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Characterization of jute fibre reinforced pine rosin modified soy protein isolate green composites

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Abstract. Very slow degradation of synthetic based polymers has created a severe environmental issue that increased awareness towards research in polymers of biodegradable property. Soy protein isolate (SPI) is a natural biopolymer used as matrix in green composites but it has limitations of low mechanical properties and high water sensitivity. To enhance mechanical properties and reduce water sensitivity of Jute-SPI composites, SPI was modified with pine rosin which is also a natural cross-linking agent. 30% glycerol on the weight basis of a matrix was used as a plasticizer. The fibre volume fraction was kept constant at 0.2 whereas the pine rosin in SPI ranged from 5% to 30% of the matrix. The effects of pine rosin on mechanical, thermal, water sensitivity and surface morphology have been characterized using various techniques. The mechanical properties and water absorbency were found to be optimum for 15% pine rosin in Jute-SPI composite. Therefore, Jute-SPI composite without pine rosin and with 15% pine rosin were chosen for investigation through characterization by Fourier transforms infrared spectroscopy (FTIR), Thermo-gravimetric analysis (TGA), X-Ray diffraction (XRD) and Scanning electron microscope (SEM). The surface morphology of the composite was influenced by pine rosin which is shown in the SEM image. TGA measurement showed that the thermal properties improved due to the addition of pine rosin. Antimicrobial test showed antimicrobial property in the composite occurring 15% pine rosin. The research paper concludes that the modification of SPI resin with an optimum percentage of pine rosin enhanced mechanical, thermal as well as water-resistant properties of jute fibre reinforced composites.

Keywords: antimicrobial; biodegradability; green composite; jute fibre; pine rosin; soy protein isolate

1. Introduction

The green composites are made of natural fibre reinforcements like sisal, banana, ramie, flax and jute, and biodegradable matrix manufactured from vegetable oils, maize starch, corn starch, corn pith, cellulose acetate, poly hydroxybutyrate-co-valerate (PHBV), polylactic acid (PLA), soy protein etc. (Chabba and Netravali 2005, Patil *et al*. 2017). These green composites are light in weight, have an acceptable specific strength, inexpensive, renewable, biodegradable, and property to enhance energy recovery. Non-renewable and expensive synthetic fibres can be replaced by inexpensive natural fibres (Manickavasagam *et al*. 2015). In comparison to synthetic-based composite; green composite has several advantages like they are environmentally friendly since they generate 68%

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fewer greenhouse gases. They are renewable, non-toxic and energy-efficient in production (Gholampour and Ozbakkaloglu 2020).

These fully biodegradable and environment-friendly composites although have several advantages also have some limitations such as low mechanical properties, high water absorption and thermal degradation properties which limit their successful adoption in many fields of applications. Many efforts have been made to improve the inherent properties of green composite by surface modification of fibre, modification of bio-based polymer using a cross-linking agent and by blending of different resin. A volume of work has already been done on developing green composites from soy protein resin reinforced with natural fibres. The objective of the present work is to enhance the performance of composites made from soy protein reinforced with jute fibre by adding pine rosin as a soy protein modifier.

Jute fibre comes under the family of *tiliaceae* and is the most commonly used natural fibre as reinforcement in green composites. It is economical and produced abundantly across the country (Singh *et al*. 2018, Boopalan *et al*. 2012). It has good mechanical properties such as tensile strength 393-773 MPa and elastic modulus 10-30 GPa (Elbadry *et al*. 2012). Several researchers like Reddy and Yang (2011) developed completely biodegradable green composites by using soy protein and jute fibre with water as plasticizer. Behera *et al*. (2012) developed a composite of non-woven and woven jute fabrics as reinforcement and soy milk as resin. Avancha *et al*. (2013) fabricated green composite which consisted of alkali modified non-woven jute fabric as reinforcement and soy milk as resin.

Soy protein is a polymer that has important features like mass availability, low cost, chemical modifiability, biodegradability and sustainability because of these features many researchers were attracted towards the green composite constituting soy protein as resin (Deepmala *et al*. 2017, Koshy *et al*. 2015). Its prime source is soybean. As per U.S. Department of Agriculture (USDA) data, total global production of soybean was 360 million metric tons in 2018 (O'Flynn *et al*. 2021).

At first soy protein is extracted from soybean which is available in three forms such as soy flour (SF), soy protein concentrate (SPC) and soy protein isolate (SPI). Among these forms SPI is the most purified form which contains more than 90% protein. Due to high concentration of protein in SPI, higher number of functional groups are available for reaction that's why in this research work SPI has been used as most important ingredient of matrix to produced green composite. The composites developed with the help of soy protein are being applied in housing, transportation, rigid packaging etc. The pictorial representation of extraction method of SPI has been shown in Fig. 1.

From the picture it is clear that, dehulled soybean when treated with hexane oil gives soy oil and defatted soybean flakes/flour. After removal of soluble carbohydrate from soy flour, soy protein concentrate is obtained. This obtained product when further processed to remove insoluble carbohydrate and dietary fibre gives soy protein isolate.

Many papers present various soy protein modifications, some of these papers are mentioned here; Soy protein concentrate (SPC) resin was modified by Chabba and Netravali (2005) presented the modification of SPC by adding glutaraldehyde to improve its mechanical, physical and thermal properties with its processability and reduced moisture absorption. Stearic acid was used by Lodha and Netravali (2005) to modify SPI to reduce the moisture sensitivity and simultaneously to enhance the tensile properties without affecting its biodegradability. Won *et al*. (2015), studied mechanical and biodegradation properties of the biocomposites prepared with Kenaf/SPI- PVA using glycerol as plasticizer and PVA modified SPI to improve Kenaf nonwoven/SPI interfacial bond and glutaraldehyde (GA) as a cross-linking agent. Mohanty *et al*. (2005) used Injection molding technique to make biocomposite from soy protein-based bioplastic and short hemp fibre. Heat

