RESEARCH PAPER

Almond-Walnut Shell Hybrid Composite: Optimization of Composition Using Mixture Design

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ABSTRACT

The current work presents the mixture design method to optimize the composition of almond-walnut shell hybrid composite. In this regard, the different numerical models were developed and realized that the quadratic & cubic are best suitable to set up a correlation between input and response parameters. The numerical equalizations and experiential outcomes authenticate that the inclusion of shell particles (almond and walnut) enhanced the thermo-mechanical and biodegradation characteristics of the polyester resin. Hybridization yielded a positive effect and exhibited better performance than the single filler strengthened ones. The validation test results revealed that the mixture design is an effective optimization tool to develop a high-performance hybrid composite.

The optimal specifications as almond shell proportion: 19.6%, walnut filler: 20.4%, polyester resin: 60%, tensile strength: 44.09 MPa, flexural strength: 58.68 MPa, impact strength: 5.60 kJ/m², Young's modulus: 1.57 GPa, flexural modulus: 1.68 GPa, moisture absorption: 5.26%, thermal decomposition temperature: 390.76 °C, and biodegradation: 51.12%.

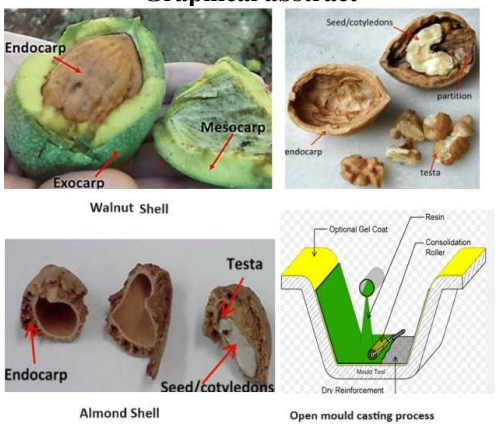
Keywords: Hybrid composite, Almond shell, Walnut shell, Mixture design, Optimization

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Graphical abstract



1.0 INTRODUCTION

Composites strengthened with biofillers are an attractive ecological substitute to synthetic filler ones. The leverage of biofillers is their availability, biodegradability, low abrasiveness, good strength/weight scale, and relatively lower price which contributes to a lower-cost product useful in various industrial applications [1-5]. It was found that the materials made of natural fillers especially powder-

like provide us huge advantages of satisfactory mechanical properties, improved fuel efficiency, high toughness, and good thermal insulation. Due to this reason, the uses of natural fillers are increasing day by day in domestic and industrial applications [6, 7]. Several natural fillers and agro-waste favorably used in composite production, such as rice husks, corn hull, hemp, coir, jute, kenaf, abaca, pineapple, peanut shells, etc. can be found in the literature [8-14]. Synthesis of materials usage of agriculture by-products is currently the point of consideration.

In varieties of agro fillers, the shell residue from edible nuts have sound strengthening ability to polymeric materials. They can easily retrieve in ample amount from the nut processing mill [15, 16]. Walnut (*Juglans regia L.*) and almond (*Prunus armeniaca L.*) are the most prominent tree nuts and their production is over 3.7 million and 1.2 million tons in 2017. As per FAOSTAT data, China and USA are the biggest producer of walnut & almond respectively [17]. The walnut shell have 25.60% cellulose, 52.30% lignin, 22.10% hemicellulose, and 3.6% ash content while the almond have 29.57% cellulose, 47.97% lignin, 17.01% hemicellulose, and 3.6% ash content. These shells are usually junked without control causing an environmental problems like air pollution, soil erosion, and decreases soil biological activity [18-22].

To overcome these problems, researchers are putting efforts for the synthesis and characterization of biofiller based composite materials. Z. McCaffrey *et al.,* (2018) found the convincing strengthening performance of almond shell fillers in recycled PP-PE blends [23]. M. Ramos *et al.,* (2020) declared the increment in strength and stiffness of polyester matrix after the inclusion of almond shell powder (ASP) [24]. V.K. Singh (2013) discovered the positive influence of walnut shell particles on the modulus and hardness of epoxy composites [25]. X. Li *et al.,* (2018) reviewed the chemical characteristics of almond shells and advocate its sound potential in composites [26]. H. Pirayesh *et al.,* (2013) witnessed the improvement in swelling and hydroresistant behavior of wood-based particleboards by the addition of walnut/almond shell fillers [27]. N.A. Sarsari *et al.,* (2016) stated the improvement in tensile & flexural strength of thermoplastic starch by the accomodation of walnut shell (WS) particles [28]. P. Sabarinathan *et al.,* (2016) checked the strengthening potential of sugarcane leaves and almond shell particles in an epoxy polymer [29]. A.H. Shah *et al.,* (2018) noticed the positive result in thermal stability, crystallinity, and storage modulus of blended Epoxy/diaminodiphenylmethane (DDM) matrix with admission of alkali-treated walnut shell [30]. M. Picard *et al.,* (2020) reported the heighten of tensile and flexural moduli of poly(trimethylene terephthalate) by inclusion of peanut hulls [31].

Significant work is available on separate almond and walnut shell composites. But no attempt was carried out on the almond/walnut shell strengthened polyester hybrid composites. In current, hybrid materials draw symbolic absorption in several fields. They provide blending of properties i.e. stiffness, ductility, and strength, that can not be retrieved through single filler composites [32, 33].

