blow direction and notch type-A. For each test, a notch (Notch Type — Type A) is made in each sample with a base radius of 0.25 mm and notch angle of 45°. Further, a set of such 10 specimens having dimensions 80 × 10 × 4 mm³ are first conditioned for 24 h at 23 °C and 50% relative humidity. The test was carried out on Tinius Olsen (Model Impact 104). The average impact information with standard deviations has been calculated and reported.

2.7. Scanning electron microscopy (SEM)

Cryogenically fractured surfaces of composite samples have been analyzed for the assessment of filler dispersion and interfacial adhesion of t-HGM and fiber with the base matrix. The SEM analysis has been performed using MIRA 3 LM (FE SEM) by TESCAN. The sputter deposition has been done on the fractured surfaces of samples with gold-palladium alloy, followed by sample analysis at 2.0 kV.

3. Results and discussion

3.1. Fourier transform infrared spectroscopy (FTIR) analysis

The spectral peaks of MA-g-PP occurring at 1781 cm⁻¹ and 1849 cm⁻¹ in Fig. 2(a), are attributed to the carbonyl (C=O) stretching of the anhydride group of MA-g-PP. Further from FTIR study of BM-B10 (Fig. 2(c)), it is clear that the birth of C=O stretching peak at 1745 cm⁻¹, (C=O)—O stretching peak in the region 1254 cm⁻¹ and χ3 bending at 1165 cm⁻¹ confirms ester bond formation [18,42] between the –OH groups of SBF and anhydride groups of MA-g-PP. These ester signature peaks are found to be very weak in BM-H10 in Fig. 2(b) which suggests the presence of relatively less number of –OH groups over t-HGM even after silane treatment. The relatively small peak at 1780 cm⁻¹ in Fig. 2(b) for BM-H10 and Fig. 2(c) for BM-B10 correspond to the peak due to unreacted C=O group of anhydride moiety in MA-g-PP which are available for further fiber incorporation and wetting. Further, the

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Base matrix (BM) ratio</th>
<th>t-HGM with respect to the BM</th>
</tr>
</thead>
<tbody>
<tr>
<td>BM</td>
<td>9:1</td>
<td>0</td>
</tr>
<tr>
<td>BM-H10</td>
<td>9:1</td>
<td>10</td>
</tr>
<tr>
<td>BM-H10-B5</td>
<td>9:1</td>
<td>10</td>
</tr>
<tr>
<td>BM-H10-B10</td>
<td>9:1</td>
<td>10</td>
</tr>
<tr>
<td>BM-H10-B15</td>
<td>9:1</td>
<td>10</td>
</tr>
<tr>
<td>BM-H10-B20</td>
<td>9:1</td>
<td>10</td>
</tr>
<tr>
<td>BM-B10</td>
<td>9:1</td>
<td>0</td>
</tr>
</tbody>
</table>

intensity of C=O stretching peak at 1781 cm\(^{-1}\) is significantly reduced in the spectra of BM-H10-B10 indicating adequate and almost complete compatibilization of SBF and \(\tau\)-HGM by added MA-g-PP.

Fig. 3 indicates the spectra of BM-H10, BM-B10 and BM-H10-B10 with quite a broad transmittance peak in the 3200–3700 cm\(^{-1}\) region. In general, O–H stretching/H-bonding show characteristic absorption in the 3200–3600 cm\(^{-1}\) region [42–44]. Further, N–H (stretch, free) and hydrogen bonded N–H also show their absorption bands at 3300–3500 cm\(^{-1}\). So, the broad range of transmittance (3200–3700 cm\(^{-1}\)) shown here is suggestive of the presence of both primarily hydrogen bonded and few free O–H groups in SBF, and likewise, primarily hydrogen bonded and few remaining free O–H and N–H groups in \(\tau\)-HGM.

