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Studies on Tamarind Seed Kernel-Based Bio Composites for Fire Performance and Degradability to Enhance Shelf Life, Under the Influence of Additives

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Abstract

Natural fibre reinforced composites have received a lot of interest in recent years as prospective building components for low-cost applications. Natural fibers offer good opportunity as composite reinforcement, as they are strong, light, cheap and renewable. Numerous experiments have been conducted to emphasize the use of bio-based materials for various applications. Considering environmental aspects, the current research is concentrated on bio-based binder and reinforcement. The objective here is to conduct various experiments for fire behaviour to justify its insulation property, fungal behaviour for degradability, moisture absorption and mechanical properties in order to tabulate results and to quantify the variations. Justify optimal composition and parameter responsible for variation by DOE-Taguchi technique. Experimental results presented reduction in burning rate with increase in Tamarind Seed Kernel Gum (TSG), attaining lowest of 8.29 mm/min at 60% Paper Cellulose (PC) and 40% TSG falling within the class of UL94HB for horizontal testing, 26.92 mm/min for vertical testing. The PC in combination with TSG influenced development of 'Mucore' category fungus resulting in rapid degradation, this is addressed by additives namely 'Boric Acid' and 'Turmeric Powder'. Poor performance observed in terms of moisture behaviour hampering the sustainability of composites.

Keywords: *Bio-Composites, Degradation, DOE, Fire Behaviour*

1.0 Introduction

Composites are materials made up of a matrix and one or more filler. Because there are so many options for matrix and fillers, the range of composites that may be is nearly limitless, and can be tailored to meet specific technical requirements. Whenever the matrix is indeed a polymer, the resultant composite is often light, inexpensive[1], and easy to create, with significantly improved mechanical qualities over the pure matrix material.

The interaction in between filler and matrix, which is affected by extent of interfacial region between them, is one distinct process that permits the composites qualities. This, in turn, is dependent on the filler content as well as the size/aspect ratio[2]. Excessive volumes of filler have a detrimental impact on the overall functional qualities of the resultant composites, and in general result in higher composites final prices. This last quality motivates the industry to seek for the smallest quantity of filler necessary to achieve the specified composite qualities. The physical characteristics of the composite become increasingly different from that of the clean matrix as the interface region grows greater. Following this idea, significant efforts have been made in recent years to move from microparticles to nano-sized fibres, which ensure substantially higher area of contact with the surrounding

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matrix, in order to achieve the maximum degree of alteration of the matrix's characteristics. This occurs at the same time as decreased filler loadings and improved composite functional qualities, allowing nano-composites to be used in everyday life. Nano-composites have been shown to be extremely successful in thermal insulation, heat radiation, electrical insulation, sound absorption, biomedical applications, sensors, energy storage, solar cells, and thermoelectricity[3].

In order to create end products with superior physical qualities, polymers are frequently treated with different fillers and additives. Fillers can take the form of fibres or particles that are evenly dispersed throughout the polymer matrix composite. Many of the qualities of fibrous composite materials are influenced by fibre properties as well as microstructural factors including diameter, length, distribution, volume percentage of fibres, alignment, and packing. Except for the extremely short, randomly dispersed fibres, the thermophysical characteristics of fibre filled composites are clearly anisotropic.

At the moment, developing a sustainable insulation material is a huge challenge[4]. This is necessary to address the requirements for the reliability, quality, and functionality of insulation materials and structures for the providing of an optimal indoor climate, as well as the new requirements for the selection and rational use of materials and energy resources.

Many research investigations focus on natural materials, biodegradable, and renewable resources as a means of generating products with strong mechanical and thermal insulating capabilities while having a minimal environmental and human health effect. Argo-crop by-products and lignocellulosic waste might be an intriguing solution for these problems[5]. Fibres and non-fibrous materials are an excellent choice for efficient reinforcing in various kinds of composites. Furthermore, lignocellulosic by-products have inherent hygrothermal qualities that make them ideal for use in constructing thermal insulation materials. Many research investigations have been conducted on composite materials depending on these fibres or particulates with lignocellulosic wastes with specialized construction uses. When compared to petroleum-based materials, these materials have a lower density and weight, as well as higher insulating qualities.

2.0 Experimental Evaluation of Fire Behaviour of PCTSG Samples

When biopolymer composites are considered for thermal insulation application, flame retardancy tests are required to establish their flammability and flame retardancy properties. Because natural fibres are very flammable, they are more prone to ignite and combust exothermically, resulting in a strong burn[6]. The flammability of biopolymer composites is influenced by a number of parameters, including the kind of natural fibre and biopolymer, the type of reinforcement, the adhesion between matrix and reinforcement, and the composite structure. The flammability of different fibres varies due to differences in chemical composition and microstructure. The ability of a material to withstand the spread of fire while maintaining mechanical integrity is known as fire resistance. Composites provide good thermal insulation and burn-through resistance. Heat conduction via composites is substantially slower than through metals, which has the advantage of slowing the spread of fire from room to room. Flame, heat, smoke, and hazardous gases can all be well protected by composites.

