Composites Part C: Open Access 10 (2023) 100337

Contents lists available at ScienceDirect

Composites Part C: Open Access

journal homepage: www.sciencedirect.com/journal/composites-part-c-open-access

Multi-objective optimization of mechanical properties of chemically treated bio-based composites using response surface methodology

Ankit Manral [a], Rakesh Singh [a], Furkan Ahmad [b], Partha Pratim Das [c], Vijay Chaudhary [d,*], Rahul Joshi [e], Pulkit Srivastava [f]

[a] Department of Mechanical Engineering, Noida Institute of Engineering & Technology, Greater Noida 201308, India
[b] Department of Mechanical Engineering, Delhi Technological University, Shahbad Daulatpur, Rohini, New Delhi 110042, India
[c] Department of Materials Science and Metallurgical Engineering, IIT Hyderabad, Sangareddy, Telangana, 502285, India
[d] Department of Mechanical Engineering, Amity School of engineering and Technology, Amity University Uttar Pradesh, Noida, 201313 India
[e] ME Department, Netaji Subhas University of Technology, Sec-3, Dwarka, New Delhi, 110078, India
[f] Department of Mechanical Engineering, Sharda University, Greater Noida 201308, India

ARTICLE INFO

Keywords:
Kenaf fiber mats
Sodium acetate
Response
RSM (CCD)
Optimization

ABSTRACT

Eco-friendly surface treatment of natural fibers using sodium acetate (CH_3COONa) affects the mechanical properties of the developed composites in many ways. In present study, geometrically different kenaf fiber mats (bidirectional (BC), unidirectional (UD) and randomly oriented (RO) were treated at different concentration (10, 15 and 20 percentage w/w) of sodium acetate aqueous solution for varying time (24, 48 and 72 hr.) at room temperature. PLA (Poly-Lactic Acid) was used for the fabrication of treated fiber reinforced bio-degradable composites. The influence of above parameters on mechanical properties were studied. Response surface methodology (RSM) module face centered central composite design was employed for the development of regression models. The relationship between chemical treatment parameters and mechanical responses were predicted by quadratic model. In this study, predicted model was developed for two numerical factors (chemical concentration (CC) and treatment time (TT)) and one categorical factor (type of mat (TOM)). Tensile strength (TS), flexural strength (FS) and impact strength (IS) are considered as response variables. The statistical analysis showed that chemical concentration, treatment time and kenaf mat type have individually and interactively influenced the response of experiments. Chemical concentration was found to be the most influencing factor among all for the changes in mechanical properties. Optimization of input variables was done based on predicted model within bounded reason of responses.

1. Introduction

From the last decade, natural fiber has been accepted as a reinforced material for thermoset and thermoplastic polymer because of their comparable properties such as low-density, high specific strength to weight ratio, availability, low cost etc. over synthetic fibers and it is available abundantly in nature. Using biopolymer and natural fibers, green composite materials are developed. As both the constituents of green composites are biodegradable in nature, it is being used to overcome the environmental problem that is being faced by the conventional polymer composites [1].

Natural fibers for green composites are obtained from various parts of plants and tress such as leaves, seeds and bast [2]. Fibers obtained from different parts of the plants exhibits distinct properties. Some most popular natural fiber that are being used as reinforcement material with thermoset and thermoplastic based composites are Jute, hemp, flax, bamboo, pineapple, kenaf etc. Among all these natural fibers, kenaf is an important bast fiber extracted from plant via mechanical retting method. It has excellent acoustic properties and higher thermal stability compared to other natural fibers. Number of automotive companies are using kenaf fibers as reinforcement material for the development of automotive parts to enhance the acoustic behavior capabilities [3].

Cellulosic kenaf fiber has some drawbacks in extension to their advantages such as its hydrophilic nature and presence of unwanted constituents which influences the mechanical properties of developed composites. Furthermore, the properties of natural fibers depend upon

* Corresponding author at: Amity University, India.
E-mail address: vijaychaudhary111@gmail.com (V. Chaudhary).

https://doi.org/10.1016/j.jcomc.2022.100337

Available online 10 December 2022

the climate condition where it grow, environment or weather condition, soil characteristic etc. [2]. The foremost drawback with natural fibers is its lower compatibility with matrix materials. Lower compatibility results in lower interfacial adhesion between matrix and reinforcement which further affects stress transfer between the constituents negatively. Lower interfacial adhesion is due to presence of excess amount of non-cellulosic content lignin, hemicellulose, pectin and waxes. These constitutes are bonded with fiber fibrils with hydrogen bonding [4]. All unwanted contents are bounded with fiber by hemicellulose matrix. But hemicellulose is hydrophilic in nature and can be easily hydrolysis by aqueous solution of acids and bases [5].

In order to achieve a good interfacial adhesion between the matrix and fiber, the surface of natural fibers is altered by chemical treatments (Silane, alkaline, mercerization and benzoylation etc.). In some recent past studies, various authors have done the chemical treatment of natural fibers for enhancement of the various properties of developed composites. Oushabi et al. [6] studied the effect of alkaline treatment on mechanical properties of date palm fiber-polyurethane composites. The fibers were treated with 2 wt%, 5 wt% and 10 wt% NaOH (Sodium Hydroxide). From given result, authors concluded that at 5 % NaOH concentration, the TS of fiber increases 76 % as compares to untreated fiber. Moreover, the pull-out test show that at 5 % concentration the interface of fiber and matrix is higher. Moreover, the interface properties drastically decrease if further increase in chemical concentration for treatment.

Accordingly, it is required to find a chemical which do not have acidic nature, economical and must be ecofriendly for the treatment of fiber. In previous findings, various authors used sodium bicarbonate for ecofriendly treatment of natural fibers. Sodium bicarbonate called as baking soda used in cooking, baking, toothpastes and in various bio-pesticide [7, 8]. Recently, Chaitanya et al. [9] used sodium bicarbonate for the treatment of short aloe vera fiber and incorporated it with polylactic acid (PLA) with the help of injection molding process. Authors reported that at 10 percentage concentration of sodium bicarbonate, among the treatment time of 24, 48, 72, 120 and 168 hr., 72 hr. is the best treatment time and exhibited better mechanical properties compared to other treatment time. Fiore et al. [10] also used sodium bicarbonate for the treatment of sisal fibers. Authors reported that among different treatment time periods (24,120 and 240 hr.) of sisal fiber, the optimized time is 120 hr. At this treated time, fiber reinforced composites showed higher flexural properties of developed composites.

Considering all the reasoning related to chemical treatment of natural fibers, the current research intent to analyze a new greener way for the development of fully degradable biopolymer composites. In present study, different kenaf mats (UD, BD, and RO) treated with sodium acetate (CH_3COONa) and incorporated with PLA by compression molding process. Sodium acetate is a type of salt used as a pickling agent, cleaning agent and as a food additive. The pH level of sodium acetate aqueous solution maintained between 7-8 that implies its non-acidic nature. Maintained pH level of aqueous solution give environmentally friendly treatment of natural fibers.

In present study, use two numeric factors: chemical concentration (CC) and treatment time (TT) and type of mat (TOM). Both numeric and categorical factor influenced the properties of developed composites. Whereas, from given experimental input factors, the optimized were existed between them that cannot be easily find from experiment or may be required a greater number of experiments. So, for minimizing the number of experiments and from economic point of view, introduce an optimizing software technique called design of experiment (DOE). In DOE central composite design module of response surface methodology (RSM) are employed for optimizing the factor. This technique develops regression model or governing equation for predicting the response for every range of input factor. The after effect of input variable (Chemical concentration, treatment time and type of kenaf mats) on mechanical properties (TS, FS and IS) of developed composites were studies based on contour and surface plots in DOE. Additionally, DOE optimized the independent variables to get maximum output response for developed composites were also describe in this research.

2. Experimental description

2.1. Fiber and matrix

Raw mats (Untreated; UD and BD) form of kenaf fiber in 220 GSM were procured from Go Green products, Alwarthirunagar, Chennai, India. RO mat was prepared from raw kenaf fibers by using hand compression molding machine. Polylactic acid (Indego 3052D) were supplied from Nature Tech. India Pvt. Ltd, Nagalkeni, Chennai, and Tamilnadu, India in pellet form. As per supplier specification the density of PLA is 1.46 cm^3 with glass transition and melting point temperature of 55-60 °C and 200 °C respectively. Sodium acetate (CH_3COONa) was procured form Krishna chemicals New Delhi, India.

2.2. Sodium acetate treatment

Kenaf fibers were treated with sodium acetate (CH_3COONa), with three different concentrations of 10%, 15% and 20%. The treatment was conducted at room temperature with three different treatment time periods of 24 hr., 48 hr. and 72 hr. As sodium acetate is not acidic, it requires more time and concentration for removal of unwanted content from the fiber surface. The reaction during treatment of natural fiber shown in Fig. 1.

After treatment, fiber mats were subsequently washed with running water to get relieve the sodium ions and dry in oven at 70 °C for 8 hr. Aqueous solution of sodium acetate is mildly alkaline due to the formation of acetate and OH^-. The disintegration of CH_3COONa into acetate and hydroxyl ions as shown in Fig. 1. Therefor CH_3COONa aqueous solution react as in same manner as NaOH react with natural fiber as illustrate in Fig. 1. Mildly alkaline nature of CH_3COONa conventionally required more concentration and treatment time for treatment to get desired result. Hence, in present studies, chemical concentration and time for treatment are being investigated to get optimized results.

2.3. Composites fabrication

Composite samples were developed by hot compression molding process by using film stacking method. For every developed composite, kenaf fiber mats fraction was maintained of 30 %. Three different geometric oriented kenaf fiber mats (BD, UD, and RO) are used in this study. Four layers of kenaf mats were incorporated with polymer for every type of composites. To remove the moisture content from fiber, it can be preheated in oven at 70 °C for 5 hr. before fabrication of composite. Polylactic acid (PLA) granules were converted in thin sheet of thickness 1 mm by compression molding machine at a temperature of 150 °C initially and at low pressure for 2 min. Consequently, pressure was increase at constant temperature for next 3 min. Finally, the thin film of PLA allowed to cool inside a mold under pressure until the mold temperature is not equal to room temperature. Thereafter, every type of treated fiber reinforced composite (bidirectional fiber reinforced polymer composite (BDFRPC), unidirectional fiber reinforced polymer composite (BDFRPC) and randomly fiber reinforced polymer composite (ROFRPC)) kenaf fiber mats and polymer sheets are stacked alternatively inside a mold. All stacked layers are put inside the mold between

$$CH_3COONa + H_2O \longrightarrow Na^+ + CH_3COO^-$$

$$CH_3COO^- + H_2O \longrightarrow CH_3COOH + OH^-$$

(Acetic acid)

$$\text{Fiber-OH} + NaOH \longrightarrow \textbf{Fiber-O}^-\textbf{Na}^+ + H_2O$$

Fig. 1. Chemical reaction during treatment of fiber.

the Teflon sheets. Teflon sheets are introduced to overcome or avoid the sticking of polymer during fabrication of composites laminates.

