

Recipe optimisation for sugarcane bagasse fibre reinforced soy protein biocomposite

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A series of biodegradable composites has been prepared using sugarcane bagasse fibres as reinforcement and soy protein isolate (SPI) as matrix. Sugarcane bagasse has been pretreated with 2% NaOH solution for improving its reinforcement. Recipe for matrix includes soy protein isolate as prime ingredient, glyoxal as crosslinking agent and glycerol as plasticizer. The composites are characterised for tensile properties. Three-factor and three-level Box-Behnken design is used to optimize the mass fraction of fibres, percentage of crosslinking and plasticizing agent. The model predicts that the best possible results would be achieved with the recipe having 20% fibres with matrix recipe of 11% glyoxal, 17.7% glycerol and 51.3% SPI by weight. The predicted and observed tensile strength of composite is found to be comparable. The glycerol content is found to play an important role in improvement of tensile property of composite.

Keywords: Biocomposites, Green composites, Soil burial, Soy protein, Sugarcane bagasse fibre

1 Introduction

Synthetic fibre based polymer composites have become popular in daily life applications due to their large scale production and easy availability. Glass fibres have been widely used in synthetic polymer composites as reinforcement^{1,2}. Natural fibres are used with non-biodegradable matrices to produce biocomposites²⁻⁵. These fibres are renewable, show higher specific strength and cause less abrasion during processing as compared to glass fibres^{2,6}. On the other hand, the recycling of thermoplastic matrices consumes energy and deteriorate their mechanical properties^{7,8}.

Biodegradable composites are composed of biodegradable components such as natural fibres and biopolymer resin, and hence these are called 'green composites'. India produces a huge amount of various types of agriculture waste every year and it is among the top producers of sugarcane in the world. The production of sugarcane has increased constantly since past few decades and so the production of bagasse⁹. Bagasse is currently being used as fuel with low calorific value¹⁰ and also in paper and pulp industry¹¹. Sugarcane bagasse is a fluffy mass with pith and fibres. NaOH treatment removes the pith and leaves behind only fibres. Moreover, the lignin and hemicellulose within the fibres are also removed by this treatment and the resulting fibres have cleaner

and rough cellulosic surface, helping better interface with matrix¹². Sugarcane fibre has moderate mechanical properties as compared to other lignocellulosic fibres such as bamboo, flax, kenaf, jute, etc¹³. Justiz-Smith *et al.*¹⁴ discussed various chemical and physical aspects of sugarcane bagasse fibres to determine its potential as reinforcement in composites. Luz *et al.*¹⁵ studied the environmental benefits of replacing talc by sugarcane bagasse fibres in polypropylene based composites for automobiles. Hozdic *et al.*¹⁶ optimised the green composites with biopolyesters and sugarcane bagasse fibres. Composites resulted in maximum of 65 MPa flexural strength. Similar green composites were discussed by Chiellini *et al.*¹⁷ and Vallejos *et al.*¹⁸, where they discussed dynamic mechanical properties of sugarcane fibre reinforced PVA and tensile behaviour of starch reinforced by sugarcane fibres respectively. Mulinari *et al.*¹⁹ and Ramraj²⁰ used sugarcane fibres with HDPE and polypropylene respectively. Trindade *et al.*²¹ manufactured and studied mechanical behaviour of sugarcane fibres in thermoset phenolic resin. Some studies are also oriented towards the use of these fibres in particle boards^{22,23}.

Commercially soy protein is available in three forms, namely (i) soy flour (50-55% protein), (ii) soy protein concentrate (60-70% protein), and (iii) soy protein isolate (>90% protein). Soy protein isolate (SPI) has the highest amount of protein content among other soy derivatives. Soy proteins are

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primarily globulins²⁴. Further, 7S and 11S globulins contribute 37% and 31% of total protein respectively and have ability to polymerise, which can result in superior mechanical properties of matrix²⁵. The reasons for selecting SPI as matrix is due to its biodegradable nature, ability to form strong interface with fibre due to polar nature, availability of various polar sites, such as hydroxyl, carboxyl, amine groups²⁶, its ability to form 3D network due to disulphide linkages from 11S proteins that help crosslinking of structure, and renewable in nature^{25, 27}.

