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Abbas Saifee Valsadwala

University of Akron

Sriram Srinivasan

Rochester Institute of Technology

Surya Rajan Balachandran

B S Abdur Rahman Crescent Institute of Science & Technology

Shamshath Begum (✉ sshamshath@crescent.education)

B S Abdur Rahman Crescent Institute of Science & Technology <https://orcid.org/0000-0002-2253-536X>

Asit Baran Samui

Institute of Chemical Technology

Sandeep Kumar Shukla

Mahindra and Mahindra Ltd

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Use of eco-benign periwinkle shell particle for making composites and study their effect on the thermal and mechanical properties of novel HDPE composites

Abbas Saifee Valsadwala^a, Sriram Srinivasan^b, Surya Rajan Balachandran^c, S Shamshath Begum^{c*} Asit Baran Samui^d and Sandeep Kumar Shukla^e

^a Department of Polymer Engineering, University of Akron, Akron, Ohio, USA

^b Department of Packaging Science, College of Engineering Technology, Rochester Institute of Technology

^cDepartment of Polymer Engineering, B. S. Abdur Rahman Crescent Institute of Science and Technology, Chennai, Tamil Nadu, India

^dInstitute of Chemical Technology, N.C.Parekh Marg, Mumbai, 400019, India

^eMahindra & Mahindra, Mahindra Research Valley, Tamil Nadu, India

*^cCorresponding author : Dr. S. Shamshath Begum, Assistant Professor (Sr.Gr.), Department of Polymer Engineering, B. S. Abdur Rahman Crescent Institute of Science and Technology, Chennai, Tamil Nadu, India.

Email: sshamshath@crescent.education

ABSTRACT

In this investigation, the shell powder of *Littorina littorea* commonly called periwinkle was used as an eco-benign filler in High-Density Polyethylene (HDPE) to form periwinkle/HDPE composites (PHPC). Understanding the effect of different particle sizes of periwinkle shell powder (PSP) and optimizing their influence on PHPC is the main scope of work. Periwinkle shell (PS) particle sizes from <53 μm to 150 μm were chosen as reinforcement. The different PSP size like <53 μm , 53 μm , 75 μm , 90 μm , 105 μm and 150 μm chosen in this study were named as PHPC_{L53}, PHPC₅₃, PHPC₇₅, PHPC₉₀, PHPC₁₀₅, and PHPC₁₅₀ respectively. The composites were fabricated by incorporating 1 weight % of PSP into HDPE matrix using compression molding technique and then subjected to morphological, thermal, and mechanical characterizations. Morphology studies using scanning electron microscope (SEM) confirms 150 μm PSP had best dispersion whereas 75 μm PSP resulted with agglomeration. PSP had little influence on the thermal stability of HDPE except for PHPC₁₅₀ which showed rise in degradation temperature when compared to the neat sample. Mechanical properties such as hardness, Young's modulus, impact strength, and flexural modulus were enhanced by the addition of PSP. Whereas, a decrease was noted in elongation at break (%) and flexural strength of PHPC indicating the stiffening effect of filler on HDPE. In order to understand the particle size influence better, the extension evaluation method (EEM) was performed for all samples and PHPC₁₅₀ was found to be the best performing among all particle sizes.

KEYWORDS : Periwinkle shell powder; HDPE; composites; eco-benign filler; extension evaluation method

1. INTRODUCTION

Polymer matrix composites (PMCs) have become ubiquitous across the globe mainly due to their high specific strength, low cost, resistance to corrosion, ease of manufacturing, and flexibility in design [1]. Such excellent properties have made it possible for these materials to be used in automobiles, aircraft, marine vessels, bulletproof jackets, electric and electronic components [2]. PMCs can be described as multiphase material wherein one of the phases is the polymer matrix and the other is the reinforcement. The continuous phase, i.e., the matrix can be either thermoplastic such as polyethylene (PE), polycarbonate (PC), polypropylene (PP) or they may be thermosetting like epoxy, ureas, and polyesters, etc. There are several techniques to develop PMCs including but not limited to, hand lay-up, vacuum infusion, pultrusion, resin injection molding, and compression molding. The dispersed phase which is the reinforcement may be in the form of particulates and fibers [3] .

