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Response of flexural strength of hazelnut shell-polystyrene composite to the input concentration ratio of its constituent materials

NE Nwankwo, CN Nwambu, CC Emekwisia, FO Osakwe, OJ Chukwu and CI Nwoye

NE Nwankwo
Department of Metallurgical and Materials Engineering, Chemical Systems and Data Research Laboratory, Nnamdi Azikiwe University, Awka, Nigeria

CN Nwambu
Department of Metallurgical and Materials Engineering, Chemical Systems and Data Research Laboratory, Nnamdi Azikiwe University, Awka, Nigeria

CC Emekwisia
Department of Metallurgical and Materials Engineering, Chemical Systems and Data Research Laboratory, Nnamdi Azikiwe University, Awka, Nigeria

FO Osakwe
Department of Metallurgical and Materials Engineering, Chemical Systems and Data Research Laboratory, Nnamdi Azikiwe University, Awka, Nigeria

OJ Chukwu
Department of Civil Engineering, Federal University of Technology, Owerri, Nigeria

CI Nwoye
Department of Metallurgical and Materials Engineering, Chemical Systems and Data Research Laboratory, Nnamdi Azikiwe University, Awka, Nigeria

Corresponding Author:
NE Nwankwo
Department of Metallurgical and Materials Engineering, Chemical Systems and Data Research Laboratory, Nnamdi Azikiwe University, Awka, Nigeria

Abstract

Response of hazelnut shell –polystyrene composite (HPC) flexural strength to input concentration ratio of the constituent materials was evaluated, using a derived empirical model; $ʃ = - ɧ(ɤ_f/ɤ_m)^N + ß(ɤ_f/ɤ_m) + Ǿ$. Validity of the derived model was rooted in the core model structure; $ʃ + ɧ(ɤ_f/ɤ_m)^N \approx Ǿ + ß(ɤ_f/ɤ_m)$, in that both sides of the structure are correspondingly near equal. The predicted results are by the trend and spread of results distribution, shown in previous research. Model-predicted results have shown evaluated correlations between the HPC flexural strength and input concentration ratio of hazelnut shell & polystyrene as 1.0. For each value of the highlighted filler: matrix ratio, the standard error incurred in predicting the HPC flexural strength, relative to the experimental results is less than 0.5%. This translates to over 99% model confidence level. The HPC flexural strength per unit input concentration ratio of hazel shell & polystyrene were 10.9955 and 9.5808 MPa, using experimental and model-predicted results. The overall maximum deviation of the model-predicted HPC flexural strength from experimental results was 4%. The derived model will predict the HPC flexural strength, within the experimental results range, on substituting into the model, values of the input concentration ratio of hazelnut shell & polystyrene, providing the boundary conditions are considered.

Keywords: Flexural strength, hazelnut shell-polystyrene composite, constituents input concentration ratio

1. Introduction

Global ecologization trends lead to the search for new "green" materials-cheap, quickly renewable resources that are safe, won't degrade properties over synthetic, artificial materials, and will help preserve the world's ecological balance while also providing a solution to the disposal issue [1, 2]. To replace synthetic fibers in compositions with natural ones, "green composites" are produced by homogenizing materials based on polymeric matrices and fillers composed of plant wastes (Shells, husks, fibers, and kernels) [3, 4].

Wastes from agro-industrial sources get particular attention. Although this positively affects the environment and the economy, they are disposed of in huge amounts and not recycled in other fields [5, 6]. The potential for recycling agricultural wastes is particularly significant in the process of creating a closed-loop economy [7, 8]. Since the demand for this resource may outweigh the supply in some areas in the future and recovery may take decades, they can provide composite materials with the required aesthetic appearance and adjust and set certain parameters while also helping to preserve the forest belt and maintain a high level of physical and mechanical characteristics of the obtained materials [9, 10]. Consequently, plant-based composites are growing in popularity [11–14] because they can replace costly materials while retaining high qualities. They are applied in a variety of industries [15, 16]: food packaging [17–19], aerospace and automotive [20, 21], construction [22–24] to create new, environmentally friendly materials while cutting costs, and as a partial replacement for fine filler in concrete and other production areas.

Large amounts of hazelnut shells are available throughout the harvest season. They are agricultural waste products known as by-products that can be utilized as sustainable raw materials for future manufacturing. Hazelnut shells possess a high degree of hardness and impact resistance, making them a versatile and renewable resource for synthesizing high-quality goods and plant-based polymers. Approximately 530 thousand tons of hazelnuts are produced worldwide each harvest season [25].