Polymer based composites are gaining higher importance due the properties offered. Although many polymer composites are combustible, they can be made more resistant to pyrolysis. Furthermore, these materials have several potentially helpful fire qualities that metals do not have[7].

According to Federal Aviation Regulations, the flame retardancy test of bio-polymer composites is usually done in a vertical Bunsen burner test (FAR). To determine flame retardancy, horizontal and vertical fire experiments are used. The ignitability and flame spreading rates may be evaluated using UL-94 vertical and UL-94 horizontal standards in line with DIN EN 60,695-11-10.

To measure the fire behaviour of PCTSG composites, composite compositions shown in the Table 1 are synthesized according to the UL 94 standard to test under horizontal and vertical orientations[8]. The behaviour of a polymer-based composite when in contact with fire is quantified in this test. Measurements based on the particular length of material burned for the time duration in minutes yield the findings.

Table 1. Paper cellulose tamarind seed gum composition

Sample	TSG %	PC %
PCTSG 1	30	70
PCTSG 2	40	60
PCTSG 3	50	50
PCTSG 4	60	40
PCTSG 5	70	30

The horizontal test is performed by clamping one end of the specimen horizontally while letting the other end free to ignite. The results of which are shown in the Table 2. The distance travelled by the flame and the time it takes to burn are used to calculate the burning rate. Paper cellulose can readily break down into carbon, releasing a considerable quantity of energy, which contains 38 to 40 % oxygen, the burning rate decreases with increasing TSG and decreases with increasing PC, whereas because tamarind seed particulate in the form of polymer is denser than cellulose, it breaks down more slowly to releases energy.

For vertical testing one end of sample is positioned vertically so that its bottom edge is 3/8' beyond a piece of wire gauge for the vertical burning test, and then a 1" high Bunsen burner is used to apply flame to the open edge

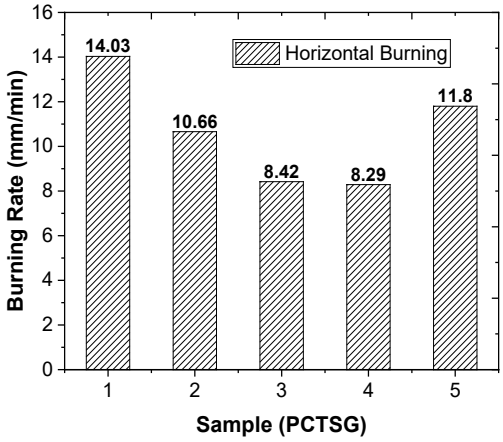

Figure 1. Burning rate of PCTSG composites for horizontal orientation.

for 10 seconds before being withdrawn. After the ignition source has been withdrawn, the time it takes for the flame to travel between the two-gauge marks is recorded, and the combustion rate is calculated. It is noticed in both cases of burning that the burnt residue forms the hard envelope, which stops further burning of the sample. Even after frequent application of flame, burning of sample did not continue after certain length. There is no particle drop in all the compositions of horizontal and vertical burning.

Table 2. Fire behaviour testing results for horizontal orientation

	Application Time (Seconds)	**Burning Tme (Minutes)**	**Burning Length (mm)**	**Characteristics**	**Burning Rate (mm/min)**	**Class**
PCTSG 1	8.91	5.43	76.2	Burning stops	14.03	UL 94 HB
PCTSG 2	11.79	7.15	76.2	Burning stops	10.66	UL 94 HB
PCTSG 3	9	9.05	76.2	Burning stops	8.42	UL 94 HB
PCTSG 4	13	9.19	76.2	Burning stops	8.29	UL 94 HB
PCTSG 5	13	6.46	76.2	Burning stops	11.80	UL 94 HB

Table 3. Fire behaviour testing results for vertical orientation

Vertical testing								
SL No	**Application Time (seconds)**	**Burning Time (sec)**	**Burning Time (min)**	**Burning Length (mm)**	**Characteristics**	**Burning Rate (mm/min)**	**Particle Drop**	**Class**
PCTSG 1	10	26	0.433333	60	Burning stops	138.46	No	94V-1
PCTSG 2	10	40	0.666667	70	Burning stops	105.00	No	94V-2
PCTSG 3	10	43 + 41	1.4	80	Burning stops	57.14	No	94V-2
PCTSG 4	10	78	1.3	35	Burning stops	26.92	No	-----
PCTSG 5	10	42	0.7	25	Burning stops	35.71	No	94V-2