The particulate reinforcements are sometimes even referred to as reinforcing fillers, which are inert in nature, that are used to make the material more cost-effective while enhancing the mechanical properties and overall performance of the composites [4]. The enhancement in the properties of filler reinforced composites depends on their intended function and some other parameters such as size (for example nano [5]), interactions, and loading. The particle size of the filler is a crucial determinant in discussions on the processing and properties of PMCs [6].

In response to the growing concern regarding the sustainability of these materials, bio-based fillers are being considered as potential replacements for their synthetic counterparts. Apart from being biodegradable, they are also cheaper, less dense, and have high specific strength. The most common bio-fillers used presently are produced from agricultural waste like soy protein, coconut husk, sugarcane bagasse, and also from various shell powders [7, 8]. The use of shell powders as reinforcing fillers in polymers has received significant traction in the last decade. In the past, the influence of treated and untreated *Portunus sanguinolentus* shell powder on the thermo-mechanical properties of jute fabric/epoxy composites has been studied. The results showed that the 10 wt% treated shell powder composites had the best overall performance [9]. Some studies have also been taken up as an application-oriented research, for example, the potential of silane-treated shell powders as reinforcement for phenolic brake friction composites [10].

Periwinkle (*Littorina littorea*) is a type of sea snail having hard shells whose hardness can be attributed to the presence of calcium carbonate [11]. HDPE combined with inorganic particulate fillers is a promising field of research as they can be made valuable in many industrial applications mainly owing to its ease of processing [12].

The potential of PSP as a reinforcing filler is yet to be fully determined as only few studies have been published so far. The results of the investigations using PSP as filler have shown a noteworthy rise in mechanical properties of the developed composites [13, 14]. However, the use of PSP in HDPE composites has not been reported yet. A composite of this type will be ideal for reducing the almost non-biodegradable portion in HDPE composite-based material and in the way help in the reduction of environmental problems. In the present study, novel PHPC samples were developed with varying particle sizes of PSP. The weight fraction of the filler was kept constant, as the main scope of the current study was to optimize the size of PSP in HDPE composites. Therefore, the weight fraction of PSP was fixed at 1wt%, in order to have minimal influence of filler concentration in PHPC. Morphological analysis of PHPC was done to understand the filler/composite interaction based on the filler size.

The developed samples were subjected to thermal and mechanical tests to analyze their corresponding response. An extension evaluation method for ranking the developed composites was also reported in this study. Using the results of the tests performed, an attempt was made to provide an optimized particle size for PSP. It also gives evidence suggesting the usefulness of PSP as potential reinforcement in thermoplastic composites.

2. MATERIALS AND METHODS

2.1 PSP – Size reduction

The periwinkle shells collected from Kovalam beach, Chennai, Tamil Nadu, India, were powdered and separated based on the difference in particle size ranging from 0 to 150 μm using a sieve separator. The PSPs were separated using a screening method with a Ro-Tap motorized sieve shaker, India. The various sizes include under 53 (<53 or L53) μm , 53 μm , 75 μm , 90 μm , 105 μm , and 150 μm .

2.2 Mixing and Compounding

Once the PSP material was separated based on their particle size, it was then mixed with HDPE purchased from ONGC petro addition Ltd., India, having a Melt Flow Index MFI (190°C/2.16 kg) of 0.04 g/10 min. The mixing was performed using a high shear blade mixer and 1 wt. % PSP was incorporated into HDPE to get PSP/HDPE mixture. The mix was then compression molded at a temperature of 190 (± 5) °C and pressure of 22 (± 2) N/mm² for 8 mins using a hydraulic press manufactured by Ravi Engineering work, New Delhi. During the molding process, breathing was done at 1st, 3rd, and 5th min to remove the water molecules and other volatile matter. Then, the mold was quenched and the composite sheets were taken out. The prepared composites for the investigation were named PHPC₀ (neat HDPE), PHPC_{L53}, PHPC₅₃, PHPC₇₅, PHPC₉₀, PHPC₁₀₅, and PHPC₁₅₀ based on the PSP size reinforced in it. The size of PSP beyond 150 μm was not used because the coarseness of the filler resulted in mixing difficulties.