The shells are almost 70% of the total mass and are of no value in reuse. Since the hazelnut shells are of low value, scientists have not discovered the full potential of this waste so far. It is used as a heat source, as a solid biofuel, or as a raw material for the production of furfural [26–28], although the area of its application can be significantly expanded. In the study [29], hazelnut shells were used as a filler for a composite with the addition of polylactic acid. Their thermomechanical and physical properties were studied. The results showed that the addition of hazelnut shells had little effect on the results, but increased the crystallinity index, which positively affects the size stability of the composite. In other studies [30], this author added epoxidized linseed oil to the polymer matrix and hazelnuts to reduce the plasticity index, which generally improves the overall properties of the composite with polylactic acid and hazelnut shells. In their work [31], Aliotta L. and others studied a synthesized composite based on PLA3251D with the addition of hazelnut shells; the resulting material shows decreased viscosity in the molten state and a low level of tensile strength. Pradhan P. and others [32] studied the physical and mechanical properties of composites with a walnut shell filler. Despite the high content of walnut shells, the density and porosity parameters of the composites remained high enough. Kufel A. and others [33] studied the physical and mechanical properties of hybrid composites based on polypropylene with the addition of hazelnut shells and basalt fiber, with maleic anhydride. The resulting material is characterized by improved physical and mechanical properties, but rather low moisture absorption. Ceraulo M. and others [24] researched the rheological properties of Bi® El51N0 polyester composites with the addition of hazelnut shells, specifically their mechanical and morphological properties, to obtain environmentally friendly biocomposites. At moderate concentrations, the stiffness and impact toughness of the material improves, and the biocomposite is easily recyclable. Even though there exist many works studying this topic, in most of them a relatively low content of hazelnut shells is introduced due to its unsatisfactory compatibility with other constituents of the polymer matrix.

Polystyrene (PS) is widely used in the construction industry in insulating materials and noise-absorbing screens, in medicine, in utilities, and in the food industry. Polystyrene is known to be poorly biodegradable [34]. Therefore, it is promising to use it for composite materials, for which, on the contrary, resistance to non-decomposition in natural conditions is important. For example, based on polystyrene, it is promising to create composite materials that can be used to create building materials for outdoor and garden furniture. Benchouia *et al.* [35] have developed a new insulating material based on date palm fibers and polystyrene. The replacement of one-third of the composition with the proposed composite showed the promise of such applications as thermal insulation, with a decrease in thermal conductivity of up to 50% [35]. Onifade *et al.* [36] showed the possibility of using reinforced biochar from psyllium stalk fibers to reinforce a polystyrene composite. The eco-friendliness of the composite gives a better solution to agro-waste disposal rather than burning [36]. Adeniyi *et al.* [37] developed a technology for the production of polystyrene composite with wood dust (Isoberlinia doka). With the addition of wood dust in the amount of 30%, an improvement in the mechanical and thermal characteristics of the composite was observed [37].

There has been a lot of research on the synthesis of composites using polystyrene and vegetable fillers, but none on the combination of polystyrene and hazelnut shell. The study aimed to enhance the compatibility between hazelnut shells and polystyrene to facilitate the shell's increased integration into the matrix and to produce highly filled composites. It will be feasible to produce a composite material with the high mechanical qualities required for use as materials for garden furniture by combining rigid polystyrene components with hazelnut shells.

According to earlier studies [43], sample width, average thickness, the force applied to the material, and the distance between the testing machine's bottom supports are all connected to flexural strength. Nevertheless, no model or mathematical expression that computes the flexural strength based on the input concentration ratio of polystyrene and hazelnut shell in the composite has yet to be developed. This served as the inspiration for the current piece, which closes the gap. The goal of this work is to develop an empirical model that, depending on the input concentration ratio of the component materials, would forecast the flexural strength of a composite made of hazelnut shell and polystyrene. As long as the input parameters fall within the boundary conditions, the model, if it is developed, should be able to forecast the composite's flexural strength within the range of experimental results.