### 3.2. Density reduction

Table 2 presents the experimental and theoretical densities of the composites prepared in this study. The density of virgin PP obtained (0.907 ± 0.003 g cm\(^{-3}\)) using the densitometer is found to be in very close agreement with the density reported (0.908 g cm\(^{-3}\)) by the supplier for the mentioned grade. It may be observed that with addition of only 10 wt% of \(\tau\)-HGM, a significant density reduction of about 8.29% with respect to the base matrix has been achieved. This is attributed to the added light-weight HGM's which possess a density of 0.46 g cm\(^{-3}\) [39]. Though HGM has a strong impact in making the composite lighter, the loading is limited due to its brittle nature that translates into a manifold deterioration of the impact strength. Using the experimental density of BM-B10, the density of SBF is found to be 1.328 g cm\(^{-3}\), assuming negligible voids presence as reported earlier [45]. This density estimate is in good vicinity of values reported earlier: 1.3–1.4 g cm\(^{-3}\) [46] and 1.4 g cm\(^{-3}\) (grinded fiber) [23] for bamboo fiber. SBF is loaded in different wt% to BM so as to compensate the effect of \(\tau\)-HGM on the impact strength. Table 2 clearly demonstrates the effect of fiber variation on composite density. From the known/calculated densities of the raw materials, theoretical densities of different composites have been calculated and compared with the experimental ones. From the data it is clear that with the increasing content of SBF the density of the resulting composite increases in line with the theoretical expectations. Also, from the density data it can be noted that the density of the hybrid
composite is crossing the density of PP between 10 and 15 wt% of SBF. The deviation of the experimental densities from the theoretical densities may be due to possibility of fractional t-HGM breakage during processing and assumption of negligible voids made in estimating BF density.

3.3. Mechanical properties

The estimation of mechanical properties of a composite is vital to understanding the utility of a composite for industrial purposes. In this regard, the volume (or weight) fraction of the filler, aspect ratio, adherence and stress transfer at the filler-matrix interface, and orientation of non-spherical filler are the main parameters that may decide the mechanical properties of a composite. This fact carries importance, specifically since the fillers considered in the study are natural fibers [47].

3.3.1. Tensile properties

It can be easily inferred from Table 3 that with addition of 10 wt% t-HGM, the tensile strength decreased by 8% as compared to BM. A decrease in the tensile stress at yield or tensile strength with increase in t-HGMs loading, compared to base matrix has been reported earlier as well [48]. Further, if the surface treatment of HGM is not done, a more pronounced decrease in tensile strength might be observed [49]. However, an enhancement in reinforcement is strongly expected as the content of relatively high aspect ratio SBF increases. The performance of fiber reinforced composites is enhanced in this work by adding MA-g-PP as compatibilizer. MA-g-PP is known to improve the interfacial adhesion between the fiber and the matrix [18,50]. The reinforcement is due to the proper stress transfer and stress distribution from the polymer matrix (in our case PP) to SBF.

In the considered study, the tensile strength and modulus of composite at 20 wt% fiber (BM-H10-B20), when compared to BM, is enhanced by 14.38% (up from 42.49 to 48.60 MPa) and 65.55% (up from 0.90 to 1.49 GPa). These values are even higher by 24.4% (up from 39.07 to 48.60 MPa) and 50.5% (up from 0.99 to 1.49 GPa) compared to BM-H10 indicating that addition of 20 wt% fiber duly compensates the marginal strength loss due to HGMs. It may also be noticed that a mere addition of only 5 wt% of SBF to BM-H10, the tensile strength of hybrid composite equaled that of BM and even crossed the strength of PP.

It is important to explore if the joint presence of different aspect ratio and different material based fillers effect their inherent property of enhancing or reducing the mechanical properties when

Table 2

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Experimental density (g cm$^{-3}$)</th>
<th>Theoretical/available density (g cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>0.907 ± 0.003</td>
<td>0.908$^a$</td>
</tr>
<tr>
<td>BM</td>
<td>0.905 ± 0.003</td>
<td>0.907</td>
</tr>
<tr>
<td>BM-H10</td>
<td>0.830 ± 0.002</td>
<td>0.832</td>
</tr>
<tr>
<td>BM-H10-B5</td>
<td>0.878 ± 0.001</td>
<td>0.846</td>
</tr>
<tr>
<td>BM-H10-B10</td>
<td>0.892 ± 0.007</td>
<td>0.859</td>
</tr>
<tr>
<td>BM-H10-B15</td>
<td>0.919 ± 0.005</td>
<td>0.871</td>
</tr>
<tr>
<td>BM-H10-B20</td>
<td>0.942 ± 0.001</td>
<td>0.883</td>
</tr>
<tr>
<td>BM-B10</td>
<td>0.932 ± 0.002</td>
<td>–</td>
</tr>
</tbody>
</table>

$^a$ Density of virgin PP as provided by supplier.