The relative vol.% of constituents alter the characteristics of a materials [34]. Therefore, the present work optimizes the proportion of three major elements (almond shell, walnut shell, and polyester resin) of a hybrid composite.

Various numerical methods i.e. RSM, ANN, GA, fuzzy logic, Taguchi, and factorial design are present that can make adequate models and optimize the design variables [35]. In the given work, mixture design (RSM) is used to optimize the composition for high performance hybrid material. To the best of my knowledge, this kind of work not been done till date.

2.0 METHODOLOGY

2.1 Materials

Unsaturated polyester with initiator [Methyl ethyl ketone peroxide (MEKP)] and catalyst (cobalt octoate) were received from M/s Sakshi Dies and Chemicals, Delhi (India). It has significant industrial applications due to favorable thermos-chemical, hydro-resistant, and low viscous characteristics. The nutshells were obtained from M/s. Go Green Products, Chennai (India). They washed in running water, then dried at 40 ± 5ºC for 48 hours in a hot air-oven. Shells were grinded in a vertical planetary ball mill machine (YKM-8L, China).

2.2 Synthesis of composites

The sampled sheets were fabricated through open mold, size of 200 mm X 100 mm X 4mm. The polymer was completely mixed with 2% initiator & 0.2% catalyst through a mechanical stirrer and no air bubbles were present. To restrict the sticking of resin mix, mold was wrapped with a Teflon sheet and sprayed with releasing gel. The dried organic fillers were manually lodged uniformly in mold space and wetted with premixed resin mixture. The desired sheet thickness and releasing of air bubbles was achieved through pressing with a steel roller. A mold was kept under dead weight (100 kg) at room temperature (25±3ºC) for curing action. The samples were post-cured at 100ºC in a hot air oven (SV Scientific laboratory, India) for 24 h. The relative proportionate range of reinforcing fillers and matrix resin is reported in Table 1. Mixture design was used to optimize the proportion of components.

2.3 Mixture design matrix

Mixture design is a statistical and numerical technique that can be employed to optimize the response variables through several models. It established the network b/w input & response parameters. The predicted & experimental values are presented in Table 2. A total number of 16 experiments were executed to figure out sum of squares (SSR, SSE, & SST).

2.4 Characterization of composites

2.4.1 Mechanical characterization

Tensile, impact, and flexural tests were conducted as per ASTM D638, D256, and D790 standards. The tensile and bending check were completed at H50KS UTM. While the impact strength was obtained at a digital pendulum impact tester.

2.4.2 Thermogravimetric analysis

Thermal analysis of synthesized material was done at analyzer machine (Perkin Elmer, TGA 4000), temp. range of 25-700ºC with 10ºC/min rate in an inert (nitrogen)

environment. The wt. loss curve gives the hint of thermal decomposition temperature.

2.4.3 Biodegradability

The biodegradation of hybrid materials was tested in natural soil burial condition. The samples were taken out after 30 days for wt. loss assessment. Four measurements of each composition were carried out and their central value was declared.

2.4.4 Moisture absorption

The hygroscopic experiment was executed as per ASTM-D570 standard. The samples wt. before and after bath immersion is taken to calculate wt. gain (%).

$$Weight\ gain\ (\%) = \frac{w_t - w_o}{w_o} \times 100 \quad (1)$$

Where w_o & w_t are the oven-dried and immersed weigh after 't' period.

3.0 RESULTS AND DISCUSSION

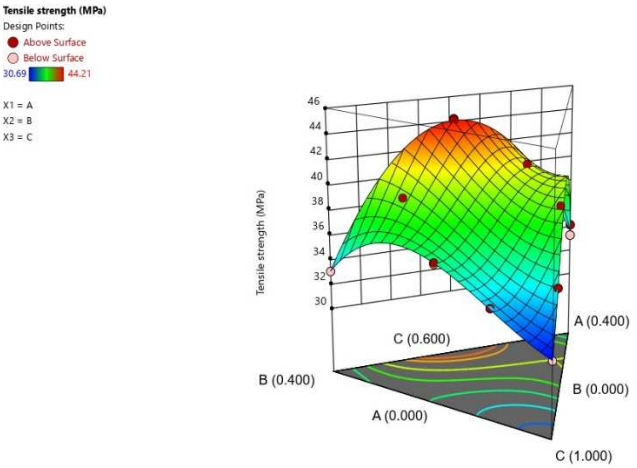
The work is settled on the optimization of composite constituents' fraction (almond shell, walnut shell, and polyester resin) through experimental and mixture design method. The experiential findings were further mapped with numerical models, formulated in DOE 12.0 software. The design matrix of several potential combinations is reported in Table 2. The different models are compared (Table 3) that resulted in cubic has best regression compliance (R^2, adj. R^2, pred. R^2) for tensile strength, Elastic modulus, moisture retention, and biodegradation. The quadratic has sensible agreement of correlation coefficients for impact strength & flexural performance. Both have decent *p*-value and adequate capacity to measure S/N ratio.