During composite fabrication whole assembly or mold initially maintained at a temperature of 170 °C for 6 min. at low pressure. Thereafter, at a same temperature of 170 °C, pressure further increased and maintained the mold for given parameters for next 3 min. After that, composites sheets were removed from the mold when the temperature of mold reached 70 °C. The average samples thickness was 3 mm. The compaction pressure range during fabrication of composites laminates were 3-5 MPa After fabrication, all composite laminates were put in a desiccator to prevent it for moisture until further use.

2.4. Tensile and flexural testing

Tensile and flexural testing of untreated and treated fiber reinforced polymer composites were carried out on INSTRO 5952 with constant cross head speed of 2 mm/min. All specimen for tensile and flexural testing were prepared according to ASTM D3039 and ASTM D790 respectively [11]. Every value reported represents average value of five specimen. The effect of different geometries of treated kenaf fiber mat reinforced composites on tensile and flexural mechanical properties of the developed composites has been studied and published [12]. This work is novel extension of the author's previous work as this work mainly focuses on the application of RSM in order to find the optimized results without spending much on the experimental work in future.

2.5. Impact test

Notched Charpy test was conducted on the impact tester (Tinius Olsen model IT-503) at IIT Delhi. The impact tester has maximum free impact energy of 50 J and has a striking velocity of 3 m/sec. All specimen for impact testing were prepared as per the standard. The effect of different geometries of treated kenaf fiber mat reinforced composites on impact properties of the developed composites was previously studied by the same authors and has been published [13].

2.6. Optimization process using RSM

Central composite module of RSM with full factorial were employed for optimization of two numerical factor (Chemical concentration and treatment time) and one categorical factor (type of kenaf mat). Addition of categorical factor in optimization, the existing runs is multiplied by categorical factor making the analysis have thirty runs.

Both numeric and categorical factor have three levels. Chemical concentration has three levels as 10, 15 and 20 percentage whereas, for treatment time it was 24, 48 and 72 hr. The three level of categorical factor are BD, UD, and RO mat types. Numerical and categorical factors have factorial, axial and center points. The developed experiments are in randomized form to overcome the unknown noise or error distorted the result of experiment. There is certain repetition in some experiment to overcome the formation of noise or error affecting during experiment. Based on the CCD, analysis was performed to develop regression models for TS, FS and IS in term of three input factors: CC, TT and TOM. Every input factor has three levels: ± 1 and 0. Table 2 shows the link between the input parameters with their corresponding selected levels. The experimental design matrix used to perform the experiment by combination of varying input variables. Experimental matrix with combination of different input variables is shown in Table 1. All experiments were strictly performed according to design Table 1.

Table 2
Input factors and their corresponding varying level.

Symbols	Input parameters	Units	Levels -1	0	+1
1.	Chemical concentration. (CC)	%	10	15	20
2.	Treatment time (TT)	hr.	24	48	72
3.	Kenaf mats	type	BD	UD	RO

Table 1
RSM randomized experimental table with experimental values.

Std	Run	Chemical concentration %	Treatment time (hr.)	Fiber mat (Type)	Response 1 Tensile strength (MPa)	Response 2 Flexural strength (MPa)	Response 3 Impact strength (J/m)
18	1	15	72	UD	83.57	73.56	67.8
24	2	20	72	RO	26.87	42.313	43.01
17	3	15	24	UD	77.29	68.46	93.8
9	4	15	48	BD	39.08	105.56	43.26
22	5	20	24	RO	45.56	74.36	62.5
23	6	10	72	RO	34.06	64.16	98.54
4	7	20	72	BD	45.9	88.4	28.75
11	8	10	24	UD	65.341	60.08	85.9
1	9	10	24	BD	32.15	89.94	54.54
3	10	10	72	BD	37.63	101.01	62.15
25	11	10	48	RO	32.46	63.16	103.9
15	12	10	48	UD	70.16	66.99	90.1
16	13	20	48	UD	90.46	81.24	40.9
30	14	15	48	RO	38.42	69.35	82.5
6	15	20	48	BD	55.37	112.45	30.65
20	16	15	48	UD	79.86	69.56	75
13	17	10	72	UD	75.56	67.5	92
29	18	15	48	RO	37.1	69.88	81.1
8	19	15	72	BD	45.02	106.06	38.95
21	20	10	24	RO	31.62	55.08	96.64
26	21	20	48	RO	52.4	76.78	52.96
2	22	20	24	BD	50.18	108.79	37.57
12	23	20	24	UD	85.709	76.832	48.4
10	24	15	48	BD	38.041	104.32	42.19
28	25	15	72	RO	40.16	70.13	75.2
5	26	10	48	BD	35.03	95.56	61.73
14	27	20	72	UD	74.326	46.53	35.5
7	28	15	24	BD	38.56	103.96	52.2
27	29	15	24	RO	35.56	66.76	97.5
19	30	15	48	UD	78.5	68	74.32

3. Result and discussion

3.1. Development of regression model

CCD methodology developed thirty experiments including few repetitions to minimize the noise arising during actual experiments. All experiments sequence is in randomized form, experimental conditions and their outcomes are shown in Table 1. Results are infused by "Design Expert (DX)'' software (student version, Stat-Ease Inc., USA). Quadratic model was perfect to fit the results, whereas cubic model is aliased for developing the regression model. In built ANOVA in DOE generated a coded and actual equation (regression model) for prediction of the response at ever bounded inputs values are given by following equation in Table 3 and Table 4.

In above coded regression, all coded values A, B and C represent chemical concentration, treatment time and type of mat respectively. The outcomes obtained from analysis of variance by ANOVA for developed models are shown in Tables 5, 6 and 7.

Table 5 shows the ANOVA variance analysis of proposed model for TS. This table include sum of squares (SS), degree of freedom (df), mean square (MS), F and P- values. Table 5 implies that fitted model are significant ($p<0.05$) and have 95 % confidence level. The P-values of input variable, lower than.05 indicates its maximum significance in output response. For TS ANOVA regression model factors, A, C and interaction of AC are more significantly affect the response output for this model. Although the P-value of variable higher than 0.1 are not significantly influenced the response. So, for TS chemical concentration and mat type are more influencing input factors. For FS the variance analysis by ANOVA shown in Table 6, same as TS the fitted model for FS is significance as its P- value is less than 0.05. The input variable which are most significance in regression model of FS is C, AC and B^2, this implies that almost all input variables influence the FS obtained by regression model. The proposed model by the variance analysis done by ANOVA for IS shown in Table 7. Model P-values indicates the proposed model is significant and most significant variable that highly influenced the response are A, B, C, AB, AC and A^2 but from the following A, B and C are highly influence the response. Predicted Vs actual values for TS, FS and IS shown in Fig. 2a, b and c respectively. Fig. 3a, b and c exhibit residual Vs predicted values for response. Actual values are the observed value during experiments, whereas predicted value are the values that generated by the regression model. Predicted values are based on semi-empirical model (Correlation) that was not equal but near by the actual value that observed during experiments. Although, Residual value is the difference between predicted and actual values. The minimum residual value shows the higher significance of model. R-squared values for the model developed for TS, FS and IS are 0.96, 0.94 and 0.97 respectively. The more the value of R^2 approaches near to unity, there are more chances to better fit of model in experimental value. R^2 value is statistical measure and explained how much independent variables influence dependent variables.

3.2. The effect of input parameters on response

All three inputs parameters were influenced the output response. The contribution of input parameters according to p-value for generated regression model may vary for output response. Some response influenced by two variable or interaction of two and some of them were influenced by all input variables. Effect of input variable on response are shown in Figs. 4, 5 and 6. These plots of individual input variable were drawn at mean value of others.

Table 3
Coded equation.

Tensile strength	53.86 + 6.26 x A + 0.0626 x B - 10.70 x C [1] + 25.68 x C [2] - 4.37 x AB + 1.51 x AC [1] + .3077 x AC [2] + 1.21 x BC [1] + 0.7901 x BC [2] + .0907 x A^2- 2.53 x B^2
Flexural strength	84.01 + 2.46 x A -2.48 x B + 23.38 x C [1]- 10.35 x C [2]- 9.19 x AB + 1.40 x AC [1]- .7844 x AC [2] + 1.27 x BC [1]- .4859 x BC [2]- 4.22 x A^2- 5.43 x B^2
Impact strength	67.56 - 19.60 x A - 4.85 x B- 19.49 x C [1] + 4.66 x C [2] - 3.52 x AB+ 7.00 x AC [1] - 3.45 x AC [2] + 1.48 x BC [1] + 0.4806 x BC [2] - 5.58A^2 - 0.1914 x B^2.

Table 4
Actual equation.

Tensile strength	For Bidirectional mat	-18.26109 + 3.19557 x CC + 1.021548 x TT - 0.036453 x CC x TT + 0.003628 x CC^2 - 0.004391 x TT^2
	For Unidirectional mat	22.57141 + 2.95537 x CC+1.00387 x TT - 0.036453 x CC x TT + 0.003628 x CC^2- 0.004391 x TT^2.
	For Randomly oriented mat	-6.12452 + 2.53057 x CC + 0.887440 x TT- 0.036453 x CC x TT+ 0.003628 x CC2 - 0.004391 x TT^2
Flexural strength	For Bidirectional mat	-16.60093 + 9.51082 x CC+ 2.00348 x TT - 0.076603 x CC x TT - 0.168762 x CC^2 - 0.009423 x TT^2
	For Unidirectional mat	-40.26106 + 9.07422 x CC + 1.93013 x TT - 0.076603 x CC x TT - 0.168762 x CC^2 - 0.009423 x TT^2
	For Randomly oriented mat	-42.8446 + 9.10826 x CC + 1.91753 x TT - 0.076603 x CC x TT - 0.168762 x CC^2- 0.009423 x TT^2.
Impact Strength	For Bidirectional mat	20.53314 + 5.58205 x CC + 0.331176 x TT- 0.029313 x CC x TT - 0.223190 x CC^2 - 0.000332 x TT^2.
	For Unidirectional mat	78.02981 + 3.49205 x CC + 0.289578 x TT- 0.029313 x CC x TT- 0.223190 x CC^2 - 0.000332 x TT^2.
	For Randomly oriented mat	93.36681 + 3.47238 x CC+ 0.187912 x TT- 0.029313 x CC x TT- 0.223190 x CC^2 - 0.000332 x TT^2

3.2.1. Effect of CC, TT and fiber mats on response

CC is a numeric factor, and it were enhanced the tensile and flexural response. The significance of CC was also shown in ANOVA Table 5 and 6. The variation of response respective to CC and mat type are linearly or curved. TS response increase with increase in CC for both BDFRPC and UDFRPC. But for ROFRPC after mean value of CC the tensile strength were almost constant. All values were examined according to the statics data at 48 hr. treatment time. Increment in tensile response after treatment is due to improve in interfacial adhesion between reinforced and matrix material. Treatment of kenaf fiber mats with sodium acetate remove the non-cellulosic content from the surface of fiber, which give higher interlocking of reinforced fiber with polymer. Mats type is a categorical factor, ANOVA table also show the significance of this categorical factor on all response. Orientation of fiber also a governing factor to handle the mechanical properties of developed composites. Manral et al. [13] study the effect of fiber orientation on mechanical properties of developed composites, tensile strength is maximum in longitudinal reinforced mats kenaf/PLA composites. In FS response the CC individually not significantly influencing the flexural response as shown in Fig 3b, it almost linear with small curvature at different chemical concentration. But the combine effect or interaction of CC and TT significant influenced the flexural response as per the ANOVA Table 6. The most dominating independent variable that boost up the flexural strength is type of fiber mat reinforced. Fig. 3b shows that BDFRPC achieved higher FS as compared to other oriented treated mat reinforced composites. Compared to CC and TT fiber mat show more significant effect for maximizing the output responses. All input variables and its interaction are significant for IS response according to the ANOVA Table 7. At mean treatment time the IS of developed composites were decrease with increase chemical concentration. ROFRPC achieved higher impact strength as shown in Fig. 4c. TT and mats type are also significant for IS response, with increase treatment time the response

Table 5
ANOVA analysis using input variable for TS.