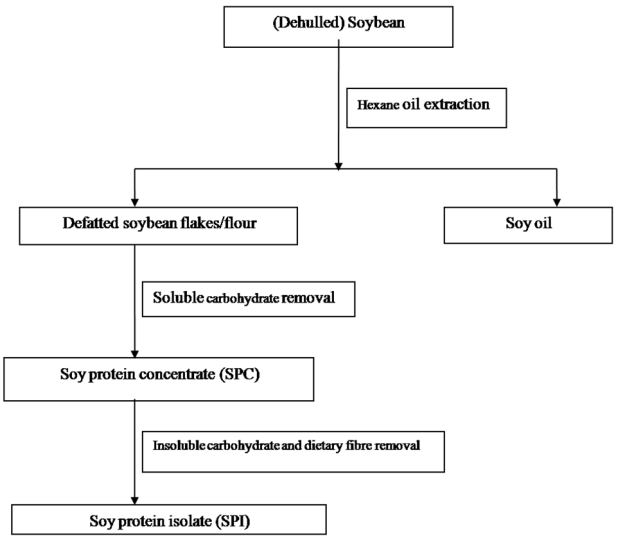

Fig. 1 Extraction method applied to produced SPI (Preece *et al*. 2017)

deflection temperature (HDT) behaviour of biocomposite is measured by Dynamic mechanical analyzer (DMA), Chabba and Netravali (2005) discussed the soy protein concentrate (SPC) modified with glutaraldehyde (GA) and polyvinyl alcohol (PVA), modified resin reinforced with spun flax yarns to fabricate green composite. Chabba *et al*. (2005), fabricated green composite using flax fibre and glutaraldehyde (GA) cross-linked soy flour (SF) and glycerol as plasticizer. These biodegradable, environmentally friendly green composites can be used in primary and secondary structure in indoor applications.

For improving mechanical and water-resistant properties, generally cross-linking agents are used. Formaldehyde, acetic anhydride, glyoxal, zinc sulfate, glutaric dialdehyde, epichlorohydrin are some cross-linking agents that have been used to modify soy protein plastics (Deepmala *et al*. 2017) but they are not ecofriendly. Pine rosin is a natural alternative to fossil-based polymer and it is abundant in nature and pine rosin act as a crosslinker as well as filler. Pine rosin is solid resinous material obtained from pine trees by heating and evaporating the pine resin. Rosin produced by this technique is semi-transparent mass and readily with a glossy appearance, varying colour from pale yellow to black, rigid, brittle and having thermoplastic behaviour. It does not dissolve in water but dissolves in light petrol, glacial acetic acid, alcohol, carbon disulphide, ether, many fixed and volatile oils, and in chloroform. Besides its availability, it possesses many other advantages such as

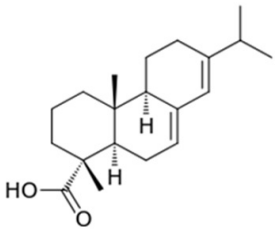

Fig. 2 Structural formula of resin acids (Kugler *et al*. 2019)

low cost, ease in converting into high-performance molecular materials, good electrical insulation, usability in cable for high voltage electricity, usability in the soldering process, usability to clean oxide compound from the surface of a metal, synthetic rubber, and chewing gums (Sousa *et al*. 2019, Aldas *et al*. 2020 and Wiyono *et al*. 2006). Other than the above advantages, rosin has also safety characteristic and the extraction of rosin from pine tree is eco-friendly due to its nontoxic behaviour (Kugler *et al*. 2019). The constituent elements of pine rosin are neutral compounds (10–20%) and resin acids (80–90%). The general molecular formula for resin acids is $C_{19}H_{29}COOH$ and its structural formula is shown in Fig. 2 (Kugler *et al*. 2019, Llevot *et al*. 2015).

Resin acids contain a tricyclic skeleton having conjugated double bonds and a carboxylic functional group. This chemical structure allows pine rosin for chemical modification for obtaining various types of derivatives (Wilbon *et al*. 2012). According to Aldas *et al*. (2020) when thermoplastic starch was blended with five derivatives of gum rosin (pine rosin), the obtained bio-composite had improved thermal stability. Bio-composites were prepared by Lam *et al*. (2012) using henequen fibres as reinforcement and pine resin as matrix. As per Sharma and Singh (2016) when biodegradable film manufactured with sesame protein isolate compared with biodegradable film with pine rosin modified sesame protein isolate, it was found that water-resistant, mechanical and thermal properties were improved for latter. These developed biocomposites could be used in rigid packaging application and usability in furniture and lightning (Ribeiro *et al*. 2018). Gennusa *et al*. (2017) studied the thermal and structural behaviour of a biocomposite material, made of vegetable fibres (hay) and natural resin (rosin). It was observed that biocomposite had adequate mechanical resistance and insulation properties.

By studying the behaviour of pine rosin it can be said that it has various beneficial properties but unfortunately, that much attention was not paid yet. If more awareness happens in future there will be large scope in the green composite research area. In this research, the fully green composite developed by using jute fibre as reinforcement and SPI (soy protein isolates) modified with a cross-linking agent (pine rosin), and 30% glycerol on a weight basis of the matrix as a plasticizer. A compression moulding machine was used to fabricate green composite. The concentration of pine rosin was optimized from 0 to 30% based on the weight of the matrix, keeping the fibre volume fraction constant at 0.2 for all the concentrations. The effects of different concentrations of pine rosin on mechanical, thermal, and hygroscopic properties were analyzed.

2. Experimental

2.1 Materials

In the present study, continuous strips of jute fibre were supplied from Central Research Institute for Jute and Allied Fibres, Kolkata. The Jute fibres strips were cut down into a staple length of 15 mm and were opened by a fibre opening machine at VJTI, Mumbai. No chemical treatment was done on jute fibres while making the composite samples. Soy protein isolates (SPI) powder of Pro Foods Nutrition brand was purchased from M/s. Chemkart importer and manufacture of food through Amazon. Analytical grade glycerol used as plasticizer was purchase from Loba Chemie Pvt. Ltd. and NaOH was supplied by Pallav chemicals & solvent Pvt. Ltd. Pine rosin in solid crystal form was purchased from M/s. Saba Associates Bhubaneswar Odisha which was converted into powder form for application.