3.1 Tensile properties

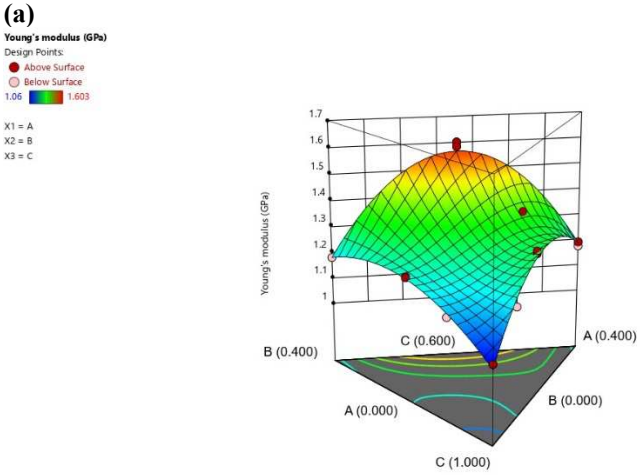
Figure 1(a)-(b) presents the tensile performance of composites where can clearly noticed that the tensile strength (30.69 MPa) & modulus (1.06 GPa) of virgin polyester was considerably elevate by inclusion of almond & walnut shell fillers. It proves their strengthening capability to polyester resin. In case of single filler strengthened composites, the almond one shows better performance than walnut due to it have compositional advantage i.e. higher cellulose fraction.

Among diverse range of filler proportionate composites, the 40% loaded one has lowest tensile strength because of shell particles jumbling which partially blocked the stress transfer.

The hybrid composite containing both shells with equal weightage (20.1% almond & 19.9% walnut shell fillers) has carried maximum tensile strength (44.21 MPa) and modulus (1.603 GPa). It proves that the hybridization is an amazing tool to innovate mechanical properties.



(a)



(b)

Figure 1 Tensile properties of developed composites (a) tensile strength (b) Young's modulus

Table 1. Mixture design for three constituent parameters

Sr. no.	Name of the components	Type	Notation	Low	High	Mean	Std. Dev.
1.	Almond shell	Mixture	A	0	0.4	0.1474	0.1347
2.	Walnut shell	Mixture	B	0	0.4	0.1249	0.1215
3.	Polyester	Mixture	C	0.6	1	0.7276	0.1313

	resin						
Study Type	Mixture		Design type	I-optimality			
Lack of fit points	5		Replicate points	5			

Table 2. Mixture design for three constituent parameters with tensile strength and modulus of composites

Sr. no.	Name of the components	Type	Notation	Low	High	Mean	Std. Dev.
1.	Almond shell	Mixture	A	0	0.4	0.1474	0.1347
2.	Walnut shell	Mixture	B	0	0.4	0.1249	0.1215
3.	Polyester	Mixture	C	0.6	1	0.7276	0.1313

Run	Actual value (wt. decomposition)	Predicted value	Actual value	Predicted value
1	53.7	53.55	387.3	388.32
2	30.1	31.31	376.1	375.88
3	48.3	48.47	385.6	385.85
4	32.7	31.31	376.3	375.88
5	36.0	35.94	375.0	374.68
6	61.7	63.27	390.1	389.77
7	11.6	11.57	364.7	365.61
8	21.6	21.99	371.2	370.89
9	39.0	39.28	384.8	383.62
10	64.7	63.27	389.6	389.77
11	42.9	43.56	382.2	381.83
12	44.0	43.56	381.0	381.83
13	37.2	37.04	384.3	385.41
14	51.7	51.84	391.8	390.80
15	50.6	51.84	390.0	390.80
16	53.0	51.84	390.8	390.80

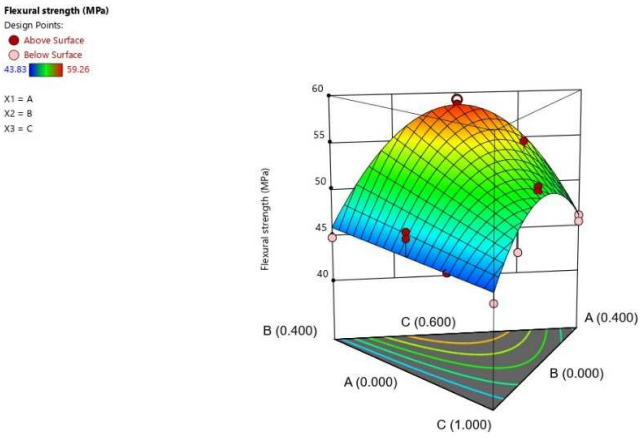
Exp. no.	shell proportio	shell proporti	r matrix proporti	strength Act.	strength Pred	modulus Act.	modulus Pred	absorption Act.	absorption Pred
1	0.264	0.071	0.665	55.3	54.1	1.35	1.44	6.85	6.85
2	0	0.203	0.797	47.9	45.3	1.29	1.24	4.65	4.69
3	0	0.4	0.6	44.7	45.8	1.20	1.21	6.09	6.11
4	0	0.203	0.797	47.2	45.3	1.28	1.24	4.78	4.69
5	0.099	0	0.901	47.0	49.2	1.26	1.26	4.31	4.26
6	0.40	0	0.6	46.2	46.3	1.20	1.22	8.13	8.19
7	0	0	1	43.8	44.9	1.17	1.27	2.31	2.35
8	0	0.104	0.896	45.2	45.1	1.23	1.26	3.02	3.02
9	0.131	0.138	0.731	53.0	53.6	1.30	1.44	5.04	5.18
10	0.4	0	0.6	45.5	46.3	1.19	1.22	8.25	8.19
11	0.197	0.004	0.799	52.1	51.0	1.33	1.26	5.99	5.84
12	0.197	0.004	0.799	51.6	51.0	1.31	1.26	5.71	5.84
13	0.069	0.273	0.658	50.0	52.2	1.30	1.44	5.11	5.10
14	0.201	0.199	0.6	59.2	58.6	1.71	1.68	5.29	5.33
15	0.201	0.199	0.6	58.7	58.6	1.69	1.68	5.43	5.33
16	0.201	0.199	0.6	58.8	58.6	1.70	1.68	5.33	5.33