Source	Sum of squares	df	Mean Square	F- values	*P*-values	
Model	11035.23	11	1003.20	46.07	< 0.0001	**significant**
A-Chemical concentration	706.43	1	706.43	32.44	< 0.0001	
B-Treatment time	0.0704	1	0.0704	0.0032	0.9553	
C-Fiber Mat	9982.83	2	4991.42	229.20	< 0.0001	
AB	229.62	1	229.62	10.54	0.0045	
AC	34.02	2	17.01	0.7810	0.4728	
BC	36.69	2	18.35	0.8424	0.4470	
A^2	0.0576	1	0.0576	0.0026	0.9596	
B^2	44.78	1	44.78	2.06	0.1687	
Residual	392.00	18	21.78			
Lack of Fit	389.67	15	25.98	33.37	0.0073	**significant**
Pure Error	2.34	3	0.7786			
Cor Total	11427.23	29				

Table 6
ANOVA analysis using input variable for FS.

Source	Sum of squares	df	Mean Square	F- values	*P*-values	
Model	9895.54	11	899.59	25.66	< 0.0001	**significant**
A-Chemical concentration	108.61	1	108.61	3.10	0.0954	
B-Treatment time	110.50	1	110.50	3.15	0.0928	
C-Fiber Mat	8234.64	2	4117.32	117.44	< 0.0001	
AB	1014.01	1	1014.01	28.92	< 0.0001	
AC	17.69	2	8.85	0.2523	0.7797	
BC	14.89	2	7.45	0.2124	0.8107	
A^2	124.60	1	124.60	3.55	0.0757	
B^2	206.20	1	206.20	5.88	0.0260	
Residual	631.08	18	35.06			
Lack of Fit	628.95	15	41.93	59.17	0.0031	**significant**
Pure Error	2.13	3	0.7087			
Cor Total	10526.62	29				

Table 7
ANOVA analysis using input variable for IS.

Source	Sum of squares	df	Mean Square	F- values	*P*-values	
Model	14406.69	11	1309.70	73.88	< 0.0001	**significant**
A-Chemical concentration	6916.84	1	6916.84	390.19	< 0.0001	
B-Treatment time	423.21	1	423.21	23.87	0.0001	
C-Fiber Mat	6212.67	2	3106.34	175.23	< 0.0001	
AB	148.47	1	148.47	8.38	0.0097	
AC	440.96	2	220.48	12.44	0.0004	
BC	37.54	2	18.77	1.06	0.3674	
A^2	217.94	1	217.94	12.29	0.0025	
B^2	.2565	1	0.2565	0.0145	0.9056	
Residual	319.08	18	17.73			
Lack of Fit	317.12	15	21.14	32.40	0.0076	**significant**
Pure Error	1.96	3	0.6525			
Cor Total	14725.77	29				

decreases linearly for all type of mats. Two factors' interactions of CC and TT or CC and mat types were also show have some significant effect on IS. Significance contribution of every input factor on response can be understood by R^2 values. If R^2 values of any factor is greater than .1 indicates that model term (input variables) is not significant.

Incorporation of different type of kenaf mat with polymer also influenced the response. Fig. 6 show the effect of mat type in composites on response generated by regression model. Geometric of mat influenced the output response, bidirectional mat enhanced the flexural properties, unidirectional mat influenced the tensile strength and for impact strength randomly oriented contribute more.

3.2.2. *Effect of factor interaction on response*

The individual and interacted effect of independent variable on response depicted in Figs. 7, 8 and 9. The interaction curved show how the responses changes with independent variables. Based on response curves tensile and flexural properties were increase with increased in CC and with TT response were slightly increase and almost constant after 48 hr. of TT. Although, impact response was slightly increased with CC and then after response start to decrease, TT does not affect efficiently on impact response. For tensile response unidirectional mat is predominating for higher tensile strength, bi-directional mat composites show high flexural properties and for impact response randomly oriented mat contributing more compared to other kenaf mat reinforced composites. Response curves clearly indicate the importance of mat type in composites for enhancing its performance.

3.2.2.1. Tensile strength. 3D Response and contour surface plots for tensile strength at varying mat type are shown in Fig. 7 which show the effect of chemical concentration and treatment time on response. The curvilinear profile of response curve is because of quadratic model fitted. From response tensile response is first increase up to a certain limit then decrease. At every CC with varying TT the tensile response was increased significantly. Chemical treatment conditions improve the

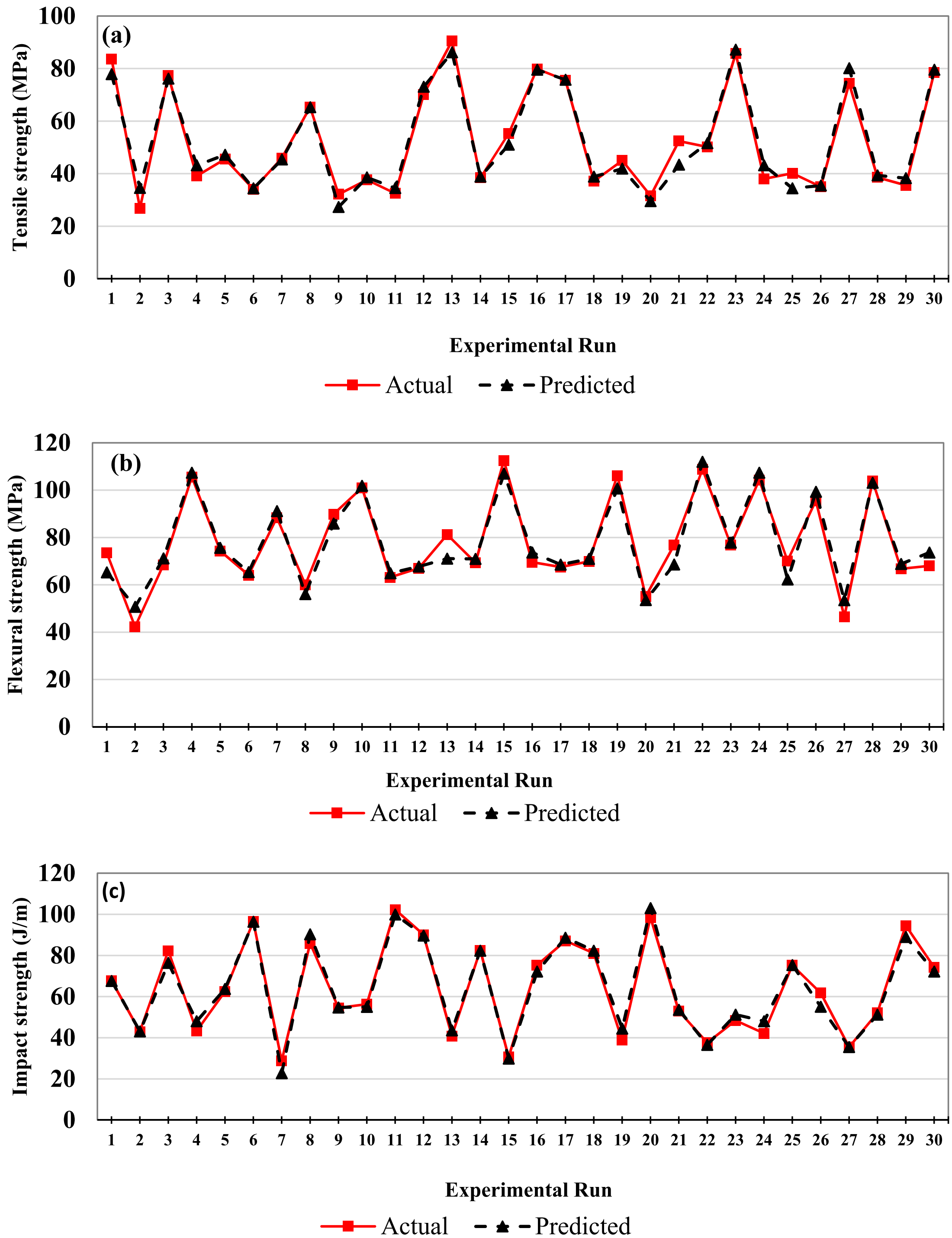

Fig. 2. Predicted vs. actual values of (a) Tensile strength, (b) Flexural strength and (c) Impact strength.

interfacial adhesion between reinforced and matrix that enhanced the response. In this study the chemical used for treatment of fiber is alkaline in nature, so it is required more time to remove the non-cellulosic constituent from the surface of fiber. Increment in response value increase subsequently with escalation in CC and TT. From the experimental observed value, the optimized condition for higher tensile response is at 20 % chemical concentration with 48hr. of treatment time. If TT is further increasing the tensile properties start to deteriorate, this is due to the damage of fiber surface. This trend of decreasing tensile response were seen in all type of kenaf mat reinforced composites. But it is interesting to note that tensile response is simply proportional to the CC and some for extent on TT if the individual effects of input variable were studies.