2.3. Characterization

2.3.1 SEM analysis

The chemical composition of the PSP powder was found by performing Energy-dispersive X-ray spectroscopy (EDX) analysis and the morphology of the PHPC samples was studied by SEM analysis, both using a Zeiss Sigma FESEM 500VP, Germany.

2.3.2 Density and Void Fraction

The Archimedes principle was used to measure the actual densities of the prepared composite samples. The density measurement was done following the standard ASTM D792, using distilled water as the liquid medium. The actual density of these samples was determined using Eq.(1).

$$\rho_a = \frac{\rho_w W_a}{W_a - W_w} \quad (1)$$

where,

ρ_a is the actual density of composite, ρ_w is the density of distilled water, w_w is the weight of the sample in water and, w_a is the weight of the sample in the air.

The theoretical density of the composites was calculated using Eq.(2) [13],

$$\rho_t = \frac{1}{\left(\frac{w_f}{\rho_f}\right) + \left(\frac{w_m}{\rho_m}\right)} \quad (2)$$

where,

' ρ_t ' is the theoretical density of composite, ρ_f is the density of filler, ' ρ_m ' is the density of matrix, ' w_f ' is the weight fraction of filler and, ' w_m ' is the weight fraction of the matrix.

The void volume fraction (v_v) percent in the composite samples was determined, [13] by Eq.(3).

$$v_v = \frac{(\rho_t - \rho_a)}{\rho_t} \times 100 \quad (3)$$

2.3.3 Thermal Analysis

The thermal properties of the PHPC samples were studied using a thermogravimetric analyzer (TA Instruments, Germany) as per the ASTM D1131 standard at a temperature range from ambient to 1000 °C temperature with a heating rate of 10 °C/min. Nitrogen (N₂) atmosphere was maintained over the samples by flowing N₂ at a flow rate of 2 ml/min while testing.

2.3.4 Mechanical Properties

The mechanical properties such as impact strength, tensile strength (TS), Young's modulus, elongation at break (%), flexural strength, flexural modulus and hardness were tested for five replicates of each composite and the average values have been reported.

Tensile properties

The tensile properties of PHPC samples were found by using a 40-ton universal testing machine (UTM) supplied by Fuel Instruments & Engineers Pvt. Ltd, India. The test was carried out by following the ASTM D638 standard, where dog-shaped samples with 3 mm thickness were used. The crosshead speed was maintained at 3mm/min.

Impact strength

Charpy impact strength of PHPC samples was measured using an Impact Tester manufactured by National Instrument, India. The testing was done with adherence to

the ASTM D6110 standard. All samples were notched, and the measurement was carried out.

Flexural properties

The flexural properties of PHPC samples were determined by using a three-point loading method as per the ASTM D790 standard [14]. A 40-ton UTM supplied by Fuel Instruments & Engineers Pvt. Ltd, India was used to conduct the flexural test.

Hardness

The hardness of the prepared samples was measured using a Shore-D durometer manufactured by PolyPlast Equipment & Accessories, India. The testing was done according to the ISO 868 standard.

3. RESULTS AND DISCUSSION

3.1 EDX analysis of PSP

EDX is a characterization technique used to determine the purity and stoichiometry of compounds [15]. Table 1 contains the EDX data for the composition of PSP. Calcium was majorly present in PSP constituting a normalized weight % of 80.28 followed by carbon constituting 16.94. The atomic % of calcium and carbon was found out to be 57.64 and 40.58 respectively. These results show that the PSP is mainly made up of calcium as depicted in Figure 1. Aluminum is present in the lowest quantity with 0.29 % by weight and 0.31 % by atomic concentration.

Fig. 1. EDX spectrum of the chemical composition of PSP

Table 1.Composition of PSP using EDX

Element	Weight %	Atomic %
Calcium	80.28	57.64
Carbon	16.94	40.58
Cobalt	2.14	1.04
Magnesium	0.36	0.42
Aluminum	0.29	0.31
Total	100.00	100.00

3.2 Density and Void Fraction of Composites

As the filler loading was the same for all the filled samples, the theoretical density, experimental or actual density, and void fraction was calculated for PHPC₀ and PHPC₁₅₀. The actual density of PHPC₀ and PHPC₁₅₀ was found to be 0.949 and 1.005 g/cc, respectively. This increase in the density of PHPC₁₅₀ can be attributed to the presence of filler. The theoretical density, as expected, was higher with the values 0.952 g/cc for PHPC₀ and 1.011 for PHPC₁₅₀, than the actual density due to the presence of voids, which may have formed during composite preparation. The void fraction was calculated to be 0.525 % and 0.593 % for PHPC₀ and PHPC₁₅₀ respectively.