3.2 Flexural properties

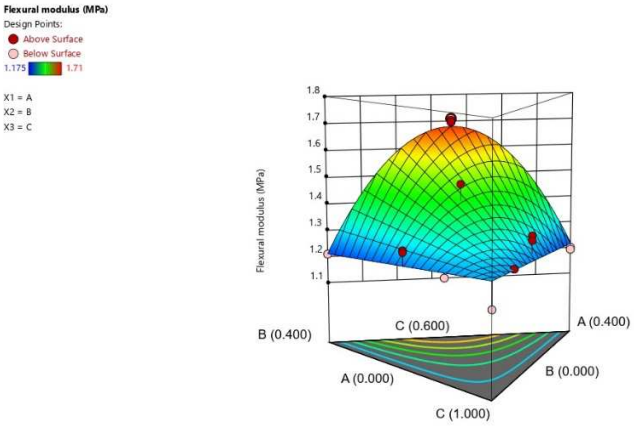
Fig.2 displayed the flexural responses of designed specimens. Similar as tensile test results, the bending strength of almond shell composite (46.26 MPa) is higher than walnut (44.73 MPa) due to lower cellulose% and difficult homogeneous dispersion of walnut shell during synthesis of composites. The accommodation of shell mass increased the bending strength & stiffness of polyester because of strong

interaction between matrix and filler that restrict their segmental motion.

The flexural behavior of walnut filled materials was considerably improved after the hybridization with almond shell fillers. The incorporation of both shells with equal weight fraction (20%) yields maximum strength (59.26 MPa) and modulus (1.71GPa). This kind of action is due to synergistic compatibilization between almond and walnut shells in viscoelastic medium.



(a)



(b)

Figure 2 Flexural properties of developed composites (a) flexural strength (b) flexural modulus

3.3 Impact strength

Fig.3 illustrate the composites performance under impact loading condition. Usually, the impact toughness of polymer was decreased by filler-reinforcement and its magnitude bet on filler type, its dispersion, and interfacial interaction [36]. But this time, positive outcome resulted in after the incorporation of shell fillers. This improvement is due to establishment of additional curing networks that hamper the crack propagation & assist energy dissipation. The native walnut shell composites have better impact strength than the almond ones.

Mixing of almond and walnut fillers yielded a positive hybridization phenomenon that leads better impact toughness than the single filler composites. The hybrid composite of 20.1:19.9 (almond: walnut) composition has carried maximum impact strength, 5.78 kJ/m^2 which is 64.20% higher than the strength of virgin matrix.

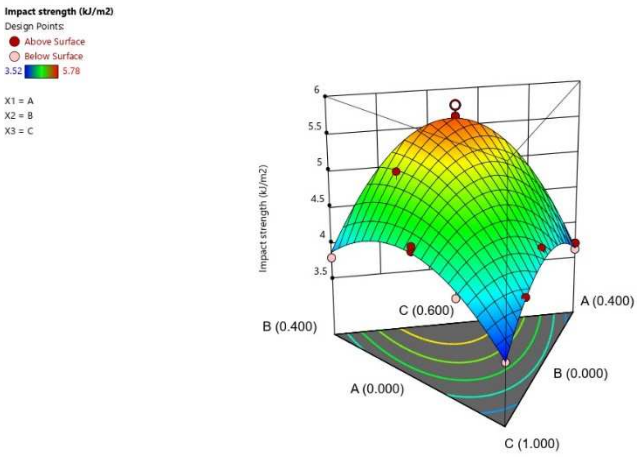


Figure 3 Impact strength of developed composites

3.4 Moisture absorption

Fig.4 shows the water soaking capacity of composites where can noticed that the unfilled polymer soaks minimum water (2.31%) than others. The increment in moisture uptake potential after filler addition is due to the presence of -OH functional group. As per Flory's theory, moisture dispersion is a two-step process where the penetrant induces elasticity then relaxation occur in polymeric chains. The Walnut shell composite absorb less moisture than the almond one and is due to residence of limited -OH & polar groups.

The experiments findings show that the material strength & moisture sorption are increased after the incorporation of almond shell in walnut shell/polyester composites. The hydro-sorption level was increased from 5.04% to 6.85% with the increment of almond filler content from 13% to 26%. Therefore. we can terminate at balanced approach i.e. central position of almond shell proportionate range for getting optimal performance composite.