Apart from two numerical factor, tensile response is also dependent on third input factor (mat type) that is categorical factor. For all three different level of mat type tensile response were vary according to it. Unidirectional kenaf mat reinforced composites achieved higher tensile response than other kenaf mat reinforced composites. Response clearly shows the importance of kenaf mats geometry on tensile strength. In unidirectional mat, fiber reinforced along the direction of load which makes them cable to convey higher tensile load. But these alignments of fibers are absent in other kenaf fiber mat reinforced composites, little bit alignment of fiber along the load were seen in BDFRPC but as compared to UDFRPC the fiber in warp direction practically just half. Additionally,

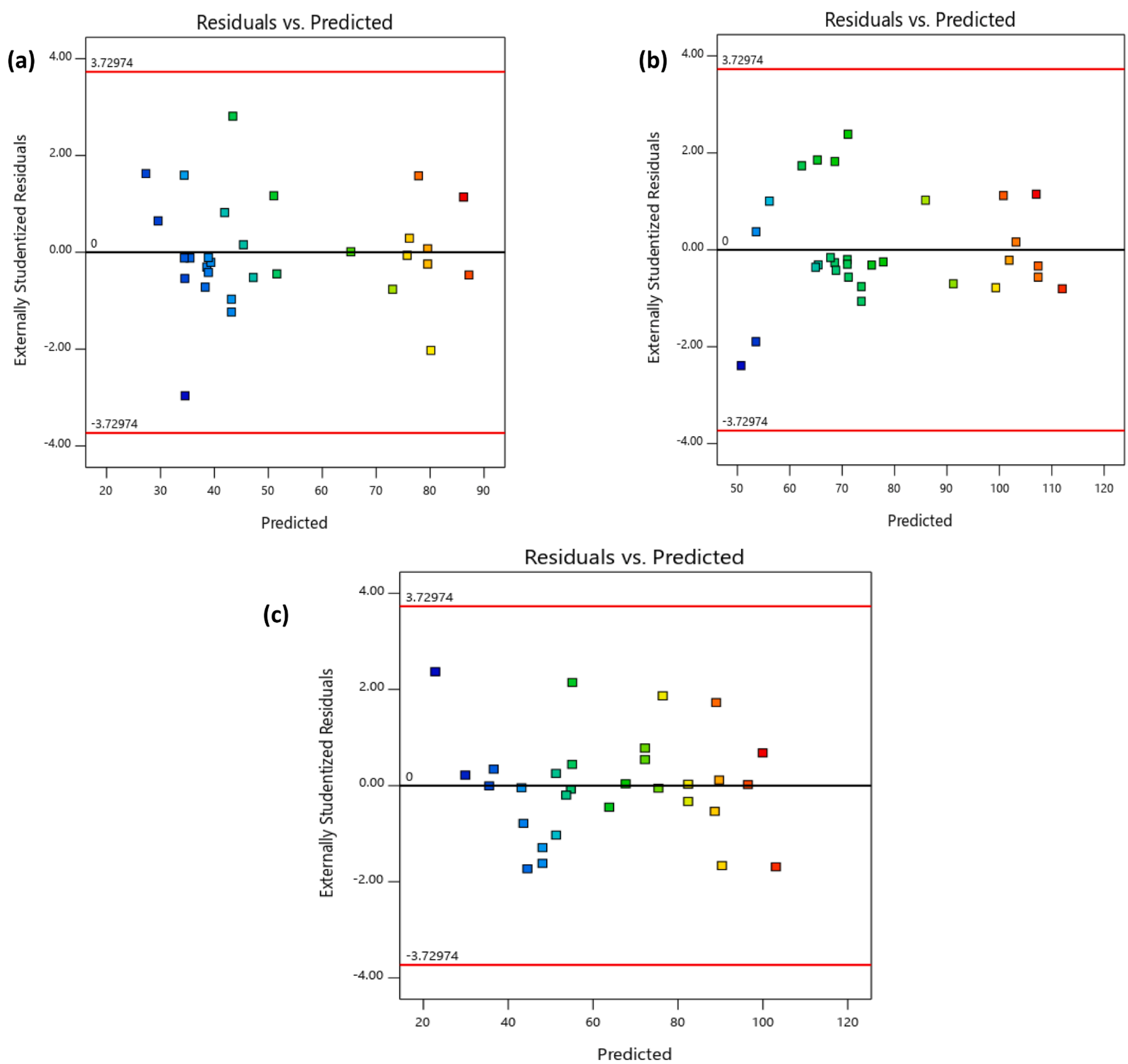

Fig. 3. Residual vs. predicted values of (a) Tensile strength, (b) Flexural strength and (c) Impact strength.

treatment of fiber with sodium acetate boosts up the tensile response. In Fig. 7 the individual effects of input variables on response can also be predict. For all type of kenaf mat reinforced composites TT show the same effect on response. Response first increases with increase in TT up to 48 hr. then further increment in TT value response remains constant and this nature behavior of tensile response were almost same for all type of kenaf mat composites. This variation of response with respected to TT is non-linearly. Although, the effect of CC on response are predominating, CC is the highly influencing factor for tensile response. The tensile response is directly proportional on CC, it was increased with CC ranges from lower to higher. This incremental variation of tensile response with respect to CC were same for all type of kenaf mat reinforced composites.

The interaction effect of CC and TT on tensile strength is shown in response contours in Fig. 7. The response curves ascertain that the increase in magnitude of CC and TT the tensile response was also increase. Increase CC with TT remove the non-cellulosic content from fiber surface sub sequentially. This interaction nature of numeric independent variables was almost same for all type of kenaf mat composites. But due to alignment of fiber in UDFRPC it has achieved higher tensile strength. At maximum CC if TT were further increased beyond approx. 48 hr. the tensile strength of developed composites was started to decrease due to damage of fiber surface. At maximum CC if fibers were further treated from optimized value fiber surface start to damage, this damage fiber surface directly influenced the interfacial adhesion between fiber and matrix material. Lower interfacial interaction reduces the tensile strength of developed composites. Response curves in Fig. 7 show the importance of all three-input factor on tensile response.

3.2.2.2. Flexural strength. Flexural strength is the bending ability of any material to resist bending load. The response plots exhibiting the flexural strength of different kenaf fiber mat reinforced PLA composites at varying CC ranging from 10 % to 20 % and TT ranging from 24 hr. to 72 hr. are shown in Fig. 8. Response curve and contour plots indicated that CC, TT, and geometry of fiber mat influenced the flexural strength of developed composites. Based on response surface curve, it is feasible that the flexural strength increases with increase the concentration of sodium acetate and treatment time. The flexural strength value is differed for every kenaf mat composites. This is the evident that the geometric of kenaf mat is also contributed to enhancing the flexural properties of developed composites. According to the response value generated from regression model, the increment in response value is up to the 20 % CC and approx. 48 hr. of TT. Further if TT were increased the flexural properties start to deteriorate that are clearly envision in

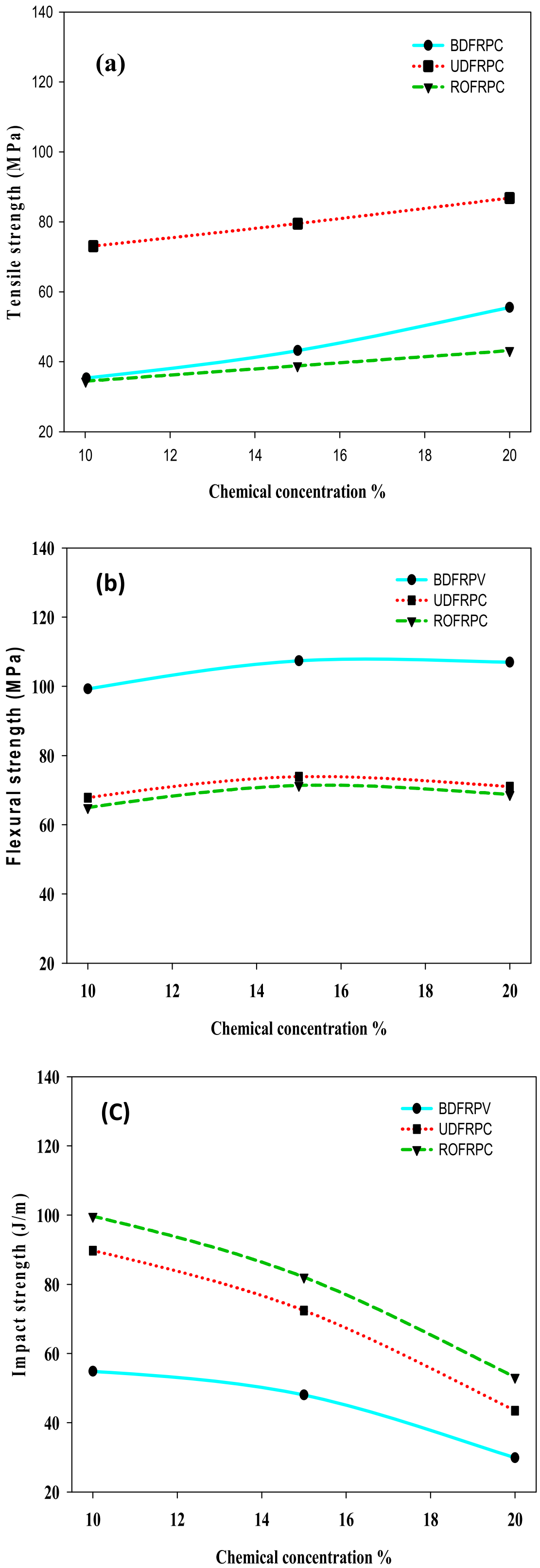

Fig. 4. Effect of chemical concentration on response (a) TS, (b) FS and (c) IS.

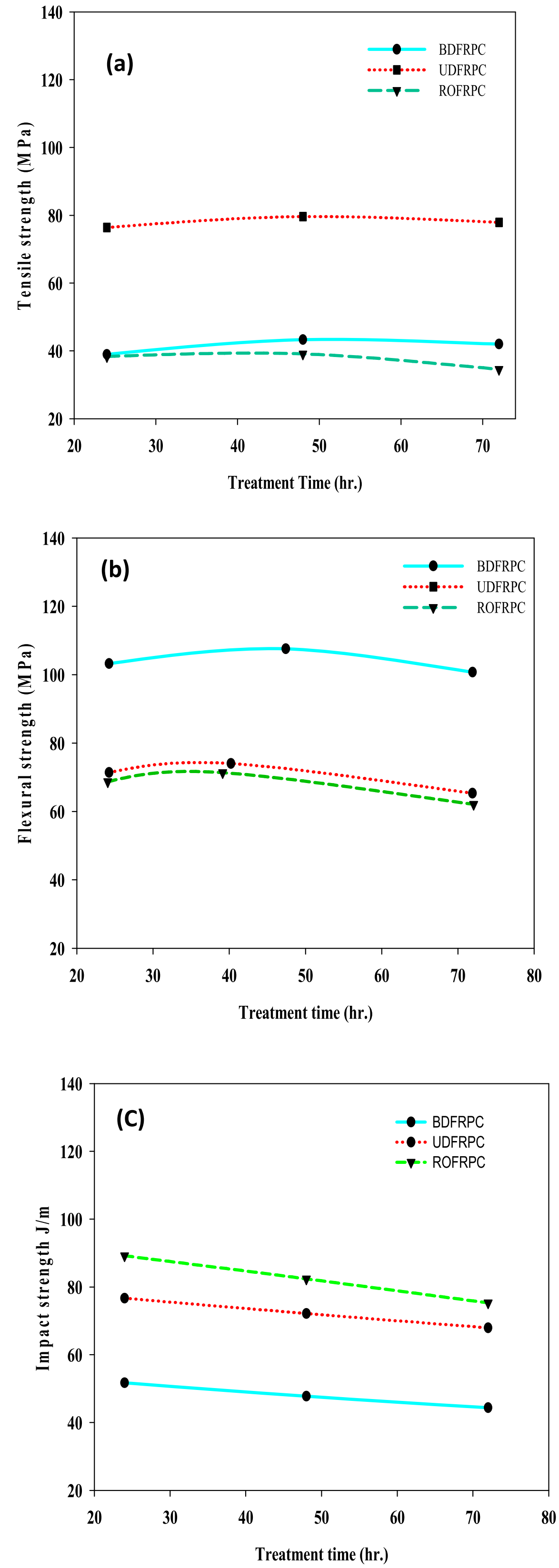

Fig. 5. Effect of treatment time on response (a) TS, (b) FS and (c) IS.

response curves. The apprehension behind is further increment in TT damage the surface of fiber which reduces the interfacial interaction between fiber and matrix material.