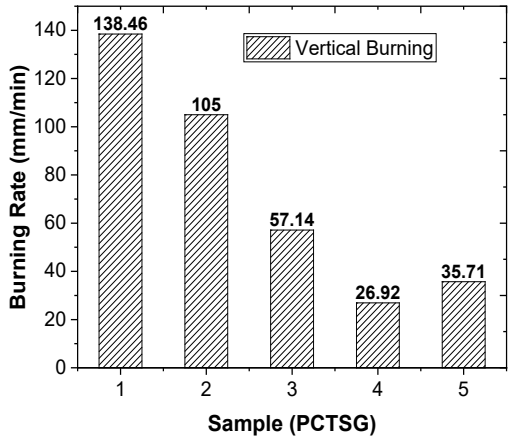

Figure 2. Burning rate of PCTSG composites for vertical orientation.

The DSC reveals three separate thermal reaction areas, two endothermic reactions and one exothermic reaction. Figure 3 (a) and (b) show the Derivative Thermogravimetric Analysis (DTA) of the samples in the most critical temperature range of 25°C-110°C. According to the chemical content of commercial and JC, the pyrolysis process is complicated, and at least two processes coexist. The DTG profile for celluloses showed just a water loss event and cellulose degradation, indicating that no cellulosic components were efficiently eliminated by extraction. The heat flow rate curve shows that the thermal rate of breakdown, as well as the middle and inflection point surface temperatures for all cellulose samples, are similar, and that higher onset temperatures are related with greater thermal stability. The considerable degree of crystallinity of cellulose might explain this phenomenon.

3.0 Moisture Absorption

In the case of thermal fibre insulation, which often exhibits high water absorption, the ability to absorb water vapor and the impacts connected with it are critical considerations. Capillary moisture movement is one of the processes of moisture flow in building materials[9]. Capillary forces the influence of adhesion forces and surface tension are to blame. Due to capillary, surfaces are wetted with liquid. Wetting is a property that describes how the surface of a substance in contact with a liquid behaves. Different degrees of wettability can be found in the fibres[10]. The contact angle between the liquid drops and the surface wetted with this liquid is used to assess whether the substance is hydrophobic or hydrophilic.

PCTSG composites contain a connected network of pores and capillaries, and the capillary surfaces are wettable. The diameter of the capillaries has a considerable impact on the dynamics of this phenomena. The composite's absorbency and water retention capacity at atmospheric pressure are of important considerations. The number and size of pores in the material have the greatest impact on this attribute.