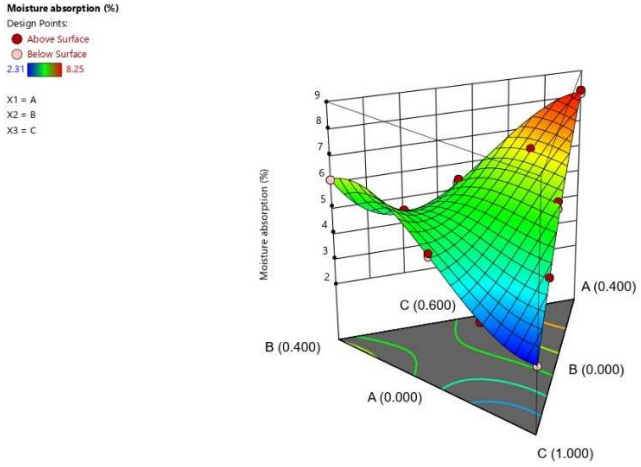


Figure 4 Moisture absorption behavior of developed composites

3.5 Thermal decomposition temperature

The prime reason behind limited application of natural-filler based materials is its poor thermal stability. The decomposition temperature (50% weight loss) of organic shell filled composites was determined through thermogravimetric analyzer. Fig.5 confirmed the rise in disintegration temperature of polymer by accommodation of shell fillers. It is due to the formation of a rigid network of shell particles within a polyester matrix that improved the restrictions in debonding of molecular chains. The almond shell composite has higher decomposition temperature (390.16ºC) than walnut shell one (385.64ºC). It is due to the existence of more crystalline cellulose in almond shell. Amongst all the developed samples, the almond/walnut shell (20.1:19.9) hybrid composite has successfully yielded a positive hybridization effect and showed the highest thermal decomposition temperature (391.85ºC) which is 7.43% higher than the virgin polyester matrix.

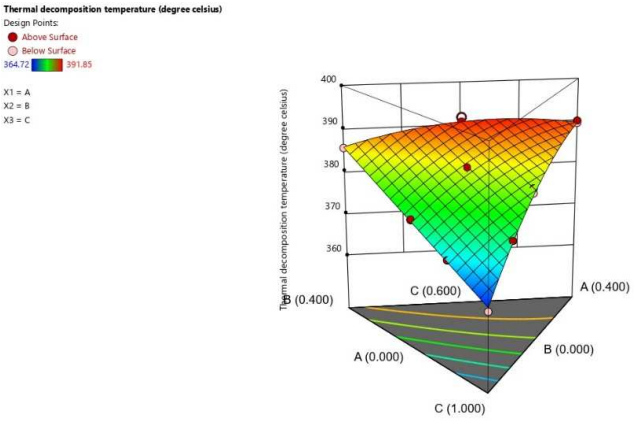


Figure 5 Thermal decomposition temperature of developed composites

3.6 Biodegradability

Fig.6 illustrates the percentage weight loss of composites where can found that the biodegradability of polymer is increased by the inclusion of organic fillers. It might be due to hydrolysis of polymeric chains that promotes bacterial action in underground conditions. Bharat K.N *et al.* [37] declared the biodegradation process wherein hydro-penetration, fracture of covalent bonds, and worsening of cellulose takes place. Among various specimens, the pure almond shell composite with 40% loading reveals the maximum weight loss (64.72%). The biodegradability of walnut shell composites was significantly improved by hybridization with almond fillers.

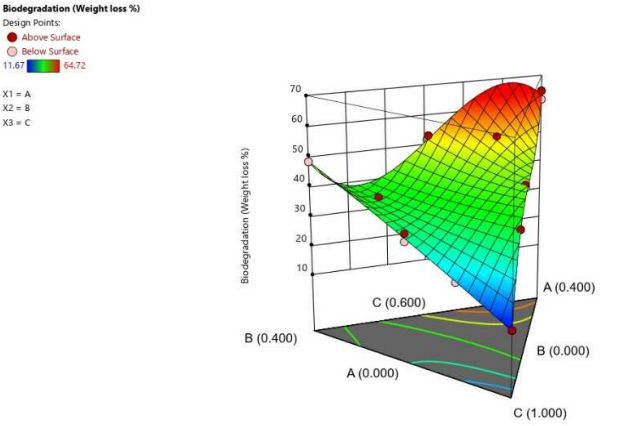


Figure 6 Biodegradation of composites in burial condition

3.7 ANOVA analysis

The given work optimized the ratio of three major constituents (almond shell, walnut shell, and polyester

resin) of hybrid composites using RSM based mixture design method. The range of constituents and values of desired responses are recorded in Table 1 & 2 respectively. The different numerical models and their coded equations as given below:

Tensile strength = 33.81 * A + 33.30 * B + 30.45 * C + 42.20 * AB + 25.80 * AC + 14.72 * BC – 91.28 * ABC + 20.12 * AC (A-C) (2)

Young's modulus = 1.19 * A + 1.18 * B + 1.04 * C + 1.53 * AB + 0.6998 * AC + 0.4445 * BC – 4.30 * ABC (3)

Impact strength = 3.64 * A + 3.87 * B + 3.52 * C + 7.38 * AB + 2.23 * AC + 2.67 * BC (4)

Flexural strength = 46.31 *A + 45.86 * B + 44.91 * C + 50.42 * AB + 21.16 * AC (5)

Flexural modulus = 1.22 * A + 1.21 * B +1.27 * C + 1.86 * AB (6)

Moisture absorption = 8.19 * A + 6.11 * B + 2.35 * C – 7.31 * AB + 2.46 * AC + 1.65 * BC + 9.08 * AB (A-B) + 6.80 * BC (B-C) (7)