Liu *et al.*²⁸ studied green composites of pineapple leaf fibres with soy. Dispersion of fibres and the interface studies were carried out for 30% fibre loaded composites. Kumar and Zhang²⁹ proposed a “dip-coating” to impart hydrophobic surface to aligned ramie reinforced soy composites. Lodha and Netravali³⁰ modified soy protein isolate by stearic acid and used it with ramie fibres. Composites displayed improved tensile strength in both axial and transverse directions than non-modified soy protein isolate based samples.

SPI is very brittle in pure state and hence plasticizers have to be added to reduce its brittleness. Among various plasticizers, glycerol was chosen because of its small and highly polar molecule. Glyoxal was used for crosslinking the SPI.

This study is directed towards determining the ratio of each of the components, glycerol, glyoxal in matrix and the fibre mass fraction to obtain maximum tensile strength of biocomposite. The interactions between these components are explored in this paper. It is also discussed that how the components and their interactions affect the tensile strength of composites.

2 Materials and Methods

2.1 Materials

Crushed sugarcane bagasse was bought from Munirka, New Delhi. Glycerol, glyoxal and soy protein in form of SPI were supplied by Plus Chemicals Pvt Ltd, New Delhi, India.

2.2 Methods

Sugarcane bagasse was thoroughly washed in warm water to remove any soluble impurity and dried in oven at 60°C for 12 h. Hard cover of sugarcane was removed manually after drying. The remaining lumps of bagasse were cut into pieces of 2cm so as to obtain the fibres of 2cm length in later stages. These pieces of bagasse were immersed in a solution of 2% NaOH

for 12 h in a closed container at room temperature. The bagasse was squeezed and individualized manually at regular intervals of 3 h. This action removed the pith sticking to the fibres. When all the fibres were free of pith, they were rinsed thoroughly in running tap water to remove the alkali. Treated fibres were stored in water to avoid agglomeration. Sheets of randomly arranged bagasse fibres were produced by water laying technique. Thick paste of SPI was made by dissolving it in heated water at 70°-80 °C along with glycerol and glyoxal, under constant stirring by magnetic stirrer; pH of the paste was maintained at 8.

Composites samples were prepared for various mass fractions of fibres, glycerol, glyoxal and SPI by hand laying the recipe paste on the fibre sheets. This setup was placed uncovered inside an oven at 65°C for 8 h. The composites were taken out and cut to desired dimensions for tensile testing.

2.2.1 Design and Analysis of Experiments

Three-factor and three-level Box-Behnken design of experiment was used in conjunction with response surface methodology of analysis. Process factors were amounts of fibre, glyoxal and glycerol. Preliminary tests for tensile strength were carried out by making films from the mixture of SPI, glyoxal and glycerol. These tests showed that soy films having glycerol 15% and glyoxal 10% on weight of SPI were stronger than other compositions. The study is carried out because the preliminary experiments on films do not reflect the effect of plasticization and cross linking of SPI on interface with fibres. Finally the study also indicates how much mass fraction of the fibres is to be used in composites for optimum results. There were three different levels for each of the process factors (Table 1).

In accordance with a 3³ Box-Behnken design of experiments, fifteen runs were conducted under identical experimental conditions. The details of these runs are shown in Table 2.

In this way fifteen samples of composites were prepared. The tensile strength of these samples was measured. The results of experiments were analyzed

Table 1– Process factors and their levels according to Box-Behnken design

Factor	Level		
	-1	0	+1
Amount of fibre (A), %	15	20	25
Amount of glyoxal (B), %	5	10	15
Amount of glycerol (C), %	10	15	20

Table 2 — Layout of runs experiments according to 3³ Box-Behnken design

Run	Coded level		
	Amount of fibre	Amount of glyoxal	Amount of glycerol
1	-1	-1	0
2	+1	-1	0
3	-1	+1	0
4	+1	+1	0
5	-1	0	-1
6	+1	0	-1
7	-1	0	+1
8	+1	0	+1
9	0	-1	-1
10	0	+1	-1
11	0	-1	+1
12	0	+1	+1
13	0	0	0
14	0	0	0
15	0	0	0

by response surface methodology using Design-Expert[®] Version 8.0.7.1 software. The single as well as interaction effect of the process factors on the tensile strength of the composites was examined. The response surfaces were modeled using following quadratic equation:

$$y = \lambda_0 + \lambda_1 A + \lambda_2 B + \lambda_3 C + \lambda_{12} AB + \lambda_{23} BC + \lambda_{31} CA + \lambda_{11} A^2 + \lambda_{22} B^2 + \lambda_{33} C^2$$