2. Materials and Methods

The polymer matrix utilized was grade 525 polystyrene, which was produced by PJSC Nizhnekamskneftekhim in Nizhnekamsk, Russia. Shells from hazelnuts were utilized as filler. Hazelnut shells from the 2022 harvest were the raw material used to make shell powder, which was then ground in planetary and vibrating mills. Hazelnut shells were modified using toluene (LLC Component-Reaktiv, Moscow, Russia) as a solvent. The density (g/cm^3), melt flow index at 200 °C at 5 kg load g/10 min and melting point (°C) of polystyrene used are 1.12, 9.0 ± 2.0 and 160 -170 respectively. Furthermore, the formular, density (g/cm^3), molar mass (g/mol) and boiling point (°C) of toluene used are C_7H_8, 0.87, 92.14 and 110.6 ^{0}C respectively [43].

2.1. Hazelnut Shell Modification

The hazelnut shells were first ground for three minutes in a WM3 vibrating mill (LLC CONSIT Holding, Moscow, Russia). They were then ground for sixty minutes in an XQM-1An planetary mill (Jiangxi Victor International Mining Equipment Co., Ltd., Shichen, China). After that, they were rinsed with distilled water and dried for sixty minutes at 150 °C in a BINDER oven (Binder, Tuttlingen, Germany). Finally, the ground shells were sieved through a 64 µm sieve. The filler was modified by creating a polystyrene coating on its surface to impart a hydrophobic finish. Polystyrene, hazelnut shell, and toluene were mixed in the ratio of 2 wt. %: 8-48 wt. %: 50 to 90 wt. %. The composition was incubated for three days. Every 24 hours the composition was treated with ultrasound using an ultrasound bath TECHMANN LABORANT L-22 Basic (ODA-Service LLC, Moscow, Russia) with 40 kHz frequency. The obtained solution was kept in a drying oven for 100-120 min at 80–95 °C. After that, the resulting material was ground in a planetary mill for at least 10 min and then sifted through a 64 µm sieve [43].

2.3. Preparation of a Composite

For the study, polystyrene-based composites were created with modified filler contents of 10%, 20%, 30%, 40%, and 50% by mass. Granules of polystyrene were previously ground for three minutes. After that, for ten minutes, the modified filler and ground polystyrene were combined in a planetary mill. The resulting homogenized mixture was loaded into a mold with further heating to 165 ^{0}C for 60 min. After that, the samples were pressed under pressure of 110 MPa with load endurance for 5 min. The method of hot pressing of the samples allows for shear deformations, which leads to a uniform distribution of the filler in the melt.

Fig 1: (a) Hazelnut shell; (b) hazelnut shell powder [43]

3. Model Derivation

Table 1: Variation of HPC flexural strength with input concentrations of hazelnut shell and polystyrene & their ratios [43]

(ʆ)	$(ɤ_f)$	$(ɤ_m)$	$(ɤ_f / ɤ_m)$
13.96	10	90	0.1111
15.32	15	85	0.1765
16.67	20	80	0.1875
18.54	25	75	0.3333
20.41	30	70	0.4286
20.56	35	65	0.5385
20.71	40	60	0.6667
17.44	45	55	0.8182
14.17	50	50	1.0000

Computational analysis of the experimental results shown in Table 1, resulted to Table 2 which indicate that;

$$ʆ + ђ(ɤ_f /ɤ_m)^N \approx Ǿ + ẞ(ɤ_f /ɤ_m) \qquad (1)$$

$$ʆ = - ђ(ɤ_f /ɤ_m)^N + ẞ(ɤ_f /ɤ_m) + Ǿ \qquad (2)$$

The expression in (2) can be re-written as;

$$ʆ = - ђ(ɤ_f /100- ɤ_f)^N + ẞ(ɤ_f / 100 - ɤ_f) + Ǿ \qquad (3)$$

Where

$ɤ_m = 100 - ɤ_f$ and $ɤ_f = 100 - ɤ_m$

The predictability of flexural strength of hazelnut shell-polystyrene composite (WPC) is assured using the empirical model expressed in 9.43.2, providing the input concentration ratio of both constituent materials are known. The variables ʆ, $ɤ_f$ and $ɤ_m$ are the HPC flexural strength (Mpa) and input concentrations of Hazelnut shell & polystyrene (wt %) respectively. The ratio $(ɤ_f /ɤ_m)$ is denoted by ɣ. The derived model is referred to as Nwoye`s Model for evaluating the flexural strength of hazelnut shell-polystyrene composite or Nwoye`s GLATTEM-WAPCO Model. The equalizing constants; ђ, N, Ǿ and ẞ are 34.3, 2.0, 9.6 and 38.5 respectively. They were generated by a software [42]. Interaction between the variables and these constants ensures that both sides of *9.43.2* are of the same units.

$$\sigma_{f,m} = \frac{3F_m .L}{2bh^2}$$

Three point flexural strength of the composite was calculated using the conventional formular [43] expressed in (4), where F_m, L, b and h are the maximum load (597N), distance between the bottom supports (15 mm), sample width (mm) and average thickness of the sample (mm) respectively determined from the experiment runs.