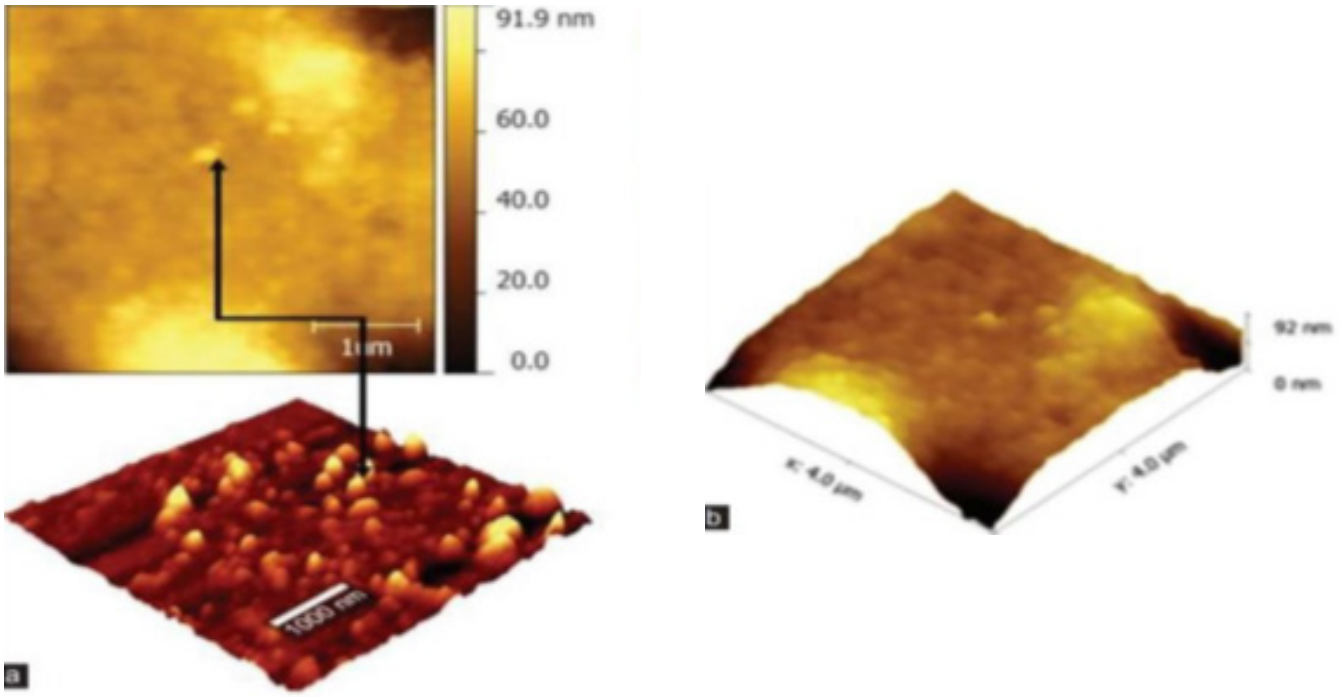

Figure 3. Morphological characterization of composite Atomic Force Microscopy Topographic image, height mode of cellulose. **(a)** CC and **(b)** JC.

The capillary interior structure of cellulose fibres is a distinguishing feature. These threads divide in several directions along a hairline, forming bigger structures that resemble plant fibres (Figure 4). As a result, the material's natural origin is confirmed. Under the SEM, a cohesive structure generated by cellulose fibres is readily visible in the image.

The shape and intricate irregular fibre structure are clearly discernible on 200X magnification. The diameters of the fibres examined range from 1 to 50 µm, while the

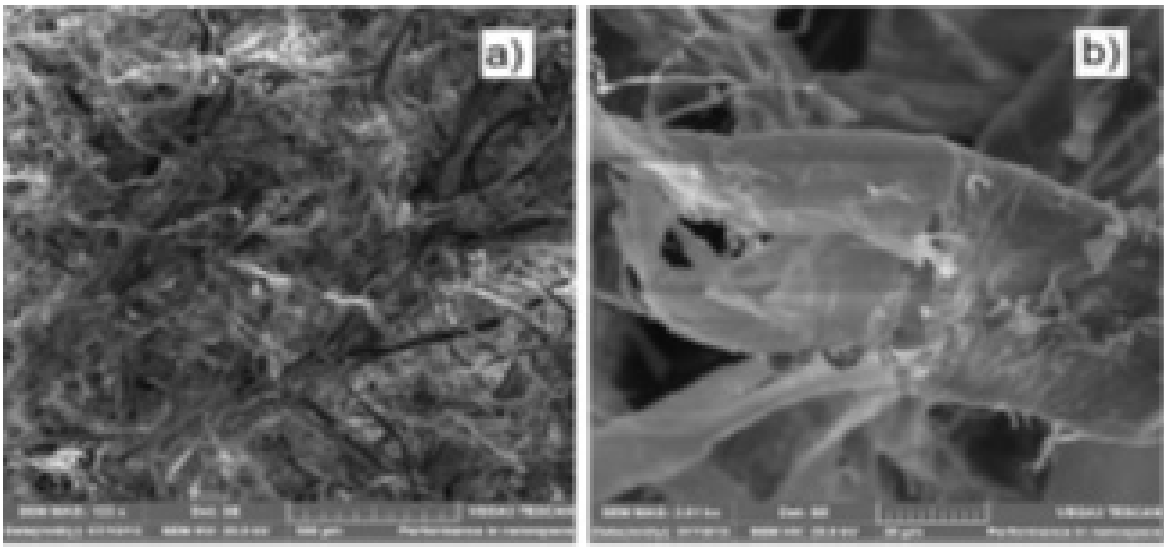

Figure 4. SEM image of PCTSG composite of composition 30:70.

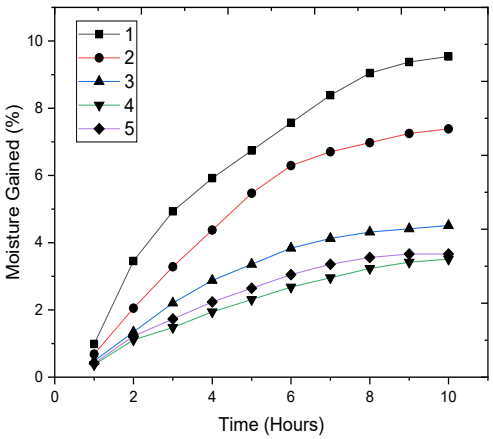

Figure 5. Moisture absorption rate of PCTSG composites.