3.3 Morphology – SEM Analysis

Figure 2 represents the micrographs of the cross-section of PHPC samples at the magnification of 500 X and 5000 X. These images confirmed the agglomeration of PS particles in PHPC₇₅, whereas PSP was found to be well dispersed within the HDPE matrix when the particle size is 150 μ m. Also, the PS particles were found to have an irregular shape. The absence of particulate filler in PHPC₀ was confirmed by the SEM micrographs (Figure 2a). At 500 X magnification, the PHPC₇₅ sample vividly displayed clusters of PS particles due to the agglomeration. The interface between the HDPE and PSP may have decreased resulting in the agglomeration of the PSP particles which can be observed at 5000 X (Figure 2b). A similar observation was made while studying the morphology of HDPE composites reinforced with marble and granite dust [16]. In the case of PHPC₁₅₀, good dispersion of PSP was observed, and the particles were embedded into the HDPE matrix (Figure 2c). Although parts of the PSP surface could be seen attached to the matrix at both sizes, it was more profound in the case of 150 μ m. Therefore, enhanced mechanical anchoring for the particulate filler could be detected for PHPC₁₅₀. This phenomenon was also reported by researchers studying the SEM micrographs of mollusk shell-filled HDPE composites [12]. As inferred, the size of the particulate filler has an important role in determining interactions between two or more components [17].

Fig. 2. SEM images of PHPC cross-section at magnifications of 500 X and 5000 X (a) PHPC₀, (b) PHPC₇₅ and (c) PHPC₁₅₀

3.4 Thermal Analysis

Thermogravimetric analysis (TGA) was done to determine the thermal stability of the polymer composites. The change in weight of the sample was measured as a function of increasing temperature [18]. Figure 3 depicts the thermograms of seven samples and Figure 4 depicts the respective first derivative curve as a function of temperature in the N₂ atmosphere.

Table 2 shows the values of T_{max} which is the temperature at maximum weight loss rate (peak of the first derivative curve), the weight loss %, and residue in milligram (mg) at near 500 °C. All samples were found to undergo single-stage decomposition. The first derivative peak temperature, which is the point of the greatest rate of change on the weight loss curve, was fairly similar for all the samples. This indicates that PSP had little influence over the thermal stability of the material, except for the PHPC₁₅₀ sample. An approximate 4.1 °C rise in T_{max} was noticed for this composite, hence establishing the role of PSP in the enhancement of its thermal stability. This particular phenomenon can be explained based on the good dispersion of PSP particles within the HDPE matrix which leads to the diffusion of volatile decomposition products being hindered resulting in the creation of carbonaceous char. Therefore, the PS particles were observed to have a physical barrier effect, obstructing heat diffusion and impeding the degradation of the volatiles from the PHPC₁₅₀. A similar inference was made by studying the thermal properties of nano CaCO₃ reinforced polypropylene composites [19]. Another indication of greater char production for PHPC₁₅₀ could be related to the comparatively higher residue obtained from its thermal decomposition.

High weight loss % and the proportionately low residue were due to low inorganic content and absence of aromatic rings in the samples. Such observations have been made earlier by other researchers [22, 23].

Fig. 3. TGA curves of PHPC samples

Fig. 4. First derivative curve of PHPC samples

Table 2. Thermal decomposition data of PHPC samples

Sample	T _{max} (°C)	Weight Loss (%)	Residue (%)
PHPC ₀	481.66	99.47	0.53
PHPC _{L53}	482.07	99.48	0.50
PHPC ₅₃	481.13	99.78	0.14
PHPC ₇₅	481.75	99.82	0.18
PHPC ₉₀	483.36	99.57	0.40
PHPC ₁₀₅	481.89	99.31	0.70
PHPC ₁₅₀	485.75	99.31	0.70

The conclusion is that there is marginal increase of thermal stability with loading of PHP particles. This is obvious as with introduction of inorganic particles there are two effects:

1. Addition of high thermally stable inorganic filler enhances the resistance for thermal degradation.
2. As the size increases, the coverage of the surface increases resulting in higher barrier properties so that the gases generated from the degraded material faces more resistance to escape and thus thermal resistance is enhanced.