Thermal decomposition temperature = 389.77 * A + 385.85 * B + 365.61 * C + 11.94 * AB + 16.50 * AC (8)

Biodegradation = 63.27 * A + 48.47 * B + 11.57 * C – 16.48 * AB + 24.82 * AC + 4.13 * BC – 81.35 * ABC + 104.65 * AB (A-B) + 73.61 * AC (A-C) (9)

ANOVA checked the impact of each factor in terms of *p* value, F-ratio, and degree of freedom (DF) in Tables 4-11. If a term has higher 'F-value' and $p \leq 0.05$ signifies that the term is significant. The models which are best fitted to responses as: Quadratic for impact strength, flexural strength & modulus, and thermal decomposition temperature, while cubic for tensile strength & modulus, moisture sorption, and biodegradation. The optimization criteria & importance level for each response is presented in Table 12. As per pre-defined goal, the point prediction tool is used and the optimal levels are declared in Fig. 7. The predicted results are validated through experiments (Table 13) that proves the selected numerical models are reliable for given problem.

Table 3. Summary of the models

Response	Model	Sequential *p*-value	Lack of fit value	R^2	R^2_{adj}	R^2_{pred}	PRESS	Precision	Remarks
Tensile strength (MPa)	Linear	0.1058	< 0.00001	0.29221	0.18332	-0.36358	369.86	Insufficient	
	Quadratic	< 0.0001	0.00073	0.95529	0.92894	0.89028	29.02	Insufficient	
	Special cubic	0.0066	0.0386	0.98002	0.96669	0.87228	34.46	Insufficient	
	Cubic	0.0133	0.5625	0.99963	0.99907	0.92241	20.55	Sufficient	Suggested
Young's modulus (GPa)	Linear	0.0506	0.001	0.36381	0.27008	-0.16175	0.4293	Insufficient	
	Quadratic	0.0001	0.04492	0.91662	0.87443	0.83	0.0625	Insufficient	
	Special cubic	0.0004	0.7101	0.98002	0.96670	0.92269	0.0269	Sufficient	Suggested
	Cubic	0.52	0.80774	0.98061	0.96552	0.92555	0.0274	Insufficient	
Impact strength (kJ/m^2)	Linear	0.1097	< 0.00001	0.28383	0.17888	-0.44418	11.41	Insufficient	
	Quadratic	< 0.0001	0.16360	0.97888	0.96683	0.86140	1.10	Sufficient	Suggested
	Special cubic	0.1076	0.22900	0.98444	0.97400	0.87449	0.9899	Insufficient	
	Cubic	0.1184	0.62950	0.99937	0.98843	0.90098	0.71360	Insufficient	
Flexural strength (MPa)	Linear	0.1716	< 0.00001	0.23750	0.12002	-0.40446	596.60	Insufficient	
	Quadratic	< 0.0001	0.00025	0.96618	0.94227	0.85390	62.09	Sufficient	Suggested
	Special cubic	0.1074	0.00034	0.97718	0.95531	0.79431	87.41	Insufficient	
	Cubic	0.0231	0.01559	0.99936	0.98841	-0.09091	467.08	Insufficient	
Flexural modulus (GPa)	Linear	0.1891	< 0.00001	0.22261	0.10770	-0.36380	0.7170	Insufficient	
	Quadratic	< 0.0001	< 0.00001	0.92007	0.88810	0.70788	0.15126	Sufficient	Suggested

	Special cubic	0.1330	< 0.00001	0.9391	0.8985	0.5411	0.2405	Insufficient	
	Cubic	0.7616	< 0.00001	0.9492	0.8729	-10.995	6.29	Insufficient	
Moisture absorption (%)	Linear	< 0.0001	0.00001	0.8014	0.7708	0.6633	12.18	Insufficient	
	Quadratic	< 0.0001	0.00167	0.9826	0.9739	0.9542	1.66	Insufficient	
	Special cubic	0.9867	0.00112	0.9826	0.9710	0.9372	2.27	Insufficient	
	Cubic	0.0031	0.5138	0.9980	0.9950	0.9513	1.76	Sufficient	Suggested
Thermal decompos ition temperature (°C)	Linear	< 0.0001	0.00078	0.95	0.9423	0.9161	79.22	Insufficient	
	Quadratic	0.0002	0.2717	0.9928	0.9893	0.9727	25.79	Sufficient	Suggested
	Special cubic	0.9200	0.2028	0.9929	0.9881	0.9574	40.20	Insufficient	
	Cubic	0.3759	0.11775	0.9956	0.9890	0.5543	420.96	Insufficient	
Biodegradation (weight loss %)	Linear	< 0.0001	0.01102	0.9346	0.9245	0.8783	366.12	Insufficient	
	Quadratic	0.0693	0.02009	0.9668	0.9502	0.8317	506.14	Insufficient	
	Special cubic	0.1026	0.02996	0.9757	0.9595	0.8384	485.97	Insufficient	
	Cubic	0.0078	0.8832	0.9962	0.9905	0.9827	51.97	Sufficient	Suggested