Bidirectional treated kenaf fiber mat composites show maximum flexural properties compared to other developed composites. In bidirectional mat fiber are aligned in warp and weft direction which develop a mat of inter-linking cross points. This inter-linking cross point mat developed composite resist the higher bending load. Whereas in other kenaf mats reinforced composites these inter-linking cross points

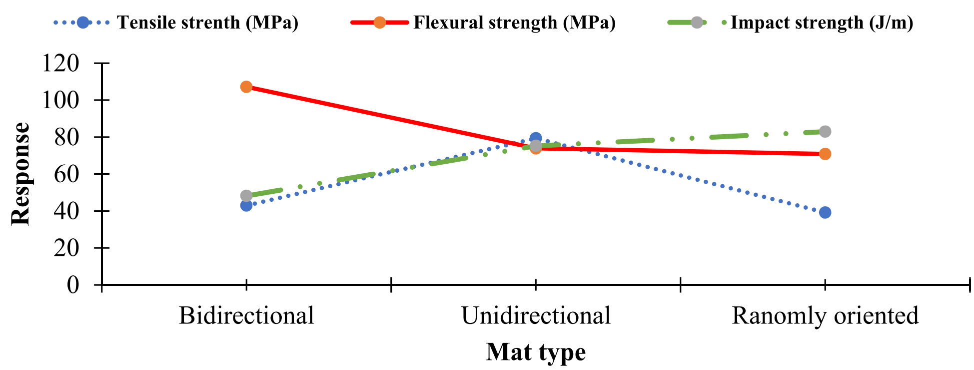

Fig. 6. Effect of mat types on response.

are absent which result drop in flexural properties. Effect of input numerical factors (CC and TT) on flexural response curve were almost the same. But the flexural response was highly affected by type of kenaf fiber mat used in reinforcement of composites. The parabolic profile of response curve is because of quadratic model fitted. As same tensile response if further TT increases the flexural properties of all developed composites start to deteriorate due to damage of fiber surface.

3.2.2.3. Impact strength. Impact response curves shown in Fig. 9, impact strength of any material tells about the energy absorbing capability of material during impact loading. Fig. 9 clearly understand that impact strength decreases with increase in CC and TT. In previous study various authors reported that, impact strength decreases with increase in CC or TT. Chaitanya et al. 2016 [9] done the experimental study on chemical treatment of Aloe Vera fiber at 10 % w/w of sodium bicarbonate with different treatment time of (24, 48, 72, 120, and 168 hr.). Authors concluded that impact strength of Aloe Vera /PLA composites is maximum up to 48 hr. TT after further increased in TT impact strength of developed composites starts to deteriorate. Fiber pullout, fiber fracture and crack propagation during impact loading are the main causes of composites failure [13, 14]. Improved bonding strength between fiber and matrix exhibited more fiber fracture instead of fiber pullout during impact loading. Fiber fracture instead of fiber pull out absorb lower energy during impact load [15]. Similar findings were observed in this study, after increase in CC with TT the impact strength of developed composites start to decrease. Response curves of impact strength with respect to input factors shown in Fig. 9. For Every impact response CC is highly influenced the impact strength, whereas effect of TT on impact strength is almost constant. But the interaction of these two factors CC and TT may influenced the impact strength of developed composites. Response contour curves indicates that ROFRPC achieved higher impact strength, the coordination of numeric input factor highly responsible for decreasing impact strength of developed composites. In ROFRPC, the arrangement of fiber in randomly form, that help to lock or arrested the crack formation arise during impact loading. Crack arresting capability of material improved its energy absorbing capability. Arresting of crack during impact load enhanced the material energy absorbing capability of material during sudden load. But this arrestment of cracks was absent or minimum in UDFRPC and BDFRPC, reason for lower impact strength compared to ROFRPC.

4. Optimization of the conditions for tensile, flexural and impact response

Regression model equation together solve to find the optimum input chemical treatment parameters. Design of experiment was used for maximization of tensile, flexural and impact response. Optimization of input parameters done based on response for individual mat and based on all comparable properties for individual mat type. The optimized output response is obtained by modeled equation by iterating several runs whenever the optimal solution was not obtained. Optimization help to reduce the number of trails to get a better result that exist between the ranging values of input parameters. Additionally, optimization helps to minimize the magnitude of input factor that is very important for economical point of view and it reduce the unnecessary used of entity for optimization during experimental study.

Fig. 10 shows the ramp response for tensile strength after optimizing the treatment parameters for all type kenaf mat reinforced composites. The obtained response value according to the regression model that may be different from experimental value due to error and noise. For BDFRPC, the optimized chemical treatment condition for tensile response are TT of 32.53 hr. and CC of 18.99 %. These optimized values give a tensile response of value 61.89 MPa, this value is according to the regression model it was less than experimental value with desirability of 0.685. Similarly, the optimization of input factors by iterating its value in regression model to get maximum output response for other kenaf mat reinforced composites. UDFRPC achieved higher tensile response of value 87.43 MPa after optimizing the input parameters, CC of 24 % and TT of 31.28 hr. The optimum condition for ROFRPC are CC of 20 hr. and TT of 31.998 give tensile response of 46.51 MPa. It is evidence from optimized parameters value all value are approximate near to each other, for CC value near to 20 % and for TT it is 32 hr. As all optimized value are near to each other but after that the tensile response are different for each mat. This is the evident not only the numeric factor, but categorical factor is also highly influenced the tensile response.

Similarly, the iteration of model equations was performed by design of experiment to find the optimum conditions for flexural response of chemical treated kenaf mats composites. Fig. 11 show the ramp response for flexural response after optimizing input numeric factor for individual kenaf mat type composites. BDFRPC achieved higher flexural strength of 112.45 MPa was experimentally observed at CC of 20 % and TT of 48 hr. But optimization according to design experiment after number of iterations of regression model. The optimized outcomes parameters are CC of 19.99 % with treatment time of 26.95 hr. give flexural response of 111.971 MPa. The difference in experimental and modeled value is due to noise and unwanted factors that are not considered in regression model design. UDFRPC and ROFRPC achieved lower flexural response value of 77.39 MPa and 75.60 MPa respectively according to regression model than BDFRPC. The optimized condition for UDFRPC is CC of 19.25 % and TT of 24 hr. whereas for ROFRPC CC of 19.93 % and TT of 24 hr. As these optimized factor values correlated with experimental input factor values the intensity of optimized factors are low. It means that optimization reduce the unwanted quantity of input factor that are unusable and have no effect on response. As same as tensile response all input optimized factor for flexural response are approx. same but have distinct flexure response value for developed kenaf mat reinforced composites. It implies that not only the input numeric but geometry of mat also contribution in enhanced the flexural response of developed composites.

Impact testing were performed to check the energy absorbing

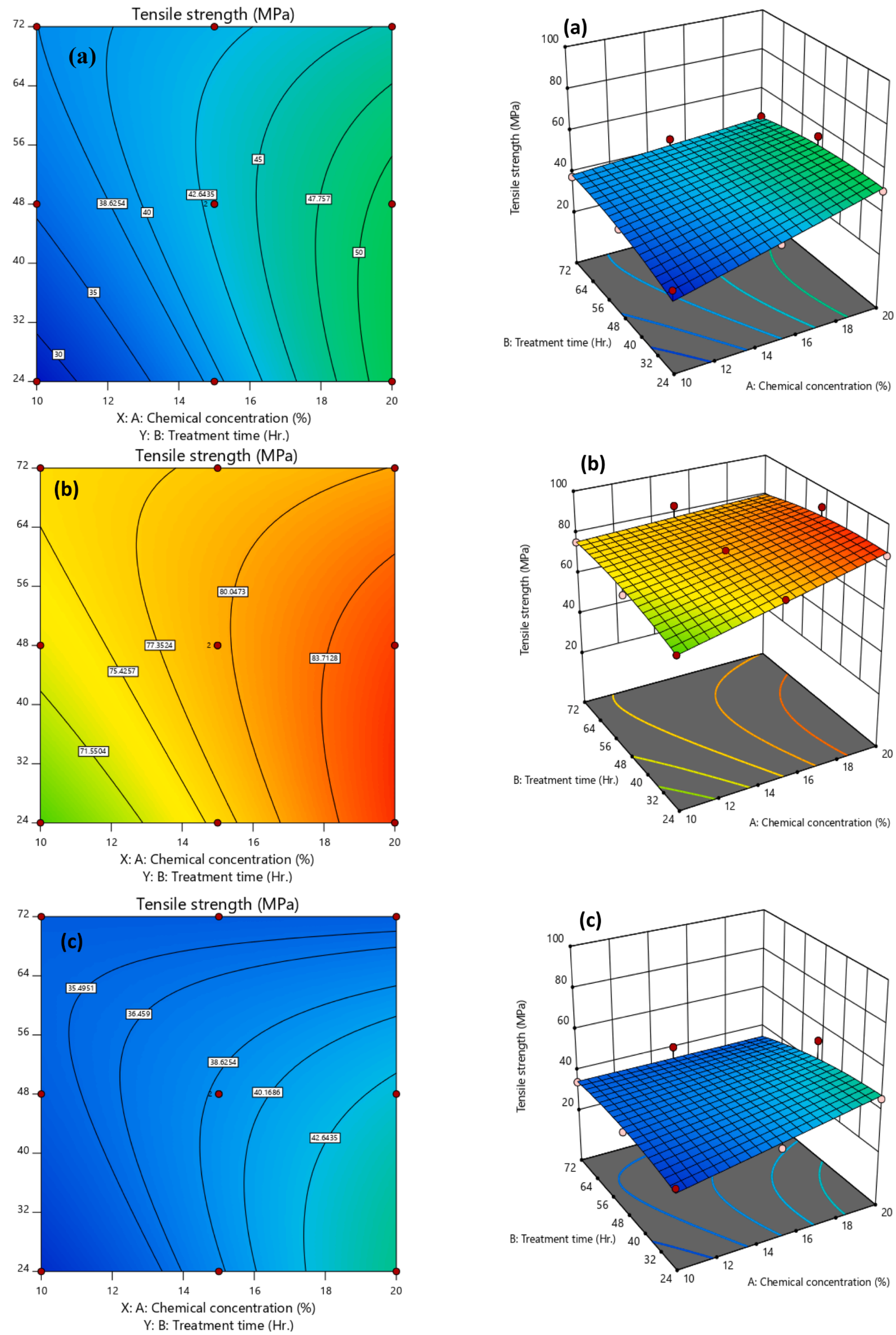

Fig. 7. Tensile Response surface of the effects two independent variables for individual mat type. (a) Bidirectional mat, (b) Unidirectional mat, (c) Randomly oriented mat.