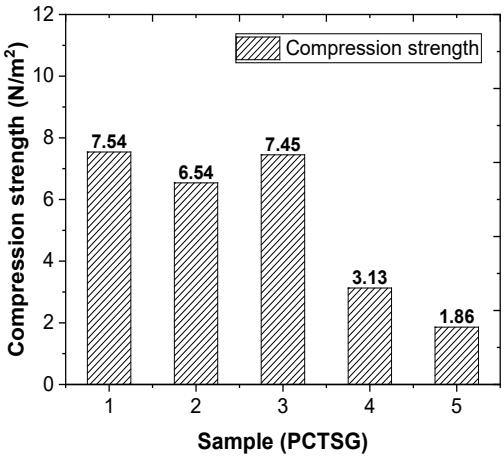

Figure 6. Compressive strength of PCTSG composites.

distance between them is between 1 and 150 µm. The cellulose fibres could not be covered with a uniform layer of conductive gold. Low stiffness and a rough fibre surface suggest this.

The graph in Figure 5, shows variation in moisture content of PCTSG composites. The composition plays a prominent role in controlling moisture content of composites. It is evident that higher fibre content in composite will result in higher moisture absorption rate. The first sample with composition 30:70 has a higher absorption rate, and goes on decreasing with increase in TSG. After time, duration of 10 hours the samples reached a threshold point where there is no longer moisture absorption.

4.0 Compressive Strength of PCTSG Composites

The samples for compressive test are synthesized based on the composition variation of PC and TSG as depicted in Table 1. The compositions with 30:70, 40:60 and 50:50 of TSG and PC respectively, possessed an average compressive strength of 7.17 N/mm^2.

The compositions of 60:40 and 70:30 TSG and PC respectively depicted lower compressive strength (Figure 6). Theoretically, compressive strength should increase with increase in binder content in the composite. In our case samples 4 and 5 were supposed to possess highest compressive strength as they contain higher TSG compared to the samples 1, 2 and 3.

After visual inspection, additional voids were noticed in the samples 4 and 5, which were induced while curing the samples, these voids tend to reduce the strength of composites. Another reason being the inherent property of TSG itself. The TSG at higher concentration shows brittle nature, which affects the strength of the composites.

5.0 Fungal Behaviour

The capacity of the material to biodegrade is demonstrated by microbial growth on the biopolymer composite[11]. Natural fibres are resistant to microbial destruction due to the presence of lignin. Less lignified natural fibres, on the other hand, are more susceptible to microbial cellulose and hemicellulose breakdown. Also, moisture infiltration and absorption encourage bacterial development. Dehydration, hydrolyses, and/or oxidation of cellulose diminish the mechanical properties of biopolymer composites.

A variety of biotic and abiotic factors can degrade cellulose[12]. For fungal spores or fragments to germinate and begin new fungal colonies, the composite must be at or near the Fibre Saturation Point (FSP), which is where the fibre cell wall is saturated with "bound" water. In most situations, fungal decay starts at around 30% moisture content reaches an optimum between 40% and 80%, and

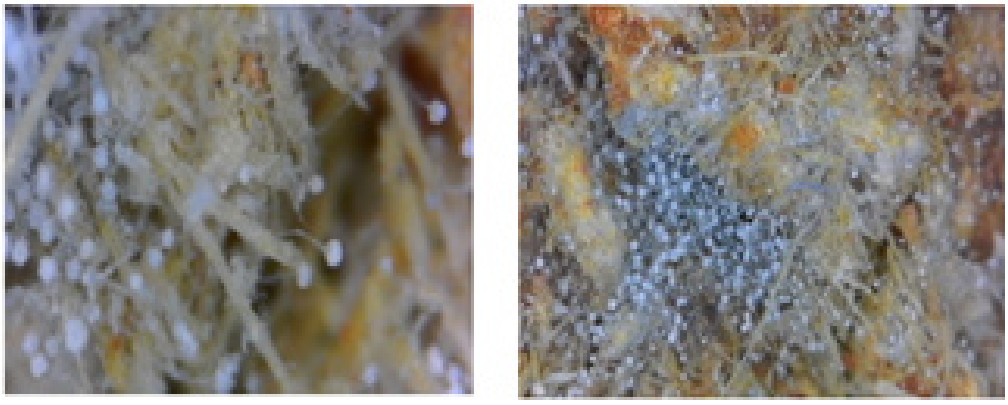

Figure 7. Fungal infected PCTSG sample at 200X (Left) and 50X (Right) magnification.

then starts to decline when moisture levels rise over 100%, as cell lumens fill with water and oxygen becomes scarce.

In order to observe the changes developed on the PCTSG composites. The samples are maintained in normal environmental conditions for 90 days. At the end of 45th day, changes were visible on the sample surface in the form of fungal development. When observed on the 90th day, colonies of mucor fungus are formed in patches (Figure 7).