Substituting (4) into (2), gives that;

$$\frac{3F_m.L}{2bh^2} = - ђ(ɤ_f/ɤ_m)^N + ẞ(ɤ_f/ɤ_m) + Ǿ$$

Equating (4) to (2) basically implies that the differential or error factor between the model-predicted and corresponding experimentally determined HPC flexural strength, must be negligible/ zero or of standard form 10^{-2}, 10^{-n-1} etc. Based on the foregoing, $\sigma_{f,m}$ becomes approximately equal to ʆ, and any of the parameters in 9.43.5 can now be evaluated, providing others are known.

Table 1 reveals the relationship between HPC flexural strength and input concentration of hazelnut shell & polystyrene as well as their ratios. These values were calculated using experimental results and conventional formular [43].

4. Results and Discussion

4.1 Boundary and Initial Conditions

Consider particles of hazelnut shell, interacting with the matrix, which is polystyrene. The flexural strength of HPC composite is affected by the input concentrations of hazelnut shell & polystyrene. The considered range of hazelnut shell, polystyrene and their ratios are 10-50%, 50-90% and 0.1111-1.0% respectively.

Table 2: Variation of ʃ + ҕ(ɤ$_{f}$ /ɤ$_{m}$)^{N} with Ǿ + ẞ(ɤ$_{f}$ /ɤ$_{m}$)

ʃ + ҕ(ɤ$_{f}$ /ɤ$_{m}$)^{N}	Ǿ + ẞ(ɤ$_{f}$ /ɤ$_{m}$)	Differential
14.3819	13.8774	0.5045
16.3902	16.3953	-0.0051
18.8138	19.2250	-0.4112
22.3507	22.4321	-0.0814
26.7109	26.1011	0.6098
30.5070	30.3323	0.1747
35.9564	35.2680	0.6884
40.4039	41.1007	-0.6968
48.4700	48.1000	0.3700

4.2 Model Validity

The model in (2) has its validity rooted in the core model structure expressed in (1). This is so because both sides of the model structure are correspondingly almost equal as shown in Table 2, which act as the numerical verificator. This table was generated through the evaluation of experimental results in Table 1. Table 2 also indicates computed differentials between the corresponding sides of the structure components. This significantly underscores the functionality of the derived model.

The derived model was also validated by comparing the predicted results with the experimental, through graphical, statistical, and deviational analysis.