Table 3

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Tensile strength (MPa)</th>
<th>Tensile modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>41.05 ± 1.57</td>
<td>0.86 ± 0.076</td>
</tr>
<tr>
<td>BM</td>
<td>42.49 ± 0.35</td>
<td>0.90 ± 0.018</td>
</tr>
<tr>
<td>BM-H10</td>
<td>39.07 ± 1.23</td>
<td>0.99 ± 0.057</td>
</tr>
<tr>
<td>BM-H10-B5</td>
<td>42.05 ± 1.18</td>
<td>1.20 ± 0.046</td>
</tr>
<tr>
<td>BM-H10-B10</td>
<td>42.54 ± 0.50</td>
<td>1.25 ± 0.065</td>
</tr>
<tr>
<td>BM-H10-B15</td>
<td>45.97 ± 1.02</td>
<td>1.36 ± 0.051</td>
</tr>
<tr>
<td>BM-H10-B20</td>
<td>48.60 ± 1.14</td>
<td>1.49 ± 0.001</td>
</tr>
<tr>
<td>BM-B10</td>
<td>44.80 ± 1.10</td>
<td>1.12 ± 0.065</td>
</tr>
</tbody>
</table>
used separately. This fact is more understood when the tensile properties data in Table 3 is looked at. The tensile strength of the BM is seen to increase by 5.4% with the addition of 10 wt% of SBF (BM-B10) whereas the strength decreases by 8% with addition of 10 wt% of t-HGM (BM-H10). If tensile strength could present itself as a simple additive property, a consequence of these two opposing behaviors from different materials should be a net tensile strength decrease of 2.6% for the composite BM-H10-B10. Further on molecular level, this expected decrease could possibly happen as with increased filler loading the number of anhydride groups of MA-g-PP available per −NH₂ group of t-HGM would decrease. This is due to tendency of −OH groups of fiber to chemically interact and form stronger ester bond with the carboxyl groups of MA-g-PP [18]. However, the −NH₂ groups of t-HGM may only interact with the carboxyl groups of MA-g-PP via relatively weak hydrogen bonding interactions. Hence, the composite BM-H10-B10 may be expected to display an even larger decrease in tensile strength than the theoretical expected (−2.6% from additive property assumption).

However, the results show that the BM-H10-B10 composite strength remains same as that of BM. This may be attributed to the well-known ball-bearing effect of HGMs during processing to improve the dispersion of fibers. The second reason is due to a probable increase in hydrogen bonding interactions between the −NH₂ groups of t-HGM and unreacted −OH groups of fiber as well as with C=O groups in ester formed.

### 3.3.2. Flexural properties

The flexural strength and modulus, with their respective standard deviations, of the prepared composites have been presented in Table 4. The addition of t-HGMs promoted an increase in flexural strength of 8.5% (up from 42.10 to 45.70 MPa) compared to BM and 16.94% (up from 39.08 to 45.70 MPa) with respect to PP. The modulus too showed substantial improvement of 17.6% (up from 1.30 to 1.54 GPa) and 25.05% (up from 1.23 to 1.54 GPa) with the addition of 10 wt% t-HGM. The addition of fillers results into greater flexural modulus due to the increase in the stiffness of the resulting composites, which is further attributed to an increase in interfacial area of contact [17]. With the addition of SBF a significant increase in the flexural strength and modulus have been observed. As the loading of SBF is increased from 0 to 20 wt%, strength increases by 18.4% (up from 45.70 to 54.13 MPa) and modulus by 39.19% (up from 1.54 to 2.14 GPa) with respect to the BM-H10. From the results presented in Table 4, treated reinforcing fillers show good flexural strength and stiffness, thereby, suggesting good interfacial adhesion with the matrix. These findings are in line with the previous inferences by Thwe et al. [50] wherein improved interfacial adhesion is reported to contribute to a stronger and stiffer material.

### 3.3.3. Charpy impact strength

It has been reported earlier by many research groups that toughness or impact strength of any rigid inorganic particulate filled polymer composite is highly influenced by the interface adhesion between the filler particles and the matrix [48,51–56].

The composite microstructure plays an equally important role and may result into poor impact strength due to a high capacity for nucleation of crystallization [57].