3.5 Mechanical Properties

3.5.1 Tensile Properties

The TS on the specimens were determined in accordance with the ASTM D 638 standard. The TS test was done to measure the tensile force required to fracture the composite samples and the elongation it possesses at the time of failure. The stress-strain curve produced was used to determine the tensile properties of the composite samples [20].

Figure 5 shows the variation of TS and Young's modulus of all PHPC samples with different PSP particle sizes. The Young's modulus values depict, that PHPC₁₀₅ (1535.54 MPa) had the highest modulus followed by other samples having lower particle sizes. A general trend can be established wherein the samples show a degradation in the modulus with the decrease in size. Compared to the neat sample, a significant rise of 112.42 MPa (7.32 % increase) was documented for PHPC₁₀₅, which brings forth the importance of PSP in the enhancement of the composite modulus. The reason is that, at lower size the distribution of filler is inferior when compared to the larger particle size.

Figure 6 illustrates the change in elongation at break (%) of PHPC samples for different PSP particle sizes. The elongation at break (%) was found to be the highest for PHPC₀ (81.36 %). Upon addition of PSP as a filler, this property was observed to have largely decreased, with the value for PHPC₇₅ being the lowest (28.01 %). This is a clear indication of the reduced ductility of the prepared composites. It can be attributed to the hardening effect of PSP on the HDPE matrix, which is confirmed by the hardness test.

The role of fillers in enhancing Young's modulus of polymer composites while decreasing ductility has been studied in the past. A similar trend was reported upon the addition of Catla fish scales as reinforcement in polypropylene composites [21]. The addition of egg and oyster shell in HDPE and linear LDPE respectively, at all filler loadings, also resulted in increasing Young's modulus while degrading the elongation at break (%) [22, 23].

Furthermore, the TS of PHPC₀ (25.61 MPa) was found to be the highest, closely followed by PHPC₇₅ (25.53 MPa), PHPC₁₀₅ (25.13 MPa), PHPC₁₅₀ (24.56 MPa), and PHPC₉₀ (24.31 MPa). For smaller particle sizes, a decrease in TS was observed, with PHPC_{L53} and PHPC₅₃ having values of 21.65 MPa and 22.92 MPa, respectively. The decrease in tensile strength upon the addition of filler can be attributed to the introduction of discontinuous domains in the composite, that would act as potential stress concentrators. Similar remarks have been made in the past by researchers studying eggshell reinforced polystyrene composites [24].

Fig. 5. Variation of TS and Young's modulus of PHPC with respect to different PSP particle sizes

After the decrease at very low filler size, there was an increase in TS with increase of size because of their better distribution in the matrix. After reaching a maximum at 75 μm particle size, there was modest decrease in TS with increase of particle size. This may be because of decrease in interface area. However, the distribution being good, there was very small decrease in TS. Also in this investigation, the loading being low the difference was found to be minimum.

Fig. 6. Variation of Elongation at break (%) of the composites for different PSP particle sizes

Elongation at break decreases with loading of filler of very small size. However, with further loading there is increase of elongation due to increase of void volume. With further increase of size of fillers there is not much variation due to very small amount of filler loading.

3.5.2 Impact Strength

The impact strength is the amount of sudden force a material can absorb before failing [25]. The effect of the particle size of the PSP on the impact strength of HDPE was studied. Figure 7 shows the impact strength of various PHPC samples. PHPC with a PSP particle size of 53 μm had the best impact strength. It increased from 25.41 kJ/m^2 for PHPC₀ to 28.61 kJ/m^2 for PHPC₅₃ composite. This increase confirms the observation that more force is required to propagate the crack that is initiated while impaction. The impact strength is higher usually when the tensile stress is lesser. Both of them are inversely proportional. In other words, slower deformation over prolonged stress, causes it to absorb a greater amount of force before breaking apart [26]. In this case, it was evident as the maximum TS was almost the lowest for PHPC₅₃ sample (21.92 MPa). The other PHPC samples followed a similar trend except for PHPC_{L53} which could be an aberration. It has also been found that the lower the impact strength, the higher is the brittleness [27].