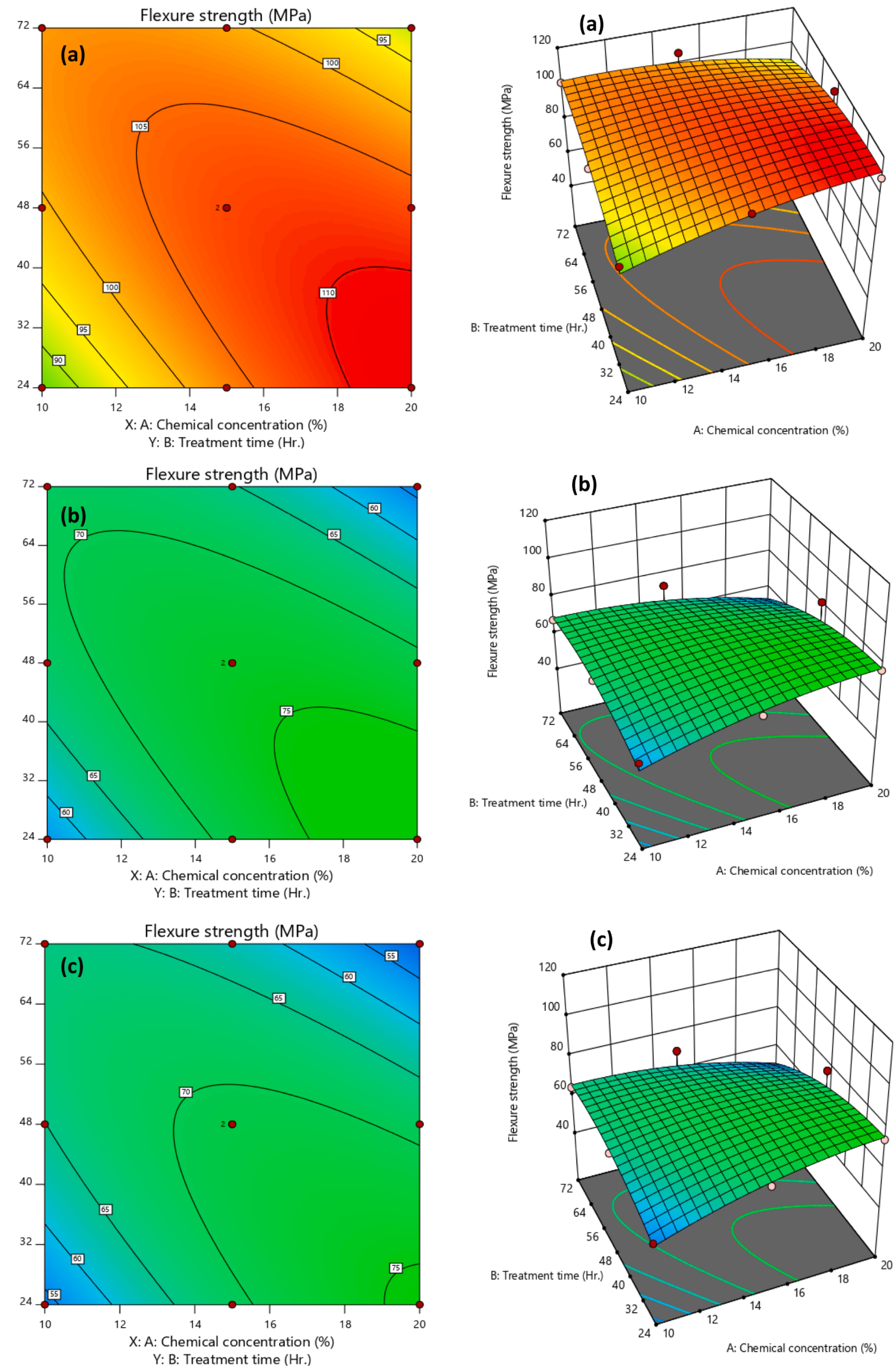

Fig. 8. Flexural Response surface of the effects two independent variables for individual mat type. (a) Bidirectional mat, (b) Unidirectional mat, (c) Randomly oriented mat.

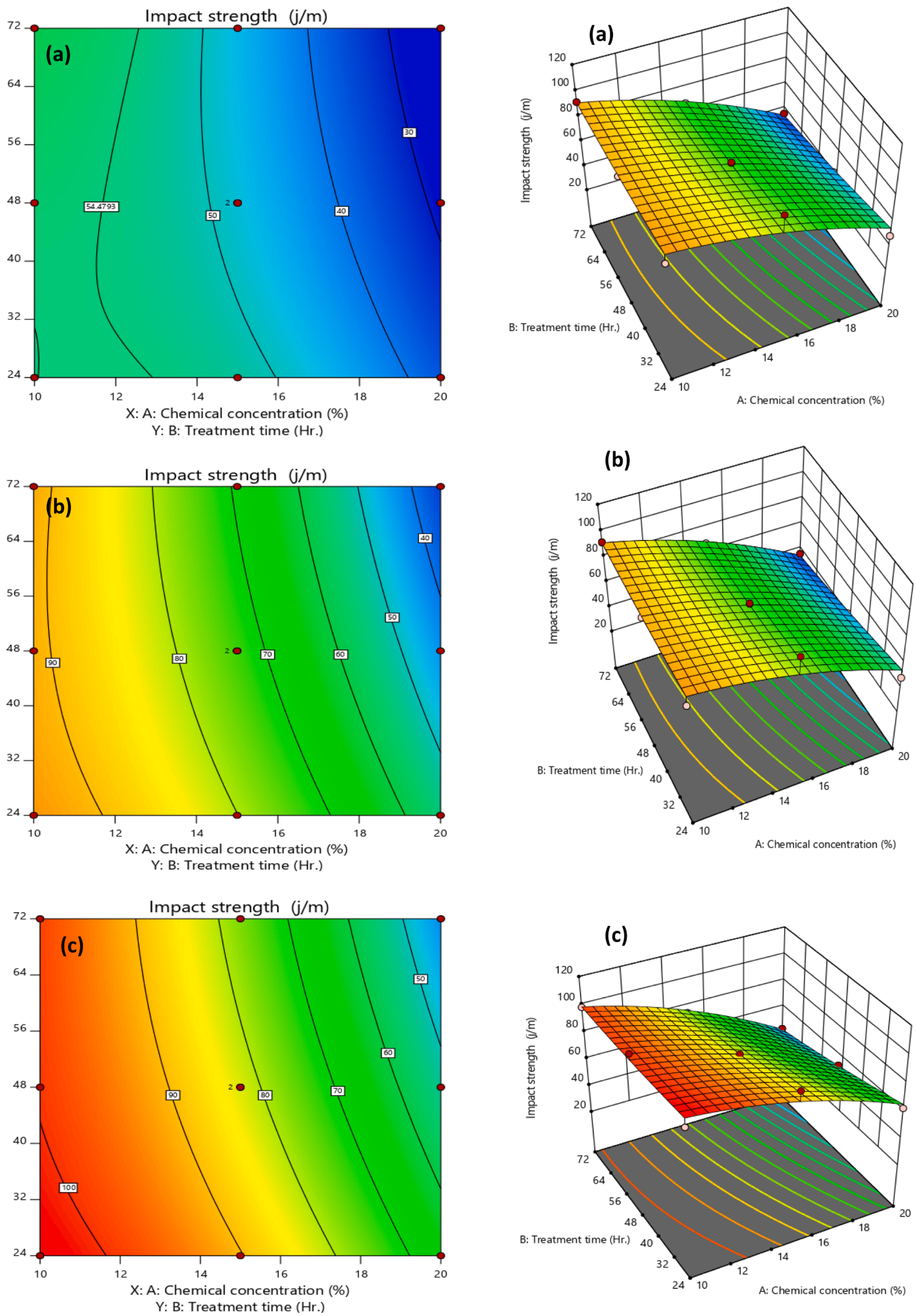

Fig. 9. Impact Response surface of the effects two independent variables for individual mat type. (a) Bidirectional mat, (b) Unidirectional mat, (c) Randomly oriented mat.

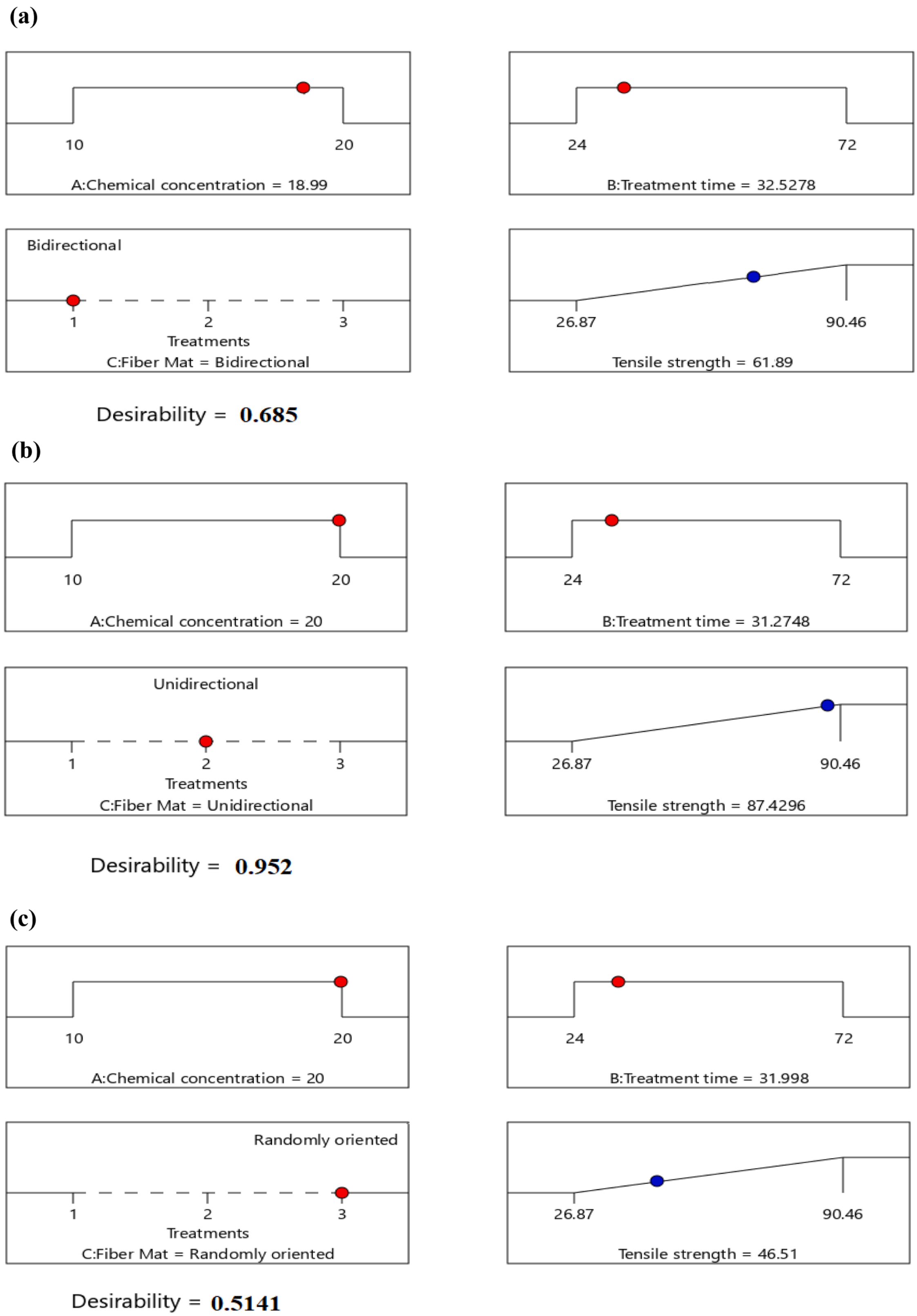

Fig. 10. Ramp function graph for chemical treatment condition and response as tensile strength for all different kenaf mat composites (a) BDFRPC, (b) UDFRPC and (c) ROFRPC.