Table 4. ANOVA result for tensile strength

Source	Sum of Squares	DF	Mean Square	F value	Prob> F (*p*-value)	Remarks
Model	268.84	7	38.41	156.21	< 0.0001	Significant
Linear mixture	79.11	2	39.56	160.89	< 0.0001	
AB	158.77	1	158.77	645.82	< 0.0001	
AC	45.96	1	45.96	186.94	< 0.0001	
BC	14.39	1	14.39	58.51	< 0.0001	
ABC	9.76	1	9.76	39.70	0.0002	
AC	3.41	1	3.41	13.8	0.0059	
(A-C)				5		
Residual	1.97	8	0.2458			
Lack of fit	1.03	3	0.3444	1.84	0.2564	Not significant
Pure error	0.9336	5	0.1867			
Cor total	270.80	15				
SD	0.4958				R^2	0.9927
Mean	37.35				Adjusted R^2	0.9864
C.V. %	1.33				Predicted R^2	0.9236
PRESS	20.68				Adeq. Precision	38.4396

Table 5. ANOVA result for Young's modulus

Source	Sum of Squares	DF	Mean Square	F value	Prob> F (*p*-value)	Remarks
Model	0.3605	6	0.0601	74.34	< 0.0001	Significant
Linear mixture	0.1354	2	0.0677	83.74	< 0.0001	
AB	0.207	1	0.20	257.	<	
	8		78	19	0.0001	
AC	0.0353	1	0.0353	43.66	< 0.0001	
BC	0.0135	1	0.0135	16.67	0.0027	
ABC	0.0235	1	0.0235	29.13	0.0004	
Residual	0.0073	91	0.0008			
Lack	0.002	4	0.00	0.54	0.7101	Not

of fit	2		06	79		significant
Pure error	0.0051	5	0.0010			
Cor total	0.3677	15				
SD	0.0284				R^2	0.9802
Mean	1.29				Adjust	0.9670
					ed R^2	
C.V. %	2.20				Predicted R^2	0.9269
PRESS	0.0269				Adeq. Precision	27.9341

Table 6. ANOVA result for impact strength

Source	Sum of Squares	DF	Mean Square	F value	Prob> F (*p*-value)	Remarks
Model	7.75	5	1.55	92.56	< 0.0001	Significant
Linear mixture	2.28	2	1.14	68.15	< 0.0001	
AB	5.21	1	5.21	311.28	< 0.0001	
AC	0.4286	1	0.4286	25.61	0.0005	
BC	0.5473	1	0.5473	32.69	0.0002	
Residual	0.1674	10	0.0167			
Lack of fit	0.1200	5	0.0240	2.55	0.1636	Not significant
Pure error	0.0472	5	0.0094			
Cor total	7.91	15				
SD	0.1294				R^2	0.9788
Mean	4.47				Adjusted R^2	0.9683
C.V. %	2.89				Predicted R^2	0.8614
PRESS	1.10				Adeq. Precision	26.20

Table 7. ANOVA result for flexural strength

Source	Sum of Squares	DF	Mean Square	F value	Prob> F (*p*-value)	Remarks
Model	398.85	4	99.71	41.98	< 0.0001	Significant
Linear mixture	100.93	2	50.46	21.25	0.0002	
AB	257.50	1	257.50	108.42	< 0.0001	
AC	41.48	1	41.48	17.47	0.0015	
Residual	26.13	11	2.38			
Lack of fit	25.36	6	4.23	27.7	0.0011	Significant
Pure error	0.7616	5	0.1523			
Cor total	424.98	15				
SD	1.54				R^2	0.9385
Mean	50.43				Adjusted R^2	0.9162
C.V. %	3.06				Predicted R^2	0.8697
PRESS	55.37				Adeq. Precision	16.0021

Table 8. ANOVA result for flexural modulus

Source	Sum of Squares	DF	Mean Square	F value	Prob> F (*p*-value)	Remarks
Model	0.4678	3	0.1559	33.22	< 0.0001	Significant
Linear mixture	0.1185	2	0.0592	12.62	0.0011	
AB	0.3493	1	0.3493	74.42	< 0.0001	
Residual	0.0563	12	0.0047			
Lack of fit	0.0560	7	0.0080	138.64	< 0.0001	Significant
Pure error	0.0003	5	0.0001			
Cor total	0.5241	15				
SD	0.0685				R^2	0.8925
Mean	1.36				Adjust	0.8657

					ed R^2	
C.V. %	5.03				Predicted R^2	0.8275
PRESS	0.0904				Adeq. Precision	13.699

Table 9. ANOVA result for moisture absorption

Source	Sum of Squares	DF	Mean Square	F value	Prob> F (*p*-value)	Remarks
Model	36.09	7	5.16	451.62	< 0.0001	Significant
Linear mixture	28.99	2	14.50	1269.91	< 0.0001	
AB	5.08	1	5.08	445.12	< 0.0001	
AC	0.4818	1	0.4818	42.21	0.0002	
BC	0.2040	1	0.2040	17.87	0.0029	
AB (A-B)	0.4087	1	0.4087	35.81	0.0003	
BC (B-C)	0.3486	1	0.3486	30.54	0.0006	
Residual	0.091	8	0.01			
Lack of fit	0.0261	3	0.0087	0.6658	0.6082	Not significant
Pure error	0.0652	5	0.0130			
Cor total	36.18	15				
SD	0.1068				R^2	0.9975
Mean	5.39				Adjusted R^2	0.9953
C.V. %	1.98				Predicted R^2	0.9499
PRESS	1.81				Adeq. Precision	77.41