4.2.1 Graphical Analysis

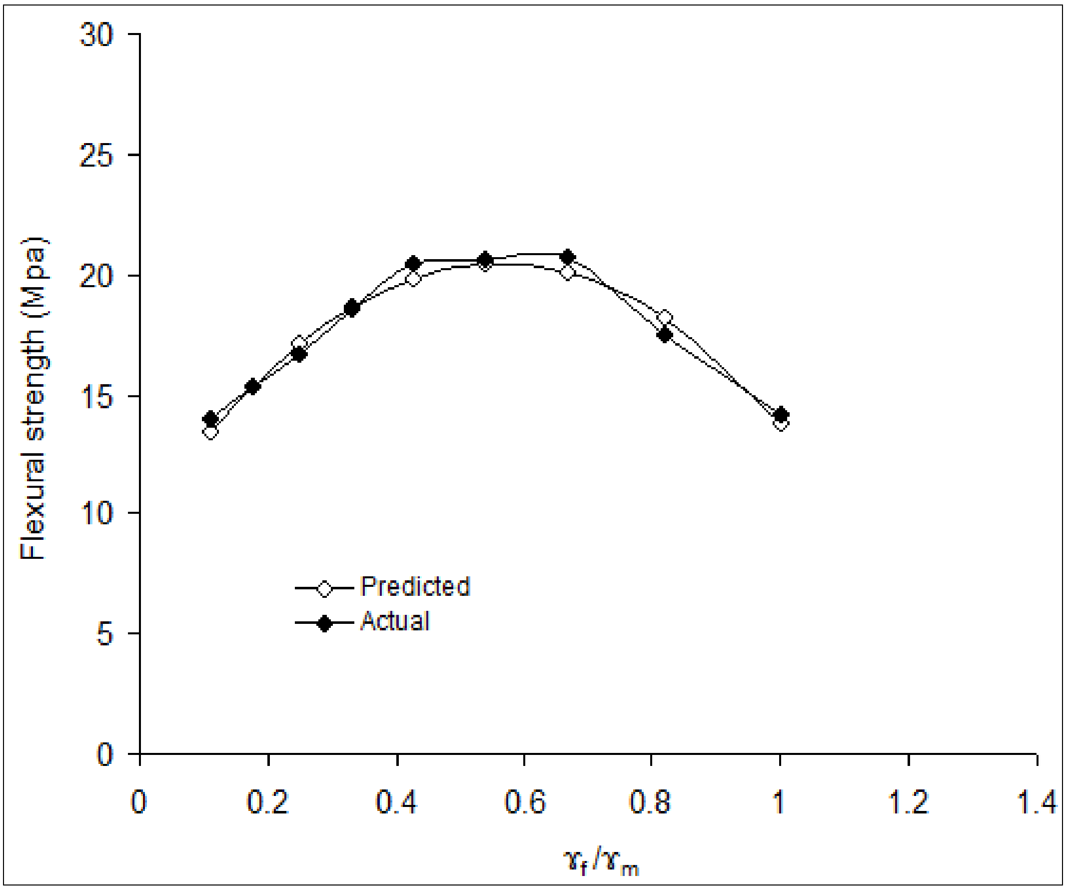

Fig 2: Comparison between HPC flexural strength (Relative to input concentration ratio of hazelnut shell and polystyrene) and as evaluated from actual results and derived model

Figure 2 shows well aligned curves of HPC flexural strength, relative to the input concentration ratio of hazelnut shell & polystyrene. These curves represent experimental and model-predicted results, which are correspondingly almost equal. The curves are also characterized by similar trend and spread of result points. Curves from the figure are all quadratic in nature and will likely emphasize positive or negative slopes, depending on part of the curves considered in the evaluation.