From the present investigation, it was also found that PHPC₅₃ had better impact strength than peanut husk/HDPE, rice husk/HDPE composite, and walnut shell/HDPE

composites [28]. Additionally, HDPE nano-composite filled with 4 wt. % talc was reported to have lesser impact strength comparatively [29].

Fig. 7. Variation of Impact strength of the composites with respect to different PSP particle sizes

During the addition of lowest size PSP ($<53 \mu\text{m}$) there is more of agglomeration rather than distribution, which does not help in enhancement of impact properties. Rather, it acts towards reduction of the impact characteristics of HDPE. However, with PHPC₅₃ samples, the size is lower as compared to most of the samples. This suggests that there is increase of interface among the PSP filler and HDPE resulting in increase of impact strength. Thereafter there is decrease of impact strength, which is justified as with increase of size there is decrease of total interface area. This results in lower extent of energy transfer from the weaker component (HDPE) to the stronger component (PSP particles).

3.5.3 Flexural properties

When the load is applied at three points, the flexural strength of the material can be measured [14]. Figure 8 depicts the flexural strength and the flexural modulus of PHPC samples respectively. PHPC₀ had the highest flexural strength, while the lowest was observed for PHPC₁₀₅ composite having a value of 28.49 MPa and 18.91 MPa respectively. The maximum flexural strength values for PHPC₀ were followed by 90 μm , 150 μm , 75 μm , 53 μm , and $<53 \mu\text{m}$ PS particle reinforced composites and had

4.1 %, 8.4 %, 8.8 %, 11.6 %, and 20.6 %, lesser values with regard to the flexural strength of PHPC₀ respectively. The poor strength of the composites in comparison to PHPC₀ can be due to poor particle-matrix debonding and easy breakage that may have occurred due to improper formation of strong bonds between the matrix and the PS particles. Similar results were reported with the use of micro-sized marble dust [30]. The higher flexural strength for PHPC₉₀ samples was observed when compared with the other -article sizes of PSP. This may be due to the better distribution of PSP in HDPE. Alike observation has been made formerly concerning filled polypropylene composites [31].

The flexural modulus was found to be highest for PHPC₉₀ composites and the least when 105 µm size particle was added to HDPE corresponding to 1084.62 MPa and 599.7 MPa, respectively. Compared to other filler reinforced HDPE composites, PHPC was found to be superior. For example, hemp fiber/HDPE composite had a flexural strength ranging from 12.27 MPa to 22.56 MPa [32]. Furthermore, the flexural strength and modulus of nano clay/HDPE nanocomposites ranged from 19.20-22.24 MPa and 656-735 MPa, respectively [33]. A recent study with waste tungsten carbide (WC) reinforced HDPE composites had approximate maximum and minimum flexural modulus as 750 MPa and 850 MPa, respectively [34]. Hence, the superiority of PHPC was established in this current investigation.

In general, for PHPC samples the tensile modulus (Young's modulus) was found to be greater than the flexural modulus. This indicates that the composite samples have a higher stiffness towards tensile loading than bending (flexural loading).

Fig.8. Variation of flexural strength and flexural modulus of PHPC samples with respect to different PSP particle sizes

As expected, there is initial decrease of flexural strength. Immediately after that there is increase of strength up to 90 μm size of PSP. This is quite possible as the filler particles of larger size are distributed uniformly along the matrix. In fact it was reported that there is best distribution of inorganic particles of size 63 μm [35]. With further increase of size there is decrease of the flexural strength because of decrease of interface area and also because of inferior distribution.

3.5.4 Hardness

The hardness of the composite sample is measured using a Shore D durometer. These values are a measure of the resistance of a material to penetration and deformation [36]. For PMCs, their hardness is mainly dependent upon the interactions present within the filler-polymer matrix interphase, filler hardness, and filler grain size [37].