The manufactured samples are examined for microscopic alterations during a two-month period under typical ambient circumstances with partial sunlight and also an average of about 60% relative humidity. The samples K4, K5, and K6, which contained 5%, 10%, and 15% turmeric powder, respectively, showed a biotic development on the surface. The samples K1, K2, and K3, which contained 5%, 10%, and 15% boric acid respectively, were stable in structure and didn't exhibit fungal (Mucor) or bacterial activity over this time period.

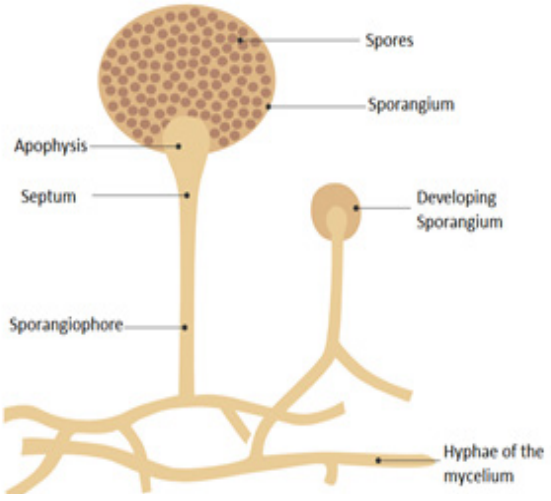

Figure 8. Mucor fungus characteristics.

Mucor species have traditionally been identified by physical traits such as sporangia size and form, as well as reproduction mechanism. Mucor's evolutionary position and relationship among its species have recently been established thanks to molecular evidence[13].

Mucor-contaminated bio materials pose just a minor health risk to healthy people. In Mucor, no particular mycotoxin has been isolated and identified. Toxins were found in extracts from specific Mucor species.

Two additives are considered in order to address the fungal development, namely Turmeric Powder (TP)[14] and Boric Acid (BA)[15] in a composition depicted in Table 4 and Figure 9, maintaining PCTSG composition at 50:50.

Table 4. Additive composition in PCTSG composite

Sample	Boric Acid %	Turmeric Powder %
K1	5	0
K2	10	0
K3	15	0
K4	0	5
K5	0	10
K6	0	15
K7	10	5
K8	5	10