4.2.2 Statistical Analysis

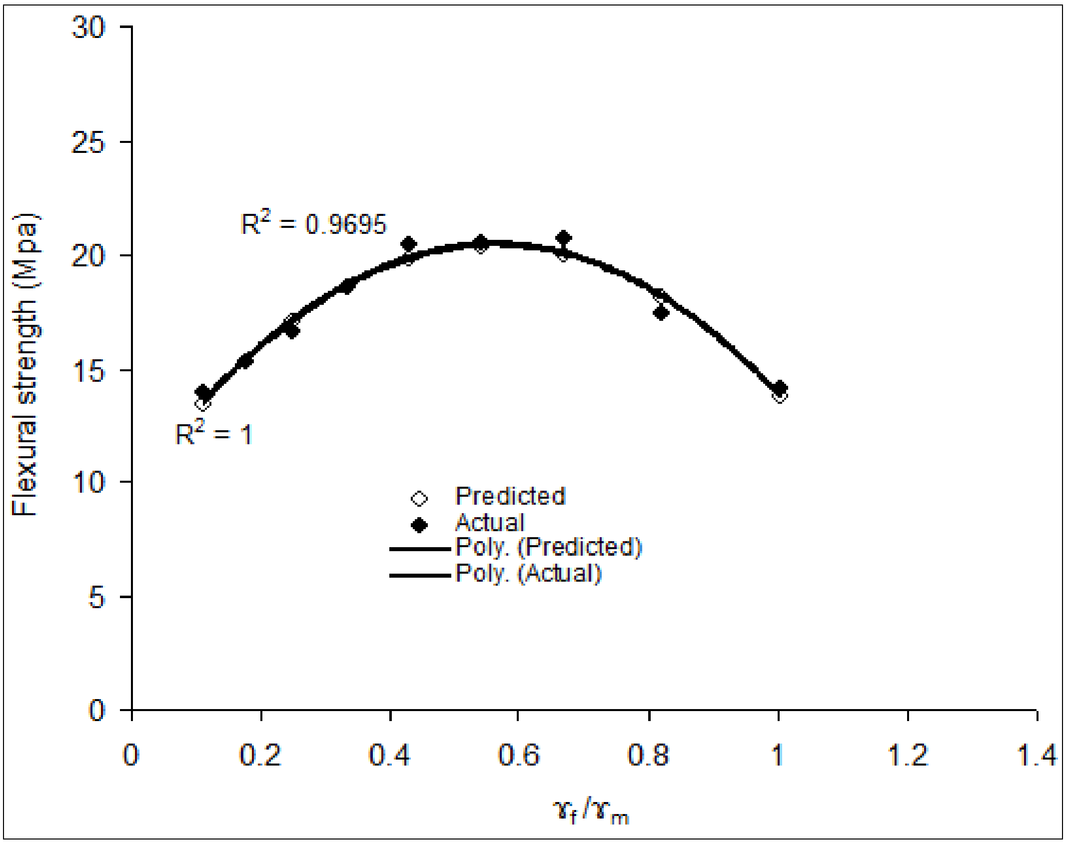

Fig 3: Coefficient of determination between HPC flexural strength and input concentration ratio of hazelnut shell and polystyrene as evaluated from actual results and derived model

The correlations evaluated from the R^2 value in Figure 3, between HPC flexural strength and input concentration ratio of hazelnut shell & polystyrene are 1.0000 and 0.9846 using model-predicted and experimental results respectively.

Relative to experimental results, the standard error associating prediction of the HPC flexural strength is < 0.5%, for every change in the input concentration ratio of hazelnut shell. This gives a model confidence level above 99%.

4.2.3 Deviation Analysis

Table 3: Variation of the input concentration ratio of hazelnut shell and polystyrene with the error fraction involving derived model-prediction of HPC flexural strength

(γ_f / γ_m)	$\varepsilon_r = (\text{ʃ}_{\text{Ɱ}} - \text{ʃ}_{\varepsilon}) / \text{ʃ}_{\varepsilon}$
0.1111	-0.0361
0.1765	0.0003
0.1875	0.0247
0.3333	0.0044
0.4286	-0.0299
0.5385	-0.0085
0.6667	-0.0332
0.8182	0.0040
1.0000	-0.0261

Table 3 shows the correspondence of error fractions to the input concentration ratios of hazelnut shell and polystyrene. Negative and positive error fractions evaluated indicate that some model-predicted values decreased below and increased beyond certain corresponding experimental results respectively. The error fractions translate into levels of model results discrepancies from corresponding experimental values. Closer margin between model-predicted results and corresponding experimental values is an indication of lower error fraction (towards negligibility). The table indicates that error fractions having standard forms within 10^{-1} confer higher disparity between experimental and model-predicted results, while those within 10^{-2}, 10^{-n-1} and lesser show much closeness between both results.