Here *y* represents dependent variable; *A*, *B* and *C* denote fibre mass percentage, glycerol percentage and glycerol percentage; λ_0 is constant; λ_1 , λ_2 and λ_3 are linear coefficients of independent variables; λ_{12} , λ_{23} and λ_{31} are mixed quadratic coefficients; and λ_{11} , λ_{22} and λ_{33} are single quadratic coefficients.

3 Results and Discussion

3.1 Tensile Strength of Composite Samples

Prepared samples were tested for tensile strength under identical conditions according to ASTM D638 standard in accordance with the Box-Behnken design of experiment. Figure 1 shows the images of composite samples after tensile testing, and the results of experiments are shown in Table 3.

Standard regression technique was used to obtain following response surface equation:

$$y = 17.63 + 1.11A + 1.19B + 1.93C - 0.47AB + 0.20AC - 0.050BC - 3.43A^2 - 1.98B^2 - 1.85C^2$$

Table 3 — Tensile strength of composites

Run	Process factors			Tensile strength, MPa		
	Amount of fibre %	Amount of glyoxal, %	Amount of glycerol, %	Experimental value	Predicted value	Error value
1	15	5	15	9.5	18.1	-8.6
2	25	5	15	12.0	18.0	-6.0
3	15	15	15	13.4	18.1	-4.7
4	25	15	15	14.0	18.1	-4.1
5	15	10	10	10.0	18.0	-8.0
6	25	10	10	12.5	18.0	-5.5
7	15	10	20	11.8	18.2	-6.4
8	25	10	20	15.1	18.2	-3.1
9	20	5	10	10.1	18.0	-7.9
10	20	15	10	12.0	18.0	-6.0
11	20	5	20	15.7	18.2	-2.5
12	20	15	20	17.4	18.2	-0.8
13	20	10	15	18.0	18.1	-0.1
14	20	10	15	16.9	18.1	-1.2
15	20	10	15	18.0	18.1	-0.1

Table 4 — Analysis of variance of response surface model

Source	Sum of squares	Degree of freedom	Mean square	F-value	P-value
Model	114.29	9	12.7	8.12	0.0164
Residual	7.82	5	1.56		
Total	122.12	14			



Fig. 1 — Ruptured composite samples after tensile testing

where *y* denotes the predicted tensile strength; and *A*, *B* and *C* represent amount of fibre, glyoxal and glycerol respectively. Based on this equation, the tensile strength of the fifteen composite samples was predicted (Table 3). The difference between the experimental and the predicted surface potential of fifteen samples is also listed as error in Table 3. The coefficient of determination (*R*²) between the experimental and the predicted results is found to be 0.9359. The summary of the analysis of variance for the model is shown in Table 4.

3.2 Effect of Various Components on Tensile Properties

3.2.1 Effect of Amount of Glyoxal and Fibre

The response surface and contour plot depict the maximum tensile strength of composites for amount of glyoxal from 5% to 15% and fibre from 15% to 25%, keeping the glycerol percentage as constant (Fig. 2). It can be seen that the lines of glyoxal at 15% fibres are not parallel to the ones at 25% fibres.

Glyoxal is responsible for crosslinking of SPI matrix. Initially, when the glyoxal content is increased, at any fibre content, the tensile strength of composite increases steadily. It is attributed to the integrity of the matrix that rises because of crosslinking and thus providing better load sharing between the fibres in the composite. After a maximum, the increase in glyoxal content decreases the tensile strength of composites. It may be due to self-crosslinking between the glyoxal molecules that results in poor crosslinking within SPI matrix. Thus, the weakened matrix does not contribute efficiently towards the load transfer between the fibres that reduces the tensile strength of composites.

Initially at a fixed amount of glyoxal, the increase in fibre content increases the total surface area for the interaction with matrix. The interface increases and strengthens the matrix around the fibres. After a certain mass fraction of fibres, the increase in fibre content decreases the tensile strength of composite because at such high level of fibre content, the matrix is insufficient to impregnate all the fibres. Certain areas appear in the composite where matrix is not present to embed the fibres. These fibre rich areas act as defects in the composite.