Table 10. ANOVA result for thermal decomposition temperature

Source	Sum of Squares	DF	Mean Square	F value	Prob> F (*p*-value)	Remarks
Model	936.72	4	234.18	333.50	< 0.0001	Significant
Linear mixture	897.25	2	448.62	638.90	< 0.0001	
AB	14.44	1	14.44	20.56	0.0009	
AC	25.23	1	25.23	35.93	< 0.0001	
Residual	7.72	11	0.7022			
Lack of fit	5.29	6	0.8817	1.81	0.2655	Not significant
Pure error	2.43	5	0.4868			
Cor total	944.45	15				
SD	0.8380				R^2	0.9918
Mean	382.61				Adjusted R^2	0.9888
C.V. %	0.2190				Predicted R^2	0.9834
PRESS	15.72				Adeq. Precision	53.767

Table 11. ANOVA result for biodegradation

Source	Sum of Squares	DF	Mean Square	F value	Prob> F (*p*-value)	Remarks
Model	2995.56	8	374.43	224.25	< 0.0001	Significant
Linear mixture	2810.36	2	1405.18	841.56	< 0.0001	
AB	24.05	1	24.05	14.40	0.0068	
AC	41.14	1	41.14	24.64	0.0016	
BC	1.13	1	1.13	0.67	0.4375	
ABC	7.50	1	7.50	4.49	0.0717	
AB (A-B	51.74	1	51.74	30.99	0.0008	
AC (A-C)	36.29	1	36.29	21.73	0.0023	
Residual	11.69	7	1.67			
Lack of fit	0.3233	2	0.1616		0.9323	Not significant
Pure error	11.36	5	2.27			
Cor	3007.	1				

total	15	5				
SD	1.29				R^2	0.9961
Mean	42.48				Adjusted R^2	0.9917
C.V. %	3.04				Predicted R^2	0.9827
PRESS	52.07				Adeq. Precision	53.34

Table 12. Optimization criteria and importance level

Response	Lower value	Upper Value	Goal	Importance level
Tensile strength (MPa)	30.69	44.21	Maximize	*****
Young's modulus (GPa)	1.06	1.603	Maximize	*****
Impact strength (kJ/m^2)	3.52	5.78	Maximize	*****
Flexural strength (MPa)	43.83	59.26	Maximize	*****
Flexural modulus (GPa)	1.175	1.71	Maximize	*****
Moisture absorption (%)	2.31	8.25	Minimize	*****
Thermal decomposition temperature (°C)	364.72	391.85	Maximize	*****
Biodegradation (wt. loss %)	11.67	64.72	Maximize	*****

Table 13. Experimental results at the optimum values of constituent elements

Response	Test 1	Test 2	Test 3	Test 4	Mean
Tensile strength (MPa)	43.70	45.37	44.62	45.09	44.69
Young's modulus (GPa)	1.528	1.590	1.548	1.521	1.546
Flexural strength (MPa)	57.97	58.08	58.19	59.15	58.35
Flexural modulus (GPa)	1.643	1.701	1.698	1.682	1.681
Impact strength (kJ/m^2)	5.17	5.89	5.48	5.75	5.57
Thermal decomposition temperature (°C)	387.19	391.07	389.46	390.12	389.46
Biodegradation (wt. loss %)	49.53	50.28	51.07	50.86	50.44

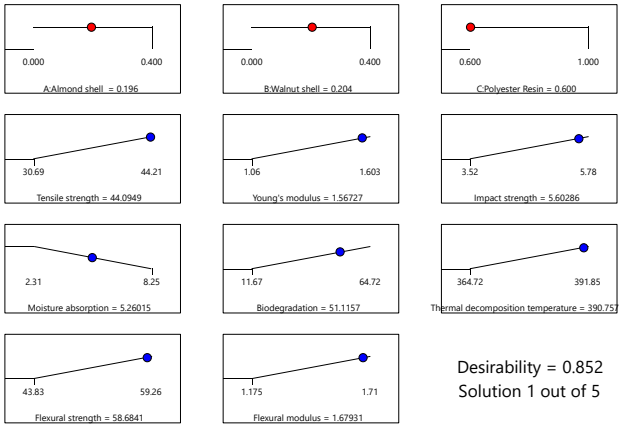


Figure 7. Optimum value of input and response parameters

4.0 CONCLUSION

The current investigation optimizes the proportion of major constituents (almond shell, walnut shell, and polyester resin) of hybrid composites using mixture design tool. The quadratic and cubic models have showed reasonable agreement in correlation coefficients (R^2, adj. R^2, pred. R^2) for different responses. The numerical equations and experiential results proved the hybridization is a best way to reinforce contravene properties in a balanced manner. The almond/walnut shell (20.1:19.9) hybrid composite showed maximum strength, modulus, and thermal decomposition temperature. The optimum level of variables is: almond filler: 19.6%,

walnut filler: 20.4%, polyester resin: 60%, tensile strength: 44.09 MPa, Young's modulus: 1.57 GPa, flexural strength: 58.68 MPa, flexural modulus: 1.68 GPa, impact strength: 5.60 kJ/m^2, moisture absorption: 5.26%, thermal decomposition temperature: 390.76^{o}C, and biodegradation: 51.12%. In summary, the mixture design provides an effective solution to develop a high-performance hybrid composite.

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