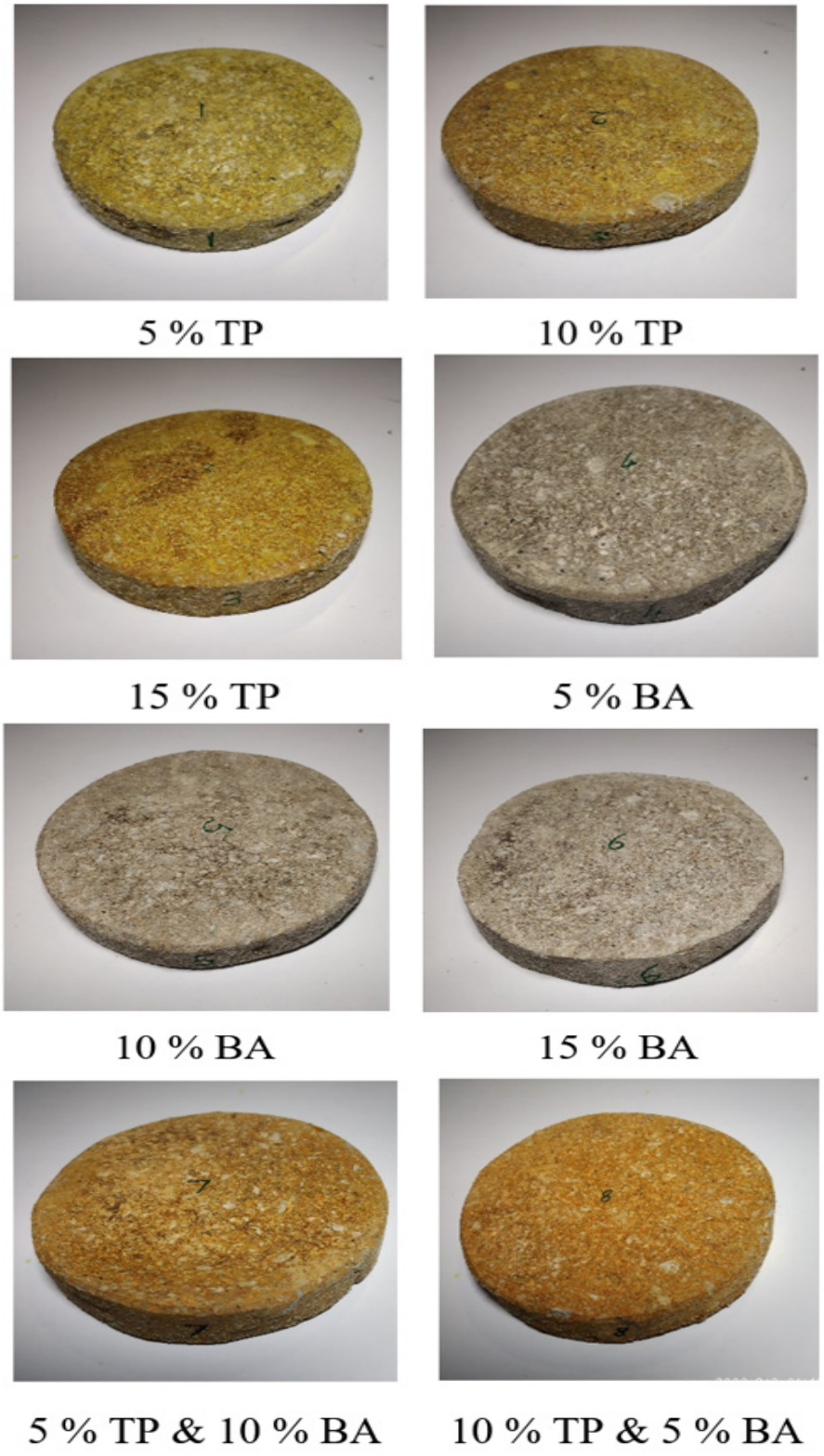

Figure 9. Additive PCTSG samples.

The samples are maintained in the environmental conditions for same duration of time as elaborated above. Further fungal development is seen in samples with TP, the samples with the BA additive did not have any impact of mucor.

6.0 Additive Sample Compression Test

Compressive test on additive samples is carried out to study the changes in strength of synthesized samples in comparison with the non-additive PCTSG samples. Figure 10 shows the pattern of variation of compressive strength of additive based PCTSG samples. An average of 6.39 N/m^2 is possessed by the additive TP, the addition of TP tends to reduce the compressive strength of samples. The additive BA based samples also depicted similar results of variation as the TP.

The compressive strength of BA additive-based composites possessed compressive strength little higher compared to TP, possessing an average of 7.12 N/m^2. The samples 7 and 8 are the mixture of TP and BA and did not show much variation in compressive strength.

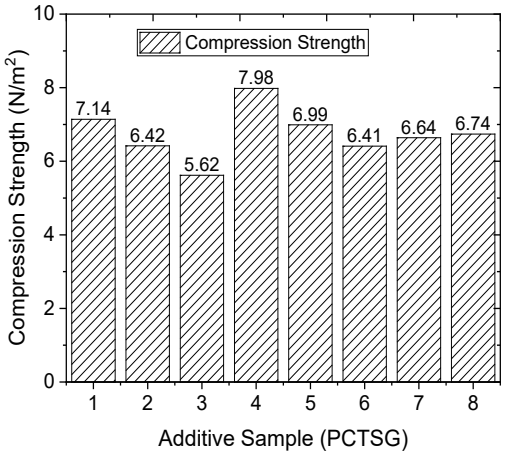

Figure 10. Additive samples compression test.

7.0 Additive Sample Thermal Conductivity

To test in Lee's and Charlton's apparatus, samples for 'k' are synthesized according to the dimensions required.

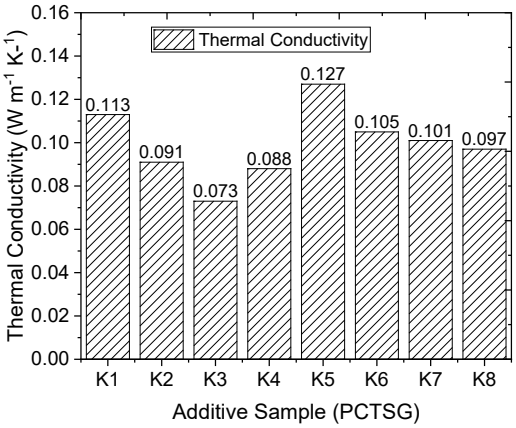

Figure 11. Additive samples thermal conductivity values.

Samples are synthesized by altering the matrix and reinforcement compositions, and are maintained at a temperature of 24°C±4°C for 24 hours before being tested. To prepare thermal conductivity samples, a 30 mm thick and 120 mm diameter mould is prepared considering shrinkage and machining allowances. The samples are created using a combination of open and compression moulding procedures.

Figure 11 shows the 'k' values of additive PCTSG samples. The BA samples depicted 'k' values nearer to the non-additive PCTSG samples. The 'k' for TP additive is seen on the higher side which is not desirable for an insulator.

8.0 Design of Experiments

The main effects plot is plotted to determining the relative influence of various inputs on the desired result. The main effects plot illustrates the mean outcome for each independent variable's value, integrating the effects of the other factors, used to assess whether or not the category variable has a primary influence in the design of experiment[16].