Table 1 Calculation and codes for composites

Codes for Jute-SPI-Pine rosin composite sample	Weight of Matrix (gm)	Concentration of SPI (%) on weight basis of matrix	Concentration of pine rosin (%) on weight basis of matrix	Concentration of glycerol (%) on weight basis of matrix	Weight of jute fibre (fibre volume fraction 0.2) (gm)	Weight of SPI (gm)	Weight of pine rosin (gm)	Weight of glycerol 30% on basis of matrix (gm)
JSP0	209.6	70	0	30	60	146.72	0	62.88
JSP5	209.6	65	5	30	60	136.24	10.48	62.88
JSP10	209.6	60	10	30	60	125.76	20.96	62.88
JSP15	209.6	55	15	30	60	115.28	31.44	62.88
JSP20	209.6	50	20	30	60	104.8	41.92	62.88
JSP25	209.6	45	25	30	60	94.32	52.4	62.88
JSP30	209.6	40	30	30	60	83.84	62.88	62.88

2.2 Methods

The composite samples made are broadly categorized into two categories, first one is jute fibre reinforced unmodified SPI matrix composites and second one is jute fibre reinforced pine rosin modified SPI matrix composites. As the main focus of the composites was on SPI modification through pine rosin, the fibre volume fraction was kept constant at 0.2 for all the composite samples. In the jute fibre reinforced pine rosin modified SPI matrix samples, the SPI powder was modified by adding with varying percentages of pine rosin. SPI was modified with 5%, 10%, 15%, 20%, 25% and 30% of pine rosin. 30% glycerol on the weight basis of a matrix was used as a plasticizer for all the samples. A hot compression moulding machine was used to fabricate the composite. Calculations and codes for all compositions have been mentioned in Table 1.

2.2.1 Preparation of resin

SPI was mixed with 2.5 times of water calculated based on the weight basis of SPI and fibre. 15 ml of 10% solution of NaOH was added to maintain pH > 10. Alkaline pH > 10 encourages unfolding of native globular structures and reorganization of unravelled globules by hydrophilic/hydrophobic regions, partial hydrolysis of asparagine and glutamine primary amides and protein chain crosslinking by the formation of lysinoalanine (Krinski 1992)**.** The mixture was stirred in a steel container to make uniform slurry with a magnetic stirrer for 15 minutes at room temperature. After that, glycerol (30% of a matrix) was added as a plasticizer to reduce the brittleness of SPI resin and to improve processability. Then slurry was stirred continuously for 5 min. Thereafter, the container was transferred into a hot water bath to the pre-cure slurry at 80°C for 30 minutes followed by cooling (Lodha and Netravali 2005). After pre-curing, the slurry became thick and consistent. After cooling, a measured amount of pine rosin was added as per the requirement and pH was kept greater than 10.

2.2.2 Preparation of jute fibre Reinforced composite

After preparation of resin, measured weights of chopped and opened fibres were slowly added to the resin manually and then the mixture was stirred manually to maintain uniform distribution of

fibres in the matrix. This mixture was kept for 24hr at room temperature in the steel pot to improve its viscosity. Then resin/fibre mixture was transferred into mould (200 mm × 200 mm × 5 mm) to make a uniform sheet of composite. The mould was kept in a compression moulding machine and the pressure was gradually applied to avoid flowing out resin/fibre mixture. The mould is kept at 80°C for 30 min for drying resin/fibre sheet. Curing was done at 120°C for 3hr under a pressure of 50 kg/cm^2.

2.3 Mechanical characterizations

The mechanical characterization was done for all the composites of Jute-SPI without pine rosin and Jute-SPI with pine rosin. The mechanical properties define the actual utility of the materials. The prime object for the mechanical characterization was to observe the effect of various concentrations of pine rosin in SPI in the composite sample and find out the best combinations. Subsequently, the optimum pine rosin-SPI combination was to be chosen for the detailed analysis. This was done to reduce loads of data and avoid perplexity. Tensile, flexural and impact properties of prepared jute composite with and without pine rosin were characterized according to ASTM D638-03, ASTM D790-07 and ASTM D256 -06a respectively.

2.3.1 Tensile testing

For tensile testing specimens of size, 115 mm × 19 mm × 4 mm was cut from composite according to ASTM D638-03. A cross-head speed of 2 mm/min and a gauge length of 65 mm were used for carrying out the test. Five replicate specimens, each of all variants, i.e., JSP0, JSP5, JSP10, JSP15, JSP20, JSP25 and JSP30 were conditioned and tested at 23°C temperature and 55% RH. Tests were performed on a universal testing machine (UTM) make SHIMADZU Autograph AGS-X series of capacity 100 KN and the software used was TRAPEZIUM.

2.3.2 Flexural testing

For flexural testing specimens were prepared according to ASTM D790-07. The 3-point bending method was adopted specified in the standard. Specimen with the nominal dimensions of 120 mm × 12.7 mm × 4 mm having span length of 80 mm and cross head speed of 2 mm/min were used. Five replicate specimens, each of all variants, i.e., JSP0, JSP5, JSP10, JSP15, JSP20, JSP25 and JSP30 were conditioned and tested at 23°C temperature and 55% RH. Tests were performed on the same universal testing machine (UTM) used in tensile testing.

2.3.3 Impact testing

This test was performed on the Izod Charpy Impact Tester of make Avery-Denison Impact meter; a 2.7-joule striker was used. The specimen dimensions were 63.5 mm × 12.7 mm × 4 mm and 'v' notch of depth 2.54 mm and notch angle 45°as per ASTMD 256-6a was made by notch cutter at the middle of the face having dimension 63.5 mm × 4 mm. Five replicate specimens, each of all variants, i.e., JSP0, JSP5, JSP10, JSP15, JSP20, JSP25 and JSP30 were conditioned and tested at 23°C temperature and 55% RH. The impact strength in KJ/m^2 was calculated by dividing the recorded absorbed impact energy by the cross-sectional area of the specimen.

2.4 Water absorbency

ASTM D570-98 method was used to test the effect of water absorbency of five replicate specimens, each of all variants, i.e., JSP0, JSP5, JSP10, JSP15, JSP20, JSP25 and JSP30 in water.