Therefore, the increase in glyoxal and fibre content initially increases the tensile strength of composite and after a certain maximum, they contribute negatively towards it.

3.2.2 Effect of Amount of Glycerol and Glyoxal

Figure 3 shows the interaction and role of glycerol and glyoxal in the composite at different amounts towards the tensile strength of composite samples. Both glycerol and glyoxal directly affect the performance of SPI matrix that finally affect the tensile strength of composite. Glycerol acts as a plasticizing agent for SPI matrix, whereas glyoxal is responsible for its crosslinking. Plasticization by glycerol reduces the brittle nature of SPI and increases the elongation at load without rupture. This plasticization plays crucial role in transferring the load from one fibre in the composite to the other through the matrix. Glycerol content from 10% to 20% slowly improves the tensile strength due to higher strain values that the matrix can achieve.

As discussed earlier, glyoxal helps in strengthening the matrix by crosslinking it. Further increase in concentration of glyoxal may lead to its self-crosslinking and it might be incompatible with the SPI matrix.

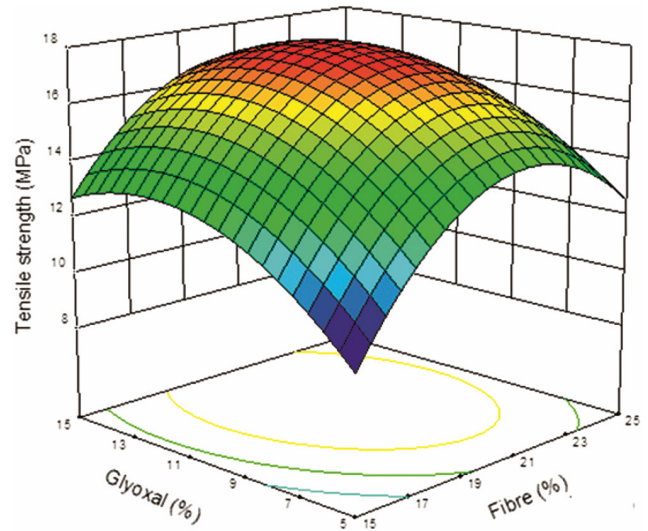


Fig. 2 — Effect of glyoxal and fibre amount on tensile properties of composite

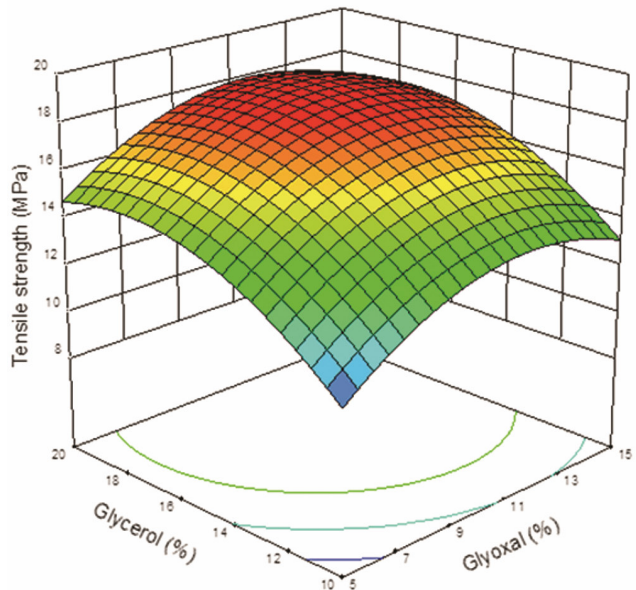


Fig. 3 — Effect of glycerol and glyoxal on tensile properties of composite

Glyoxal crosslinks pure soy effectively. It is possible that the increasing amount of glycerol hinders the cross linking by glyoxal because glycerol is intimately mixed with the soy due to its highly polar nature and small molecular size. This is evident from the lowering of tensile strength at higher mass fraction of glycerol. As seen in Fig. 3, both glycerol and glyoxal contribute positively towards the matrix performance. Although the higher amount of glycerol is avoided as it has a tendency to leach out and hinders the interaction with fibre.