capability of material during impact. Fig. 12 shows the effect of optimized parameters on impact strength of developed composites. ROFRPC composites achieved higher impact strength value of 102.3 J/m at CC of 20 % with treatment time of 48 hr. as experimentally observed. As per design experiments, the highest impact strength value is 101.239 J/m under the optimized conditions at 10 % of CC and 27.09 hr. TT. Difference in optimized impact response value compared to experimental value due not consideration of unwanted parameters during chemical

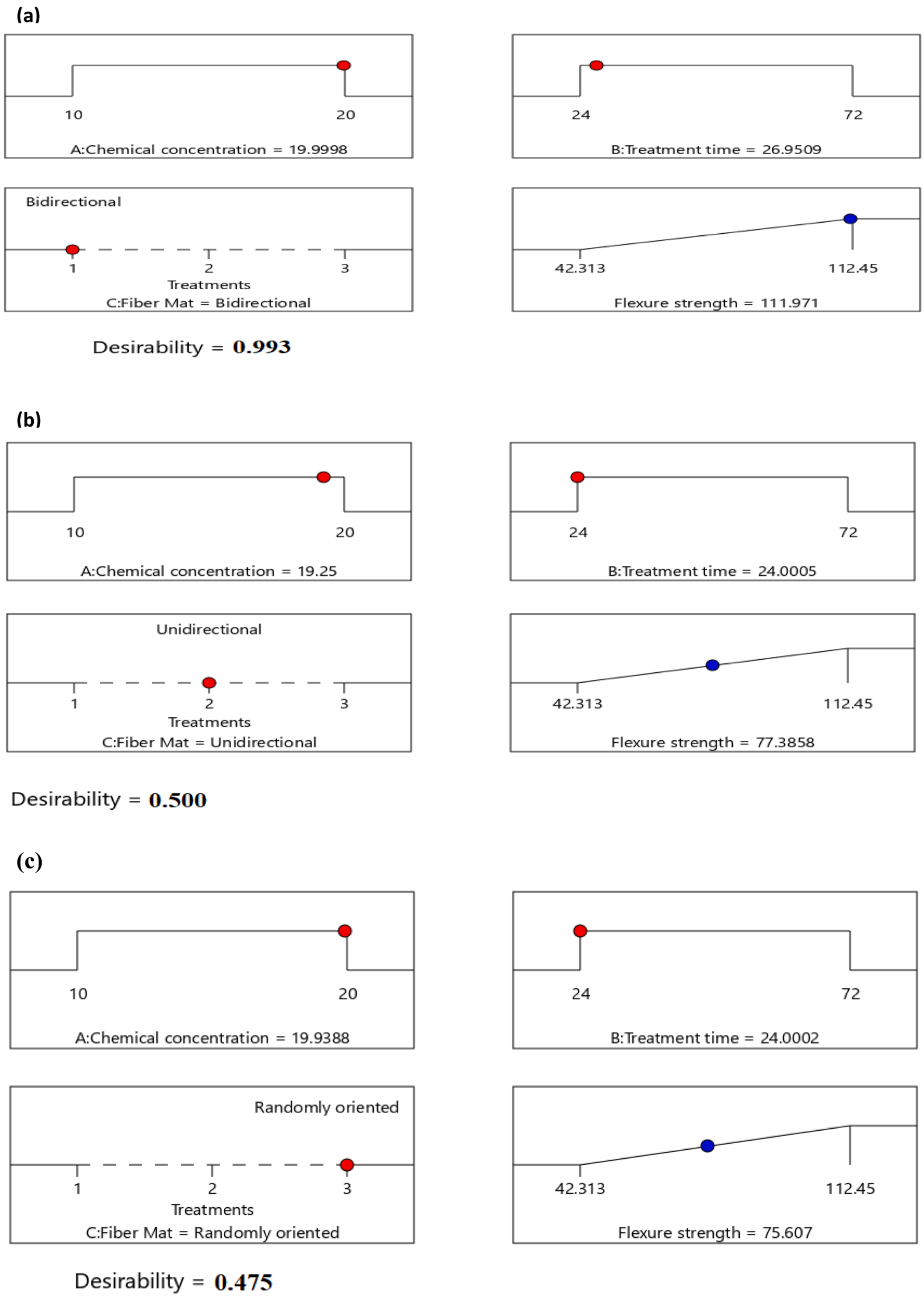

Fig. 11. Ramp function graph for chemical treatment condition and response as Flexural strength for all different kenaf mat composites (a) BDFRPC, (b) UDFRPC and (c) ROFRPC.

treatment, optimization reduced the unnecessary TT during experimental study. BDFRPC and UDFRPC achieved lower impact response as compared to ROFRPC. As shown in Fig. 12 the optimized parameters are approx. near to each other, but the impact response is different for each type of kenaf mat reinforced composites. It is the evident not only the input parameter, but fiber geometry may influence the impact response. Increase in chemical removed non-cellulosic content from surface of fiber and improved the interfacial adhesion between fiber and matrix material. Higher interfacial adhesion minimized the fiber pullout chances during impact loading instead fiber fracture is generally seen in

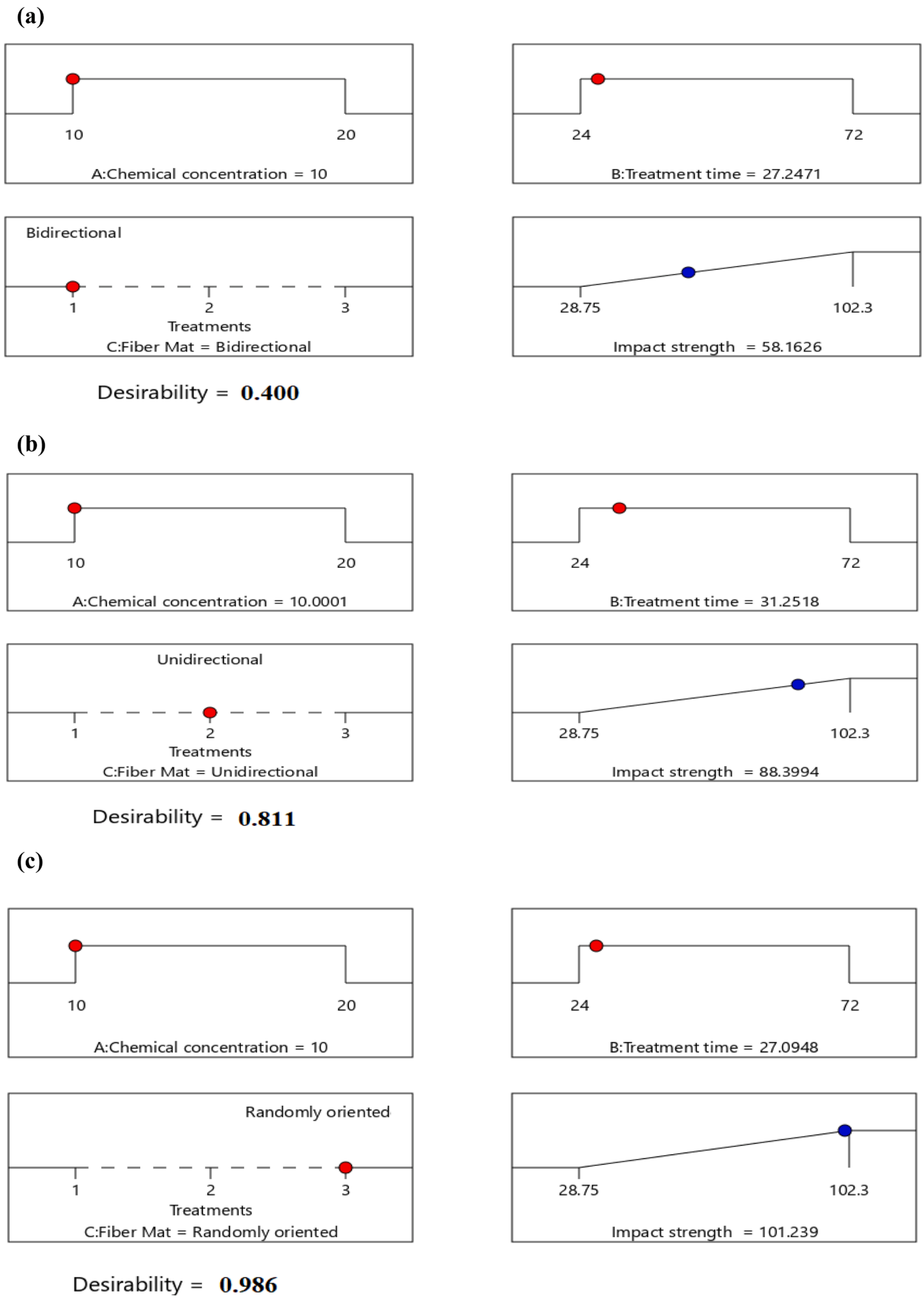

Fig. 12. Ramp function graph for chemical treatment condition and response as Impact strength for all different kenaf mat composites (a) BDFRPC, (b) UDFRPC and (c) ROFRPC.

that condition. Fiber pullout in composites during impact loading absorb higher impact energy instead of fiber fracture. This is the evident that composite materials have higher impact strength at lower CC and treatment time. Higher CC and TT increase the interfacial adhesion, results low energy absorption due to fiber fracture. This trend of decreasing impact strength with respect to increasing CC were seen in all type of kenaf mats reinforced composites. The fiber geometry is also a judging factor to decide its impact response.

Randomly arrangement of fiber in ROFRPC arrest the crack propagation during impact loading that enhanced the energy absorbing capability of material. But the arrangement of fiber in UDFRPC and BDFRPC are different from ROFRPC, and they are not cabled to arrest the crack during impact loading. This is the reason for Unidirectional and bidirectional mats achieving least impact value than ROFRPC. The concentration of fiber in warp direction of UDFRPC is very high that helps to arrest the fiber fracture for some extent and absorb high impact energy hence UDFRPC exist impact strength between BDFRPC and ROFRPC. Generated regression model equation helps to find out the response values at every range of response values.