Figure 9 shows the variation in hardness of PHPC samples. The addition of PSP to HDPE resulted in the enhancement of the hardness of the developed composites. This can be attributed to the introduction of the hard and brittle PSP phase into the HDPE matrix and the microstructure of the prepared composites. Similar phases have been introduced in polyester resin and HDPE matrices by hardwood charcoal particulates and coconut shell powder respectively [38, 39].

The reasoning for PHPC₇₅ having the highest hardness value could be correlated with the SEM micrographs, which illustrates distinct clusters or agglomeration of the PSP particles which form hard filler grains in the composite microstructure. An approximate 9.1% increase in hardness from the lowest (PHPC₀) to the highest value (PHPC₇₅) has been recorded. Beyond that, the size does not alter the behavior; rather at same loading the value reaches a plateau. This may be due to the coverage of the surface by the filler remains similar. All PSP reinforced samples were found to have a greater hardness than PHPC₀. This is in accordance with other research work done which observed an increase in hardness upon the addition of filler [40].

Fig.9. Variation of hardness of PHPC samples with respect to different PSP particle sizes

3.6 Extension evaluation method for ranking polymer composites

Based on the extension theory, the extension evaluation method (EEM) was performed to establish the non-linear relationship between the particle size of PSP filler and the mechanical performance of the composites. EEM aids in the ranking of developed composite materials and allows for the prudent selection of the best composite sample [41].

The most crucial part of developing the extension theory involves the construction of a mathematical model/dependent function ($K(x)$). Assume $M \in X$, where X is an interval consisting of $X = [a, b]$. Eq.(4). defines $K(x)$ of any point within a limit $x \in [-\infty, +\infty]$, conforming to the interval X and the point M .

$$K(x) = \begin{cases} \frac{x-a}{M-a}, & x \leq M \\ \frac{b-x}{b-M}, & x \geq M \end{cases} \quad (4)$$

The properties of the dependent function $K(x)$ are listed below:

- $K(x)$ reaches a maximum value, $K(x) = 1$ at $x = M$
- $x \in X$ and $x \neq a, b \Leftrightarrow K(x) > 0$
- $x \notin X$ and $x \neq a, b \Leftrightarrow K(x) < 0$

Table 3 shows the model calculation for PHPC₁₅₀ with different parameters chosen for ranking the sample ranges and optimum (required) points which is common for all seven samples. The parameters chosen for evaluation can be classified as follows:

- The elongation at break (%) (parameter 2: Table 3) reached its optimum point of the dependent function $K(x)$ in the left extreme of the selected interval X . $K(x)$ for this parameter is calculated by using Eq. (5).

$$K(x) = \begin{cases} \frac{x-a}{b-a}, & x < a \\ 0 \vee 1, & x = a \\ \frac{b-x}{b-a}, & x > a \end{cases} \quad (5)$$

- The remaining seven parameters were found to have reached their respective optimum point of $K(x)$ in the right extreme of X and the dependent degree is calculated by using Eq. (6).

$$K(x) = \begin{cases} \frac{x-a}{b-a}, & x < b \\ 0 \vee 1, & x = b \\ \frac{b-x}{b-a}, & x > b \end{cases} \quad (6)$$

Table 3. EEM Model calculation for PHPC₁₅₀

Sl. No.	Parameter descriptions	Interval X_i [a, b]	M_i	x_i	$K(x_i)$	w_i	$\overline{K(x_i)}$
1	Impact Strength	[12.81, 28.61]	28.61	14.08	0.08	1/8	0.772
2	Elongation at Break (%)	[18.705, 81.359]	18.705	28.011	0.851	1/8	
3	Young's Modulus	[1232.528, 1647.968]	1647.968	1639.049	0.978	1/8	
4	Max. Tensile Stress	[21.652, 25.616]	25.616	24.563	0.734	1/8	
5	Flexural Modulus	[599.7, 1084.62]	1084.62	1025.54	0.878	1/8	
6	Hardness	[77, 84]	84	81.6	0.657	1/8	
7	Residue (TGA)	[0.020, 0.2]	0.2	0.2	1	1/8	
8	Peak Temperature (TGA)	[481.13, 485.75]	485.75	485.75	1	1/8	