The experimental results of thermal conductivity for each variation are considered to plot main effect for means and signal to noise ratio for inputs BA, TP and output of thermal conductivity. The influence of both parameters is depicted in the Figure 12, where positive influence of BA persists on the thermal conductivity with increase in its content. The average 'k' value of BA additive is 0.099 W/

Table 5. Response Table for signal to noise ratios (Smaller is better)

Level	BA %	TP %
1	21.78	19.49
2	20.46	19.77
3	18.88	20.81
4		23.87
Delta	2.90	4.38
Rank	2	1

Table 6. Response table for means

Level	BA %	TP %
1	0.08307	0.10779
2	0.09500	0.10271
3	0.11450	0.09159
4		0.06402
Delta	0.03143	0.04378
Rank	2	1

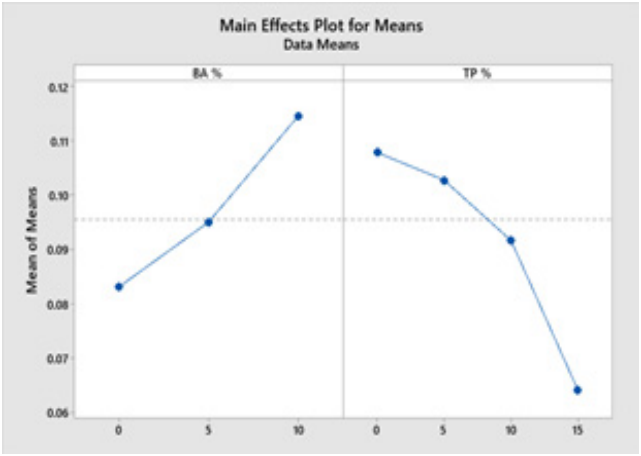

Figure 12. Main effects plot for means (Input- BA, TP and output - Thermal Conductivity).

mk. The TP has negative influence compared with BA in terms of thermal conductivity gaining an average 'k' value of 0.106 W/mk. This proves BA has an advantage over TP in terms of 'k'.

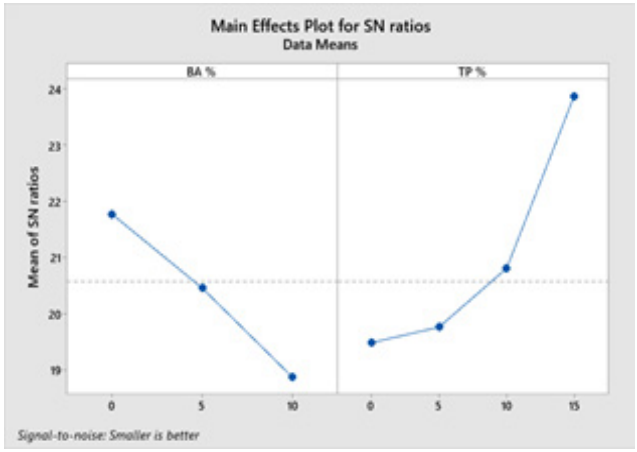

Figure 13. Main effects plot for signal to noise ratio (Input- BA, TP and output - Thermal Conductivity).

9.0 Conclusion

Bio-polymer composites represent an innovative and sustainable approach to building insulation materials in the mining industry, offering a unique blend of environmentally friendly characteristics and enhanced thermal performance. These composites exhibit desirable thermal and mechanical properties, making them suitable for a range of applications within the mining sector. The research in bio-polymer composites for the mining industry is also exploring their potential as an alternative to conventional materials in mine site infrastructure.

PCTSG composites evaluation towards fire behaviour under the standard UL94 for horizontal and vertical testing depicted promising results falling in the class of UL 94 HB for horizontal orientation, 94V-1 and 94V-2 for vertical orientation. Higher moisture absorption in case of PCTSG1, whereas reduction in absorption and higher moisture retention is observed at higher TSG content, which makes it not suitable for applications where high humidity persists. Voids in the samples of compression test showed reduction in strength and increase in brittleness at higher TSG, whereas better results can be seen at higher PC content in the samples. Degradation due to fungal attack on the PCTSG composites addressed by BA and TP, the BA proved a better additive with 0% infection by 'Mucor' fungus and other ailments even at 5% composition. This predicts, at compositions less than 5% BA, similar results can be obtained. Average 'k' value

determined for PCTSG samples without additives is 0.057 W/mk, correspondingly for additives based PCTSG samples 'k' value obtained is 0.099 W/mk, which shows an increment of 0.042 W/mk by using additives. The two independent variables BA and TP had interaction at 20.5 which depicts the effect of constituents on 'k' value. Adequate results are generated through this research to support our argument regarding the use of PCTSG composites for thermal insulation application.

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