The impact strengths for the various prepared composites have been reported in Table 5. A 37.6% decrease in the impact (down from 4.95 to 3.23 kJ m⁻²) has been observed with the addition of 10 wt% t-HGM illustrating the undesired and detrimental effect of addition of t-HGMs on the BM. Although, the treatment of HGMs is expected to promote better filler-matrix interfacial adhesion, but the interaction has not been found sufficient to reinforce the BM (attributed to a decrease in tensile strength also as explained earlier in section 3.3.1) or to make the BM tough. This decrease in impact strength may also be ascribed to the brittle nature of HGM. A notable increase in impact strength is observed as the loading of SBF is increased from 0 to 20 wt%, with the 20 wt% SBF reinforced composite (BM-H10-B20) displaying a substantial increase of 22.2% (up from 4.95 to 6.05 kJ m⁻²) in the impact strength over BM. The failure mode in all the impact tests has been observed to be brittle.

A comparison of mechanical properties mentioned above for t-HGM and SBF based composite (BM-H10-B10) verses virgin PP presented in Table 6 clearly indicates an improvement in selected hybrid composite strength. Although, the tensile and impact strengths of composite show marginal increase of 3.62% and 3.42% respectively, the flexural strength is significantly improved (~30.17%) despite addition of 10% t-HGM which is known, in general, to reduce mechanical strength. The modulus values for both tensile and flexural test environments show significant improvements of ~45% and ~60% respectively, with a mere 10% addition of fiber. The contribution to modulus improvement is provided by both the fillers. A look at the density values indicate that the density of PP is not increased, rather shows a ~2% decrease, despite 10% SBF addition which has much higher density than base matrix (1.32 g cm⁻³ versus 0.90 g cm⁻³).

### 3.4. Morphological studies via Scanning Electron Microscopy (SEM)

A study on morphology using FE-SEM is attempted to explore the dispersion characteristics and matrix wetting of the fillers. Fig. 4(a) reveals that t-HGM is nicely wetted by the polymer matrix (BM), and the same is seen for all the composite samples (BM-H10, BM-H10-B5, BM-H10-B10 and BM-H10-B15) in Fig. 4(b)–(d). The
possible formation of hydrogen bonding of $\text{--NH}_2$ groups of $t$-HGMs with the carboxyl group of MA-g-PP carries responsibility of such an appropriate matrix wetting. This indicates that there has been no physical hindrance to the dispersion of $t$-HGM by the fiber. These morphological snapshots help to infer that $t$-HGM showed good level of dispersion and matrix wetting, and also that the treatment of HGMs successfully supported their dispersion.

Fig. 4(c) shows fibrils breakage perpendicularly to the cleaved plane while fibril has been in the direction of plane of paper. Fig. 4(b) and (d) provides a snapshot of fiber bundle cleaving or tearing in the plane of fractured plane. The fiber pull-out has not been noticed in any of the snapshots taken. These observations suggest that there is sufficiently good interfacial adhesion of fiber with base matrix resulting into strong BM reinforcement, as also reported earlier [17]. Further, there is a good number of uniformly dispersed $t$-HGMs that are seen in the vicinity of SBFs supporting our hypothesis that $\text{--NH}_2$ group of $t$-HGMs tends to show hydrogen bonding with the available hydroxyl groups of the fiber. This results into its improved spatial spread around fiber along with a better dispersion in remaining matrix without any evidence of aggregation. This translates into improved mechanical properties of fiber based composite.

4. Summary and conclusions

Treated hollow glass microspheres and short bamboo fiber based PP composites have been prepared and investigated in this study for their mechanical properties and morphology. While the use of SBF improved the mechanical properties of virgin PP significantly, HGMs controlled the increase in density due to SBF addition. For example, the tensile strength of virgin PP has been found to increase by a maximum 18.39% and tensile modulus by 73.25% for a 20% SBF addition. Likewise, the improvement in flexural strength and modulus has been 38.51% and 73.98%
respective, while the impact improved considerably by 47.92%. The enhancement in mechanical properties is attributed to the addition of high modulus SBF and also due to the good interfacial adhesion due to the pre-treatment of SBF and HGMs. The morphological studies further provide evidence to this interfacial wetting and good dispersion of r-HGMs and SBF in the matrix. The composites are proposed as suitable for use in industrial applications such as in automotive parts for replacing PP with enhanced strength and relatively environment friendly materials with similar or reduced density.

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