The first weight of the conditioned specimen was measured for each sample then distilled water was used for the immersion of above mentioned seven specimens. For each specimen sample size of five was chosen. After immersion, the specimen's container was kept at temperature 23.6°C for 24 hrs. Specimens were removed from water one at a time; excess water was wiped off with a dry cloth and weighed again to the nearest 0.001 g immediately. Water absorbency was calculated using an Eq. (1)

$$\text{Increase in weight } \% = \frac{\text{Wet weight} - \text{Conditioned weight}}{\text{Conditioned weight}} \times 100 \quad (1)$$

2.5 FTIR, TGA, XRD and SEM characterization

Based on the results of the mechanical test, two variants i.e., Jute-SPI without pine rosin (JSP0) and Jute-SPI with 15% pine rosin (JSP15) were chosen for the FTIR, TGA, XRD and SEM characterization to reduce complications in analysis.

2.5.1 Fourier transforms infrared spectroscopy (FTIR)

Fourier transform infrared spectrum (FTIR) was done with Perkin Elmer Spectrum 100 FT-IR Spectrometer. Spectra of the samples were recorded in the region of 4000-650 cm^{-1}.

2.5.2 Thermo-gravimetric analysis (TGA)

Thermal characteristic of samples were studied using DTG 60H TGA (Shimadzu, Japan) instrument in a nitrogen atmosphere and analyzing thermogravimetric data from 30°C to 600°C at heating rate 10°C /min under 100 ml/min flow rate of nitrogen gas. During the test, samples were kept in aluminium pan.

2.5.3 X-Ray diffraction analysis (XRD)

X-ray diffraction analysis was carried for green composites with the help of Shimadzu XRD 6100; voltage and current for the test were kept at 40 kV and 30 mA respectively. Symmetrical reflection mode with Cu Kα radiation of 1.54060 Å was used to carry the test. The angular range for 2Θ was taken from 10° to 60°. Sampling pitch and scanning rate for continuous measurement were set at 0.02° and 2° per minute respectively.

2.5.4 Scanning electron microscope analysis (SEM)

The surface morphology of the longitudinal surface and the cross-sectional surface of fractured samples were observed with the help of SEM (Philips XL-30 SEM, The Netherlands). The samples were sputter-coated with gold before recording the micrographs.

2.6 Antimicrobial analysis

From previous researches it has been observed that pine rosin contains antimicrobial activity, so the composite having pine rosin as cross linker should also have antimicrobial property up to some extent. To confirm this property of pine rosin modified soy protein isolate and jute composite (JSP15), AATCC 147 standard was used against two bacteria Staphylococcus aureus (gram positive) as per inoculum ATCC 6538 and Klebsiella pneumonia (gram negative) as per inoculum ATCC 4352. As per test standards two swatches for two bacteria was cut into rectangular shape of dimension 25 mm × 50 mm, and sterilized in autoclave by using free steam and incubated for 24 hrs at 37 ± 2°C

temperature. An Eq. (2) was used to evaluate antibacterial activity of composite sample

$$W = T - \frac{D}{2} \tag{1}$$

Where, W = Width of clear zone of inhibition in mm
T = Total diameter of test specimen and clear zone in mm
D = Diameter of test specimen

3. Results and discussions

3.1 Mechanical properties

Mechanical properties such as tensile strength, tensile modulus, flexural strength, flexural modulus and impact strength were studied for JSP0, JSP5, JSP10, JSP15, JSP20, JSP25 and JSP30.

3.1.1 Tensile properties

Tensile properties of the composites were improved by the addition of pine rosin to SPI. It was observed that the tensile strength and tensile modulus increases with an increase in pine rosin percentage up to 15%. However, beyond 15% of the pine rosin in SPI, there is a decreasing trend of strength and modulus but the lowest values are higher than that of SPI without pine rosin. The tensile strength and tensile modulus of composites without pine rosin found to be 11.78 MPa and 1302 MPa respectively whereas, the tensile strengths and tensile modulus of composites with 15% pine rosin found to be 21.04 MPa and 2395 MPa respectively. The tensile strengths and tensile modulus of composites with 30% of pine rosin found to be 12.95 MPa and 1584 MPa respectively, which is the lowest among the pine rosin variants. Fig. 3 shows the tensile strength and modulus properties of all the composite samples.

Improvement in tensile strength and tensile modulus may be due to, pine rosin having major content of rosin acids which consist of abietic acid. Abietic acid is comprised of carboxylic group. The carboxylic groups form peptide linkage with amino groups of soy protein isolate. This reaction is highly responsible for strong covalent linkages. An expected crosslinking reaction between SPI and pine rosin has been presented in Fig. 4.

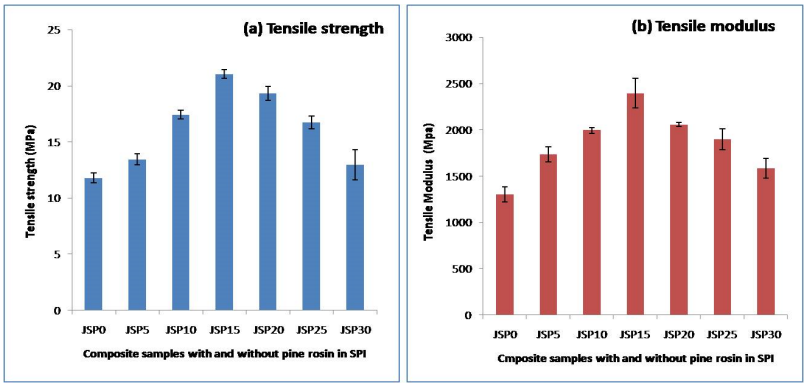

Fig. 3 (a) Tensilel strength; (b) Tensile Modulus of different concentration of pine rosin composite