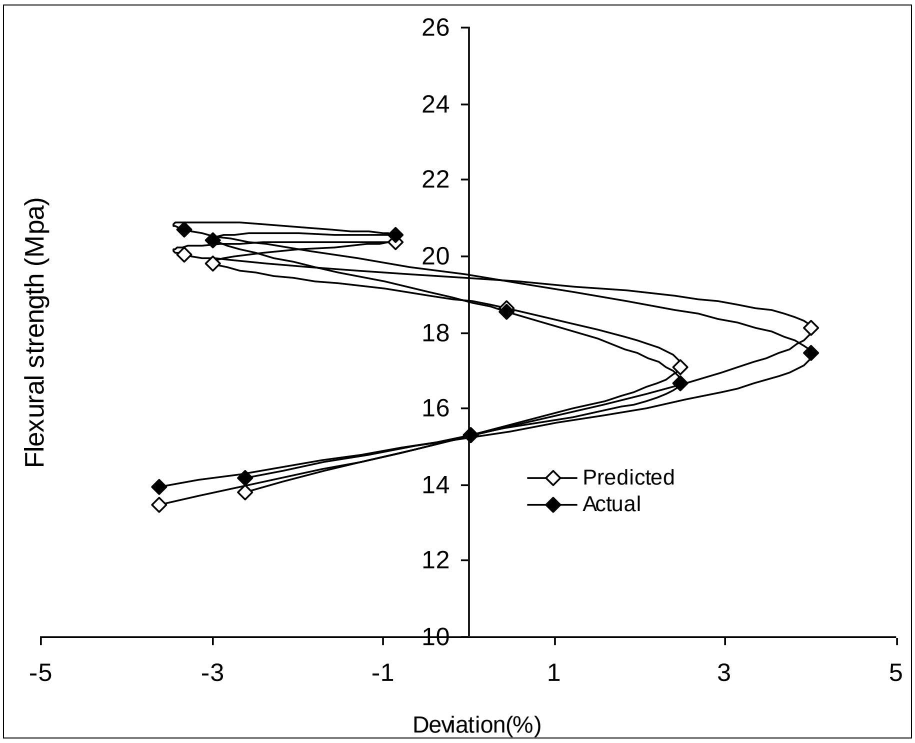

Fig 4: Variation of model-predicted HPC flexural strength with its corresponding deviation from experimental results

Figure 4 shows the graphical interaction between model-predicted HPC flexural strength and the corresponding experimental results, relative to the associated deviation between them. The figure indicates that maximum deviation of model-predicted HPC flexural strength is 4%, prompting derived model operational confidence levels at 96%. The figure also revealed least and highest deviations of the model-predicted HPC flexural strength as 0.03 and 4% respectively. These correspond to HPC flexural strength: 15.3251 & 18.1368 and input concentration ratio of hazelnut shell and polystyrene: 0.1765 & 0.8182 respectively. Based on the foregoing, the overall model confidence level places between 96 and 100%, following results generated from correlations, standard error and model deviation.

The deviation Dv, of model-predicted HPC flexural strength from the corresponding experimental result was evaluated from the expression.

$$\mathrm{Dv} = \left(\frac{f_{\mathrm{m}} - f_{\mathrm{E}} \qquad \mathrm{x}}{f_{\mathrm{E}}}\right) \cdot 100$$

Where

f_{E} and f_{m} are flexural strengths of the composite evaluated from experiment and model-predicted results respectively. Correction factor which overcomes the deviation is calculated as the negative of equation (6)

$$\mathrm{C_f} = -\left(\frac{f_{\mathrm{m}} - f_{\mathrm{E}} \qquad \mathrm{x}}{f_{\mathrm{E}}}\right) 100$$

HPC flexural strength per unit input concentration ratio of hazelnut shell and polystyrene $ʆ_{ɣ}$was calculated from the expression;

$$ʆ_{ɣ} = ʆ / ɣ \tag{8}$$

Re-written as

$$ʆ_{ɣ} = \Delta ʆ / \Delta ɣ \tag{9}$$

The expression (9), is detailed as

$$ʆ_{ɣ} = ʆ_{2} - ʆ_{1} / ɣ_{2} - ɣ_{1} \tag{10}$$

Where

$\Delta ʆ$ = Change in the HPC flexural strength $ʆ_2$, $ʆ_1$ at two input concentration ratios of hazelnut shell and polystyrene $ɣ_2$, $ɣ_1$

A plot of points (0.1765, 15.32) & (0.6667, 20.71) and (0.1765, 15.3251) & (0.6667, 20.0216) shown in Figure 2, designated as ($ɣ_1$, $ʆ_1$) and ($ɣ_2$, $ʆ_2$) for experimental and derived model results, and substituted into the expression (10), gives the slopes: 10.9955 and 9.5808 Mpa, as their respective HPC flexural strength per unit input concentration ratio of hazelnut shell and polystyrene.

5. Conclusion

The response of hazelnut shell–polystyrene composite (HPC) flexural strength to input concentration ratio of the constituent materials was evaluated, using a derived empirical model. The validity of the derived model was rooted in the core model structure since both sides of the structure are correspondingly near equal. The correlation between the HPC flexural strength and input concentration ratio of hazelnut shell & polystyrene were evaluated as 1.0 using model-predicted results. For each value of the highlighted filler: matrix ratio, the standard error incurred in predicting the HPC flexural strength, relative to the experimental results was less than 0.5%. This translates to over 99% model confidence level. The HPC flexural strength per unit input concentration ratio of hazel shell & polystyrene were 10.9955 and 9.5808 Mpa, using experimental and model-predicted results. The overall maximum deviation of the model-predicted HPC flexural strength from experimental results was 4%. Based on the foregoing, the derived model will predict the HPC flexural strength, within the experimental results range, on substituting into the model, values of the input concentration ratio of hazelnut shell & polystyrene, providing the boundary conditions are considered.

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