The various variables used for calculation using EEM are as follows:

i → parameter number (1-8),

x_i → measured parameter value of the sample,

M_i → optimum point of the x_i ,

$K(x_i)$ → dependent degree,

w_i → parameter weights,

$\overline{K(x_i)}$ → mean of $K(x_i)$ based on Eq. (6)

Table 3 shows the model EEM calculation for PHPC₁₅₀

Eq. (7). weighs all parameters equally as each one of these criteria are important factors for evaluating the performance of the PHPC composite samples.

$$w_1 = w_2 = w_3 = w_4 = w_5 = w_6 = w_7 = w_8 = \frac{1}{8} \quad (7)$$

The weighted mean required to calculate the overall performance of the PHPC samples is calculated using Eq. (8).

$$\overline{K(x)} = \sum_{i=1}^{11} w_i K(x_i) \quad (8)$$

The EEM results of all PHPC samples are shown in Table 4.

Table 4. Results of extension evaluation for all PHPC samples

Dependent Degree	PHPC ₀	PHPC _{L53}	PHPC ₅₃	PHPC ₇₅	PHPC ₉₀	PHPC ₁₀₅	PHPC ₁₅₀
K(x ₁)	0.797	0.268	1	0.049	0.398	0	0.08
K(x ₂)	0	0.876	0.663	1	0.735	0.794	0.851
K(x ₃)	0.729	0	0.605	0.748	0.841	1	0.978
K(x ₄)	1	0	0.319	0.978	0.670	0.876	0.734
K(x ₅)	0.871	0.528	0.752	0.855	1	0	0.878
K(x ₆)	0	0.314	0.771	1	0.485	0.914	0.657
K(x ₇)	0.222	0.333	0	0	0.333	0.444	1
K(x ₈)	0.114	0.203	0	0.155	0.482	0.164	1
$\overline{K(x)}$	0.466	0.315	0.513	0.598	0.618	0.524	0.772

The result of this computation was used in the ranking of seven PHPC samples based on their overall performance. The best performing sample has the highest weighted mean, while the worst one has the lowest weighted mean. Ranking from best to worst is as follows:

$$\text{PHPC}_{150}(0.772) > \text{PHPC}_{90} (0.618) > \text{PHPC}_{75} (0.598) > \text{PHPC}_{105} (0.524) > \text{PHPC}_{53} (0.513) >$$

$$\text{PHPC}_0 (0.466) > \text{PHPC}_{L53} (0.315)$$

It can be inferred from this evaluation that PHPC₁₅₀ is the most preferable, while PHPC_{L53} is the least preferable sample for high strength, low flexibility applications. The experimental results show and confirm that the developed composites may be applied in automotive body and chassis part fabrication [42].

4. CONCLUSION

This study confirms the effectiveness of PSP as reinforcement in PHPC. The particle size of the filler (PSP) was varied while the filler loading was kept constant (1 wt%). This was done to understand better the influence of the particle size of PSP on the properties of developed PHPC samples. PHPC sheets were successfully prepared by compression molding, and were subjected to different thermal, mechanical and morphological analysis. The cross-sectional SEM micrographs of the PHPC samples were carefully examined and it was found out that filler agglomeration was observed for 75 μm PSP particles. Whereas, PSP particles of 150 μm showed excellent dispersion in the HDPE matrix. The outcome of SEM analysis provided significant

support in expounding upon the results of the hardness test in which PHPC₇₅ was found to have the highest hardness with a value of 84 shore D. The efficiency of PSP as a reinforcing filler was further bolstered by the various mechanical tests which showed promising results upon the incorporation of PSP. The Young's modulus of PHPC₁₀₅ was approximately 112 MPa greater than the neat sample (PHPC₀), while the flexural modulus was around 62 MPa higher for PHPC₉₀ with respect to PHPC₀. In terms of thermal stability, a marked increase of 4.1 °C in T_{max} was observed for PHPC₁₅₀ sample with regard to PHPC₀. Finally, the ranking of composites using the extension evaluation method helped in choosing the best performing composite, which in this case was PHPC₁₅₀. The developed composites exhibited high strength at low weight and hence could be used in the automobile sectors. The eco-friendly attribute associated with PSP made it an excellent filler for HDPE composites.

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Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article.