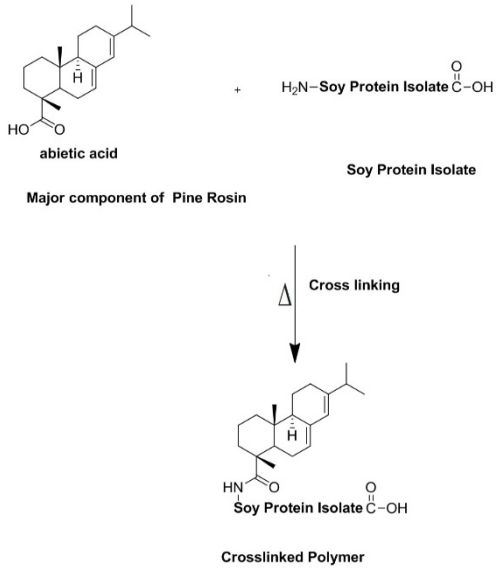

Fig. 4 Crosslinking reaction between SPI and Pine rosin

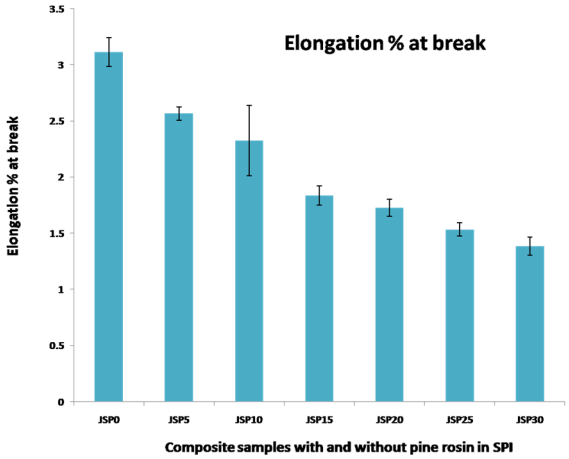

Fig. 5 Elongation % at break of different concentration pine rosin composite

Intermolecular cross-linking and intramolecular interactions between gum rosin and protein molecules produce the compact structure of composite with a strong network which might be responsible for increased tensile strength and modulus of composite (Sharma and Singh 2016). The compactness of the composite can also be seen in the SEM image (Fig. 11(d)). From Fig. 11(b), it can be seen that there is a strong presence of pine rosin on the surface of the composite, which indicates good bonding between jute fibre and rosinated resin. This may be due to the polar nature of rosinated resin and jute fibre. A good bonding of fibres and the matrix leads to a higher load for fibre breakages due to load transfer from matrix to reinforcement which reflects in total tensile strength of the composite. In addition, a higher molecular weight of pine rosin also responsible for increased tensile strength and modulus. The reduction in tensile strength and modulus above 15%

of pine rosin in a matrix may be due to a reduction in cross-linking density and building brittle structure of composite. Reduction in crosslinking density might be affected due to the increasing amount of pine rosin and decreasing amount of SPI in the overall matrix. The brittleness of composite increases with increase in percentage of the pine rosin which is, brittle in nature leading to reduction of plasticizing effect of the matrix.

In general, brittle materials have less elongation percentage at break. The diagram of elongation percentage at break for samples such as JSP0, JSP5, JSP10, JSP15, JSP20, JSP25 and JSP30 shown in Fig. 5 justifies that the composites are being more brittle as the concentration of pine rosin is increased. From the Fig. 5, it is clear that elongation percentage at break is decreasing with increasing concentration of pine rosin in the composites and therefore the brittleness of composite is increasing. Up to 15% concentration of pine rosin the increased brittleness of composite supports the strength of composite while after 15% concentration of pine rosin creates an adverse effect on the strength of composite due to very less amount of absorption energy before fracture. This contributes to the reduction of strength of composites beyond 15% of pine rosin content.

3.1.2 Flexural properties

The flexural strength and flexural modulus have a trend similar to the tensile properties. Fig. 6 shows that the flexural strengths and modulus increase with the increase in pine rosin percentage up to 15% and reduces thereafter but the lowest strength and modulus values are higher than that of samples without pine rosin. The flexural strength and flexural modulus of composites without pine rosin found to be 10.1 MPa and 1000 MPa respectively. Whereas, the flexural strength and flexural modulus of composites with 15% pine rosin found to be 16.25 MPa and 1816 MPa respectively. However, the flexural strength and flexural modulus of composites with 30% pine rosin found to be 11.42 MPa and 1130 MPa respectively which is still higher than that of composites without pine rosin in SPI. The increased flexural strength and modulus obtained due to increased fibre-matrix adhesion. Better fibre matrix adhesion provides increased stress transfer between them (Rahman *et al*. 2008). Adhesion of fibre–matrix increases due to good interfacial bond between them. The increase in pine rosin percentage beyond 15% probably reduces the cross-linking between pine rosin and SPI and increases the brittleness of composite due to brittle behaviour of pine rosin which results in decreasing flexural strength and modulus.

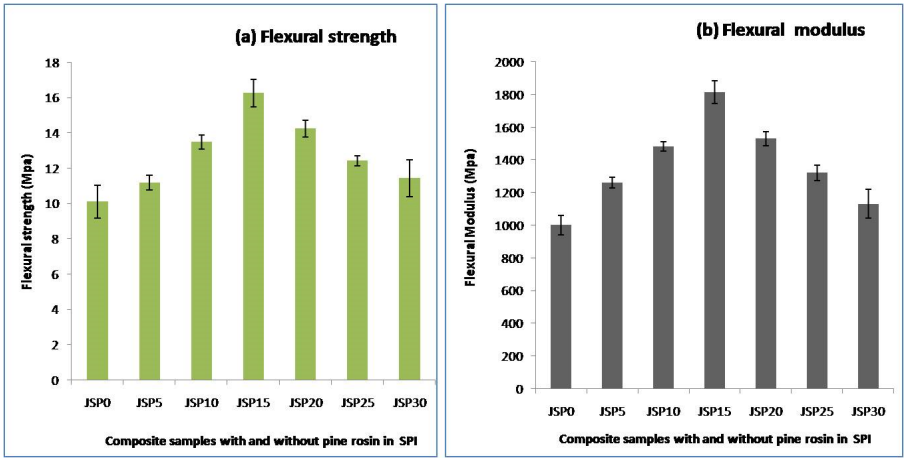

Fig. 6 (a) Flexural strength; (b) Flexural Modulus of different concentration of pine rosin composite