4.1. Optimization of parameters for individual kenaf mat composite

Individual composites have distinct mechanical propoperties. UDFRPC have higher tensile properties and for flexural and impact

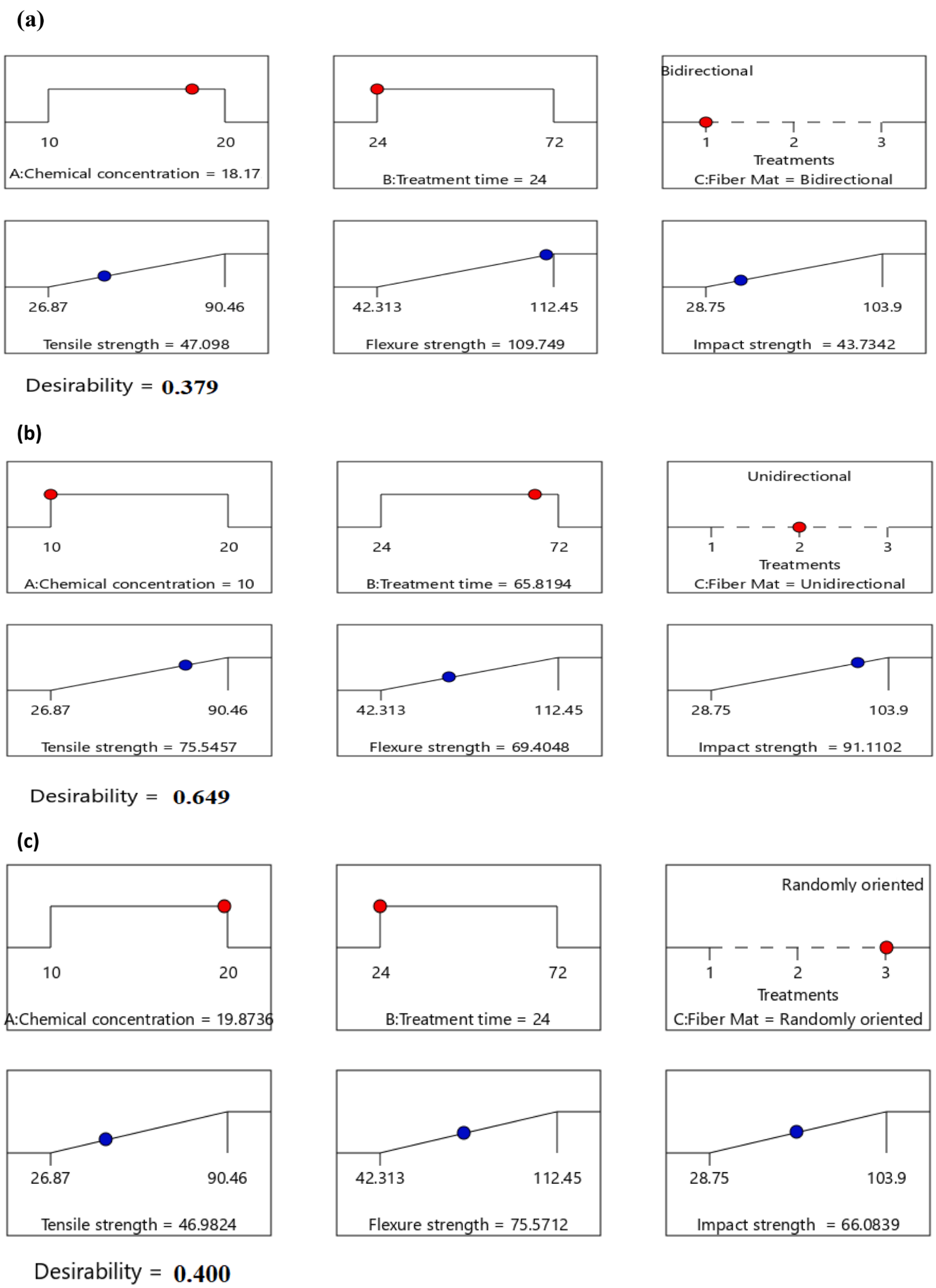

Fig. 13. Ramp function graph for chemical treatment condition and responses for all different kenaf mat composites (a) BDFRPC, (b) UDFRPC and (c) ROFRPC.

strength BDFRPC and ROFRPC are better options respectively. It means that every geometrically different kenaf mat composites is better option for individual appliaction accoding to the type of load acting on it. Practically, materials are considered under varying type of load during application. So, it is required for every material that it can bear all type of loading condition. Design experimentaion provide an environment to give an optimized condition for individaul mat have permissible in all loading conditions. Fig. 13-a,b,c shows the optimized condition for higher mechanical properties for all kenaf mats composites. Fig. 13a. shows that at 18.17 CC with TT of 24 hr. BDFRPC achieved optimum mechanical properties (Tensile stregth- 47.09 MPa, Flexural strength- 109.74 MPa and impact strength- 43.73 J/m). At these optimum parameters the BDFRPC achieved higher mechanical properties. As same as BDFRPC other kenaf mats reinforced compoistes optimized conditions are shown in Fig. 13b. and 13c. In Fig. 13b the optimized parametrs for UDFRPC are CC of 10 % and TT of 65.81 hr. give optimum mechanical properties (Tensile stregth- 75.5457 MPa, Flexural strength- 69.40 MPa and impact strength- 91.11 J/m). Similarly, for ROFRPC the optimized parameters are shown in Fig. 13c. at CC of 19.87 % with TT of 24 hr. the composite achieved higher mechanical properties (Tensile stregth- 46.98 MPa, Flexural strength- 75.57 MPa and impact strength- 66.08 J/m). For given optimized input paramters maximum output responses were obtained for individual kenaf mat reinforced composites.

5. Conclusion

In order to optimize the chemical treatment conditions for maximized output responses, a set of experiments based on RSM central composite module was conducted. The response results recommended that this technique for optimization is compelling to minimize chemical concentration and treatment time without immolate the output response (Tensile, flexural and impact strength). Chemical treatment of kenaf fiber with sodium acetate enhanced the properties of developed compoistes. Experimental results indicated all three independent factor chemical concentration, treatment time and type of kenaf mat (categoric factor) contributed to enhance the properties of developed composites. For tensile, flexural and impact responses, the predominating numerical factor to enhanced the response is chemical concentration as compared to treatment time. The reponses were successfully concluded from second order polynomial equation generated by RSM in built ANNOVA. This technique was also used to interrogate the effect of interaction of factors such as chemical concentration and treatment time for individual mat on response. Optimization of input parameters for maximizing the output responses were also predicted by RSM. The optimum conditions were obtained for individual kenaf mat compoistes as follows. For UDFRPC, the optimized condition for maximum tensile response of 87.43 MPa have chemical concentration of 20 % and treatment time of 31.27 hr. BDFRPC achieving high flexural response of 111.97 MPa have chemical concentration of 19.99 % and treatment time of 26.95 hr. and for maximum impact response of 101.239 J/m have chemical concentration of 10 % and treatment time of 27.09 hr. All values are obtained by number of iteration of regression equation. These values are mathematically generated and it have some error/difference in comparision to experimental values. For maximizing all properties of individual kenaf mat reinforced composites, the optimized condition are as follows: At 18.17 % of chemical concentration with 24 hr. of treatment time BDFRPC achieved maximum tensile, flexural and impact response of value 47.09 MPa, 109.75 MPa and 43.73 J/m respectively. Although, UDFRPC optimum conditions are at chemical concentration of 10% with treatment time of 65.81 hr. has corresponding output response tensile, flexural and impact are 75.55 MPa, 69.40 MPa and 91.11 J/m respectively. Similarly, for ROFRPC the optimized conditions for maximum response are chemical concentration of 19.87 % and treatment time of 24 hr. give tensile, flexural and impact reponse of 46.98 MPa, 75.57 MPa and 66.08 J/m respectively. This approch neccessarily helped to minimize the number of experimental trail for optimizing the responses.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

References

[1] A. Chamas, H. Moon, et al., Degradation rated of plastics in the environment, A*CS Sustain. Chem. Eng* 8 (2020) 3494–3511.
[2] N Chand, M Fahim, Natural fibers and their composites, tribology of natural fiber polymer composites. Woodhead Publishing Series in Composites Science and Engineering, Woodhead Publishing, 2008, https://doi.org/10.1533/9781845695057.1.
[3] F. Hassan, R. Zulkifli, et al., Kenaf fiber composite in automotive industry: an overview, Int. J. Adv. Sci. Eng. Inform. Technol. 7 (1) (2017) 315.
[4] M.M Kabir, H. Wang, et al., Chemical treatments on plant-based natural fibre reinforced polymer composites: An overview, Compos. Part B Eng. 43 (2012) 2883–2892.
[5] F Delbecq, Y Wang, et al., Hydrolysis of hemicellulose and derivatives—a review of recent advances in the production of furfural, Front. Chem. (2018), https://doi.org/10.3389/fchem.2018.00146.
[6] A Oushabi, S Sair et al. (2017) The effect of alkali treatment on mechanical, morphological and thermal properties of date palm fibers (DPFs): Study of the interface of DPF–Polyurethane composite. 23; 116-123.
[7] T. Lakhanisky, SIDS Initial Assessment Report for SIAM 15 (2022). http://www.inchem.org/documents/sids/sids/sodbicarb.pdf (Accessed 20 April.
[8] Potassium bicarbonate (073508) and sodium bicarbonate (073505) fact sheet, https://www3.epa.gov/pesticides/chem_search/reg_actions/registration/fs_G-135_01-Oct-04.pdf (Accessed 20 April 2022).
[9] S Chaitanya, I Singh, Ecofriendly treatment of aloe vera fibers for PLA based green composites, Int. J. Precis. Eng. Manufact.Green Technol. 5 (2018) 143–150.
[10] V. Fiore, T. Scalici, et al., A new eco-friendly chemical treatment of natural fibres: Effect of sodium bicarbonate on properties of sisal fibre and its epoxy composites, Compos. Part B Eng. 85 (2016) 150–160.
[11] J.K. Wells, P.W.R. Beaumont, Crack-tip energy absorption processes in fibre composites, J. Mater. Sci. 20 (1985) 2735–2749.
[12] A Manral, P Bajpai. Effect of non-acidic chemical treatment of kenaf fiber on physico mechanical properties of PLA based composites. J Natural Fiber.
[13] Manral A, P.K Bajpai, Static and dynamic mechanical analysis of geometrically different kenaf/PLA green composite laminates, Polym. Compos. (2019), https://doi.org/10.1002/pc.25399.
[14] M.J.A. Van den Oever, H.L. Bos, K. Molenveld, Appl. Macromol. Chem. 272 (1999) 71.
[15] S chaitanya, I singh, Sisal fiber-reinforced green composites: effect of ecofriendly fiber treatment, Polym. Compos. (2017), https://doi.org/10.1002/pc.24511.