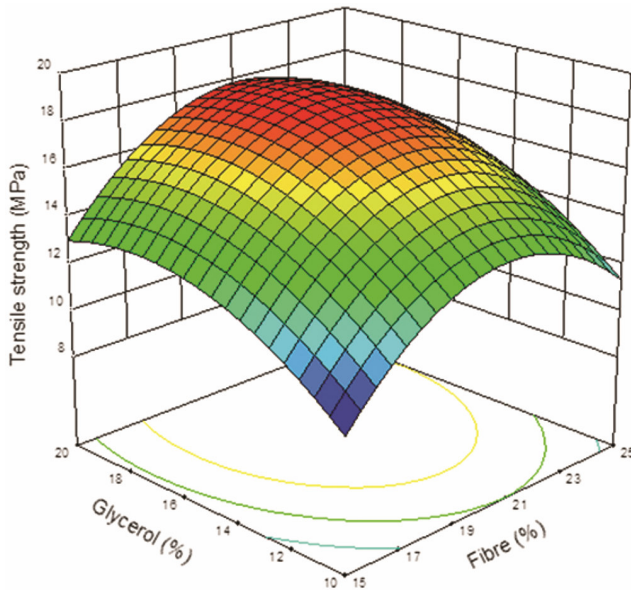


Fig. 4 –Effect of glycerol and fibre on tensile properties of composite

3.2.3 Effect of Amount of Glycerol and Fibres

It can be seen from Fig. 4 that the composite samples have lower tensile strength at a lower amount of both glycerol and the fibres. Tensile strength of composite samples reaches maximum when the amounts of both glycerol and fibres are increased further, and a decrease is observed at even higher amounts of glycerol and fibres. It can be noted that the fibres contribute directly towards the strength of composites, whereas glycerol improves the performance of matrix. Less number of fibres provide less area for interfacial interaction. This interfacial area is increased when more fibres are added because more surface area of fibres is available to interact with the matrix. Glycerol reduces the brittleness of SPI matrix and therefore helps in efficient load transfer between the fibres. Thus, at the initial stage, both glycerol and fibres contribute positively towards the tensile strength of composite.

Fibre content shows same trend with glycerol as it does with glyoxal. At desirable amount of glyoxal or glycerol, the increase in fibre content above 20% deteriorates the tensile strength of composite because although the matrix is performing well, but it is unable to impregnate all the fibres at such a high fibre content. This creates imperfections in the structure of composite.

The glycerol initially makes the SPI flexible but when increased above 17%, it hinders the effective interface between fibres and SPI matrix. Glycerol has a tendency to leach out to the surface, and fibres

cannot bind to the matrix due to this. Leached out glycerol makes the surface slippery and effective interface formation cannot take place between SPI matrix and fibres. At higher glycerol amount the leaching becomes prominent and diminishes the interfacial adhesion, leading to drop in tensile strength of composite. Therefore, the leaching of glycerol to the surface limits its content in the composite.

3.3 Optimization of Process Factors

It is observed that glycerol plays the most effective role in deciding the tensile properties of the composite. Response surfaces show the higher values of strength when higher levels are used. Glycerol reduces the brittleness of soy protein resin and therefore it allows much improved interaction between fibre and matrix. Plasticized SPI can reach the fibre bed and results in much improved bonding and consequently superior strength values. The optimum recipe is found to consist of 20% fibres, 11% glyoxal, 17.7% glycerol and 51.3% SPI. The predicted tensile strength of the composite of this combination is 18.28 MPa. In order to verify this, a sample was prepared using this combination and the tensile strength of the sample was determined as 18.4 MPa with a standard deviation of 0.2 MPa.

4 Conclusion

This study is directed towards optimizing the composition of soy based biocomposite using 3^3 Box-Behnken design of experiments and response surface methodology of analysis. The effect of glycerol, glyoxal and fibre mass fraction on tensile strength of composite was observed. All the three constituents show positive contribution up to a certain amount and then drop at higher amounts. The amount of glycerol is found to play the most effective role in determining the tensile strength of the composites. According to the model the composite attains its maximum tensile strength of 18.28 MPa at fibre fraction 20, glyoxal 11%, glycerol 17.7% and SPI 51.3% by weight. When practically tested, this recipe shows the strength of 18.4MPa that is very close to the predicted value.

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