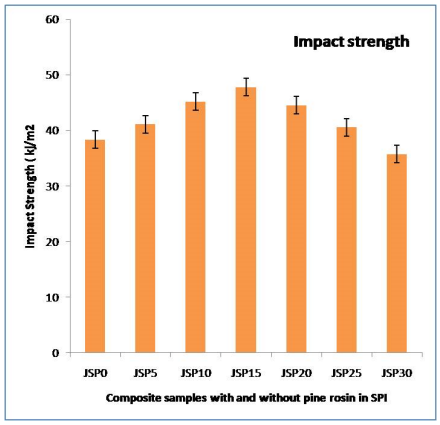

Fig. 7 Impact strength of different concentration pine rosin composite

3.1.3 Impact properties

The impact strength of the fibre reinforced polymeric composites depends on the nature of the fibre, polymer and fibre-matrix interfacial bonding (Joseph *et al*. 2003). It has been reported that high fibre content increases the probability of fibre agglomeration which results in regions of stress concentration requiring less energy for crack propagation (Karmarkar *et al*. 2007). As presented in Fig. 7, the impact strength increased with an increase in the pine rosin up to 15% and reduced thereafter. The impact strength of composites without pine rosin in SPI was 38.34 KJ/m^2. Whereas, the impact strength of composites with 15% pine rosin was 47.78 KJ/m^2. The impact strength of samples with 30% of pine rosin was the lowest among all the composite variants including composites without pine rosin in SPI. These results suggest that the fibre was capable of absorbing energy because of the strong interfacial bond between the fibre and matrix for the pine rosin up to 15% and it declines thereafter due to decreasing plasticizing effect of increased pine content in SPI. With increasing plasticizing effect impact strength increases and vice versa (Kormin *et al*. 2019).

3.2 Water absorbency

Effect of varying concentrations of pine rosin on water absorbency of soy protein isolate composite has been shown in Table 2. Water absorbency for composite without pine rosin is 54.48%, with 15% pine rosin is 44.75% and with 30% pine rosin is 52.83%. Pine rosin acts as an excellent barrier to water absorption due to its hydrophobic nature. The hydrophobic nature of pine rosin was responsible for a substantial decrease in water absorption of composite as compared to composite without pine rosin. Also, the crosslinking effect of pine rosin makes the composite compact which leads to a reduction of water absorption. However, an increasing amount of pine rosin beyond 15% makes the composite weak due to insufficient crosslinking and allows the passage for a water

Table 2 Water absorbency

Time (hrs.)	Water absorbency (%)						
	JSP0	JSP5	JSP10	JSP15	JSP20	JSP25	JSP30
24	54.48	52.70	49.39	44.75	50.03	51.76	52.83

molecule. The carboxylic acid group of abietic acid is showing linkage with soy protein isolate through peptide linkage thus there is practically less number of carboxylic groups that remains free. Another reason is that abietic acids consist of mainly ring structure which also plays an important role in reducing water absorption (Vevere *et al*. 2020).

3.3 FTIR, TGA, XRD and SEM study

Based on the mechanical performance of the composites Jute-SPI composite with 15% pine rosin was chosen for the analysis and Jute-SPI without pine rosin was treated as a reference sample for comparison purpose. Hence, JSP0 and JSP15 were characterized by FTIR, TGA, XRD and SEM analysis.

3.3.1 FTIR

In Fig. 8 graphs of FTIR have been shown. The graph which is shown at the top is for jute-SPI composite with 15% pine rosin (JSP15) and the graph at the bottom is for Jute-SPI composite without pine rosin (JSP0), from both the graphs we can interpret that both the composites have hydroxyl group which may have been come from the cellulose of jute fibre. O-H stretching is seen near 3350 cm^{-1} but the intensity of peak for the O-H group of JSP15 has been reduced. It might be due to a reduction in the number of O-H groups and the presence of other materials. This result also indicates that the water-absorbing property of JSP15 has been reduced in comparison to JSP0. This theory has also been supported by the water absorbency test. Peaks around wave number 2920 cm^{-1}

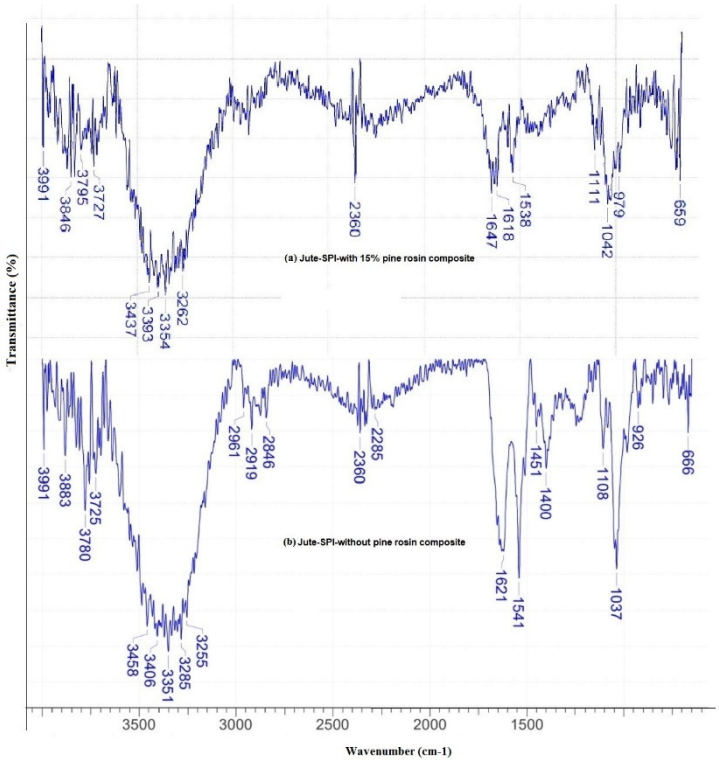

Fig. 8 FTIR Analysis of JSP0 and JSP15

show C-H stretching in both the composites due to the presence of CH_2 or CH_3. Peaks at 1621 cm^{-1} and 1647 cm^{-1} indicate C = O stretching which confirms the presence of amide in both the composites but the intensity of peak has been reduced for JSP15 which might be due to the mixing of pine rosin with SPI and decreasing amount of SPI. Crosslinking between pine rosin and SPI is being reflected from the presence of the carboxylic group and reduction in hydroxyl groups in JSP15.The carboxylic group present in JSP15 has come only from amide group present in SPI or newly formed amide groups generated through crosslinking of pine rosin with SPI because acidic group present in pine rosin may have been reacted with SPI and OH group of cellulose, so there is no sign of (COOH) group in JSP15.

3.3.2 TGA

The thermo-gravimetric analysis curves for Jute-SPI composite without pine rosin (JSP0) and Jute-SPI composite with 15% pine rosin (JSP15) are shown in Fig. 9. Both composites exhibited weight loss in three temperature stages ranging between 74°C and 601°C. The first weight loss of about 8-10% was observed between 74°C and 160°C which was due to removal of moisture from the composites. Jute-SPI with15% pine rosin composite showed next two-stage degradations with temperatures between 220°C and 300°C with weight loss of 24.8% and between 320°C and 410°C with weight loss of 40.47% respectively. Similarly, the Jute-SPI without pine rosin composite showed next two-stage degradations with onset temperatures from180°C to 280°C with weight loss of 25.6% and from 300°C to 384°C with weight loss of 43.6 % respectively. The decomposition of Jute-SPI with15% pine rosin composite at 600°C is found 78.48%, leaving 21.52% char residue. The decomposition of Jute-SPI without pine rosin composite at 600°C is found 86.07% leaving 13.93% char residue. The weight losses at progressive temperatures (100°C, 200°C, 300°C, 400°C,

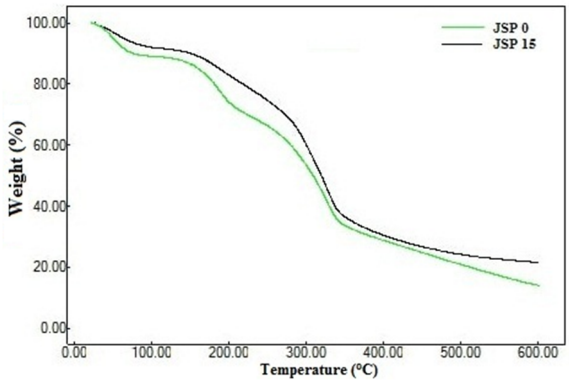

Fig. 9 TGA analysis of JSP0 and JSP15

Table 3 Percentage weight loss of composites at increasing temperatures

Weight loss (%) against temperature						
Samples	Temperature					
	100°C	200°C	300°C	400°C	500°C	600°C
JSP0	10.88%	26.04%	46.79%	71.41%	79.24%	86.07%
JSP15	8.15%	17.19%	40.17%	69.64%	75.93%	78.48%

500°C, 600°C) for Jute-SPI without pine rosin composite seem to be more rapid than Jute-SPI with15% pine rosin composite which is shown in Table 3.

Second stage of thermal decomposition is due to evaporation of glycerol which was used as a plasticizer, due to cleavage of the covalent bonds of amino acid groups present in protein and, acidic group present in pine rosin and non-acidic components of hemicellulose in jute (Rana *et al*. 1997, Verma *et al*. 2019). It was found that the temperature of thermal degradation of composite material is increased due to addition of pine rosin. At 15% pine rosin there may be formation of crosslinking between soy proteins isolate and pine rosin which makes composite more thermally stable. High molecular weight (302.44 g/mol) (Sharma and Singh 2016) of pine rosin may also play an important role in increasing thermal stability of 15% pine rosin Jute- SPI composite (JSP15).

Third stage thermal decomposition occurred due to breaking of S-S, C-N, C-O linkages of protein and degradation of abietic acid, pimaric acid, and some non-acidic materials present in pine rosin. (Sharma and Singh 2016, Rana *et al*. 1997)

3.3.3 XRD

XRD data were obtained for Jute-SPI without pine rosin and Jute-SPI with 15% pine rosin shown in Fig. 10. It was noticed that X-ray diffraction pattern of 15% Pine rosin Jute-SPI composite gave a broad peak at 2Θ equal to 21.85° corresponding to crystal d-spacing of 4 Å and a small shoulder peak at 2Θ equal to 15.9° corresponding to crystal d-spacing of 5.5 Å. Similarly, the X-ray diffraction pattern of Jute-SPI without pine rosin showed a broad peak at 2Θ equal to 22.4° corresponding to crystal-spacing of 3.9 Å and a small shoulder peak at 2Θ equal to 15.3° corresponding to crystal d-spacing of 5.78 Å. With the addition of 15% pine rosin, it is seen that the second peak is slightly shifted towards a lower angle with an increased in d-spacing and the increase in full width at half maximum (FWHM) of the diffraction peak. The intensity of diffraction was more for Jute-SPI with 15% pine rosin as compared to without pine rosin. It indicates a slight

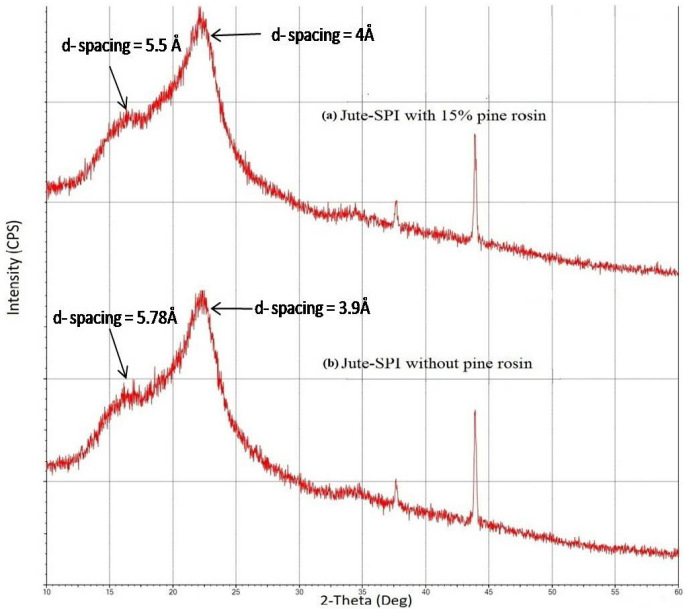

Fig. 10 XDR Analysis of JSP0 and JSP15

increment in crystallinity with the addition of pine rosin i.e., from 10.53% to 10.92%.

3.3.4 SEM

To observe surface morphology, SEM was performed for Jute-SPI without pine rosin (JSP0) and Jute-SPI with 15% pine rosin (JSP15). Images of surface morphology of the longitudinal surface of the fractured sample have been shown in Figs. 11(a) and 11(b) respectively, in Fig. 11(a), it is seen that the surface of the Jute-SPI composite without pine rosin is smoother than the surface of the Jute-SPI composite with 15% pine rosin shown in Fig. 11(b). The expected reason behind this may be due to the presence of pine rosin in the sample. Since pine rosin makes the surface rougher, therefore, surface shown in Fig. 11(b) looks more irregular. It leads to better adhesion between jute fibre and matrix along with the betterment of strength and rigidness. Similarly, SEM images of cross-sections of fractured samples, Jute-SPI without pine rosin and Jute-SPI with 15% pine rosin have been shown in Figs. 11(c) and 11(d) respectively. From Figs. 11(c) and 11(d), we can interpret that the fractured portion of composite developed with the help of pine rosin is denser due to the adhesion of pine rosin on jute fibre which leads to better strength and rigidness.

3.4 Antimicrobial property

From the value of clear zone of inhibition (W) and Figs. 12(a) and 12(b) it can be said that there

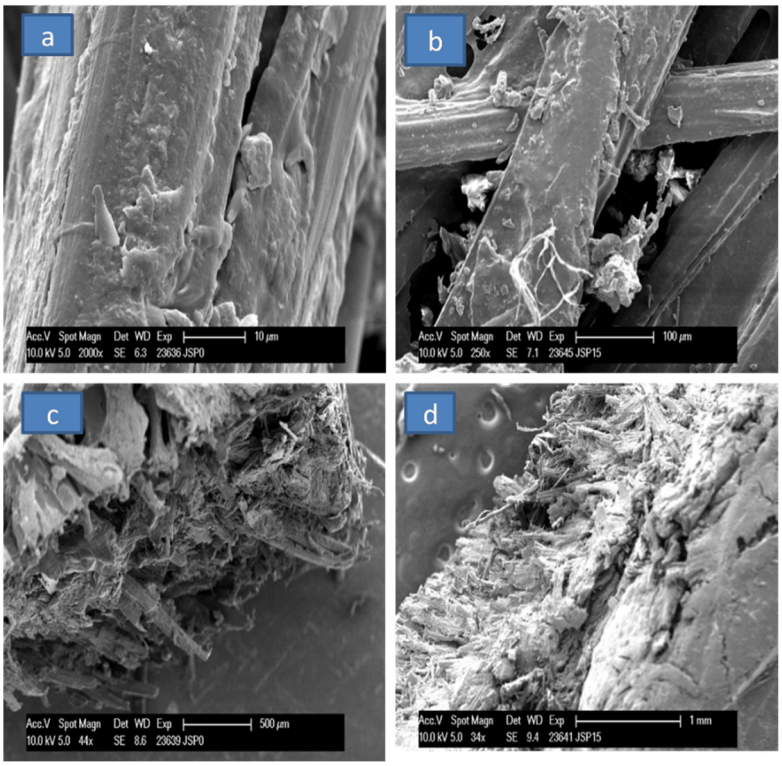

Fig. 11 SEM Photographs (a) Longitudinal section view of fractured sample of JSP0; (b) Longitudinal section view of fractured sample of JSP15; (c) Cross section view of fractured sample of JSP0; and (d) Cross section view of fractured sample of JSP15

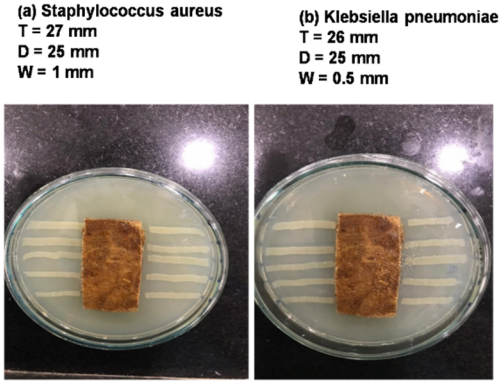

Fig. 12 (a) Antimicrobial analysis for Staphylococcus aureus; (b) Antimicrobial analysis Klebsiella pneumoniae

is slight zone of inhibition around composite sample for both the bacteria. Thus, it can be concluded that composite exhibits antimicrobial activity which may have been come from pine rosin that affects the cell wall of bacteria such as Staphylococcus aureus (Kanerva *et* al. 2019, Niu *et al*. 2018). Because of this property composite can be used in food packaging.

4. Conclusions

Green composites made from jute fibre and SPI modified with pine rosin by compression moulding technique were studied for mechanical properties, hygroscopic nature, thermal behaviour and surface morphology. SPI was modified with 5%, 10%, 15%, 20%, 25% and 30% of pine rosin then this modified SPI was used to fabricate composite and was compared with SPI composite without pine rosin. Mechanical properties are found to be improved for jute-SPI modified pine rosin composite (JSP15) when compared with Jute-SPI composite without pine rosin (JSP0). Tensile strength and tensile modulus of Jute-SPI composite with 15% pine rosin found to be 21.04 MPa and 2395.53 MPa respectively which are highest among other concentrations. Similar trends were found for flexural strength and modulus of JSP15 which are 16.25 MPa and 1816.67 MPa respectively that are also maximum. The impact strength of JSP15 was found to be 47.78 KJ/m^2 which is also the highest. FTIR results show that the samples of JSP15 there are decrease in the peak area around 3350 cm^{-1} which indicates a reduction in the number of free hydroxyl groups by the addition of 15% pine rosin. This is also supported by the water absorption tests conducted for JSP0 (54.48%) and JSP15 (44.75%). TGA analysis of JSP15 and JSP0 indicates that the thermal degradation rate of JSP15 is lower than JSP0. It indicates higher thermal stability of JSP15 in comparison to JSP0. XRD results show that the water desorption peak temperature for JSP15 is slightly higher as compared to JSP0 which indicates a slight increase in crystallinity (10.53%.to 10.92%) with the addition of pine rosin. SEM image shows that surface morphology has been changed due to the addition of pine rosin. From the antimicrobial test it has been observed that the composite having 15% pine rosin exhibits antimicrobial property. Finally, we can conclude that the modification of SPI resin with the optimum percentage of pine rosin can enhance the mechanical, thermal as well as water-resistant properties of the jute fibre reinforced composites.

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