Agri-residual Filler Based Bio-Composites: Synergistic Effect of Organo-sulfide Coupling Agent and Alkali Treatment on Mechanical Properties

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Abstract. With growing consumer awareness, carbon footprint and waste disposal challenges, there is an increasing demand for the use of agricultural wastes in developing value-added structural components. In this current study, commercially available epoxy resin has been reinforced with chemically modified wheat straw filler. Particulate wheat straw fillers were undergone alkaline treatment to remove selective and non-essential components. Alkaline modified samples were then treated with organo-sulfide based coupling agent to enhance filler/matrix interfacial compatibility. The bio-composite samples were developed using casting technique. The cast samples were tested for their mechanical strengths using compression and flexural tests. The results indicated that the use of coupling agent and alkaline treatment led to improvement of mechanical strength in a synergistic manner. Optical micrographs of fractured surfaces also revealed morphological features which could be correlated to the mechanical performance of the bio-composites.

1. Introduction

With the growing population, the demand for food crops is ever growing, thus leading higher production agricultural crops. Rice, wheat, corn are some the major agricultural crops worldwide. Looking into Indian scenario, a big part of Indian economy depends on agricultural production. Annually around 500-550 million tonnes (Mt) of crop residue is generated in India of which majority is wheat and rice. Even after cattle feed, animal bedding, cooking fuel, organic manure, more than 30 percent of the total residue remain unused [1]. Waste management of such a large quantity of unused wheat straw is a very big challenge. It is often found that farmers have no option but to burn it which contributes to air pollution. Thus, for sustainability reasons this huge amount of agricultural waste are being used in manufacturing greener products for different applications. Agricultural waste is available abundantly and it is renewable resource. As the oil resources are depleting, researchers are shifting towards green/natural resources because of social and environmental concern [2]. Use of natural fibre in manufacturing of composite in various industries has been there for some time as agricultural waste has shown potential as filler in the polymer matrix be it thermoset or thermoplastic polymer [3-4]. Natural fibres are slowly becoming an alternative to glass fibre and carbon fibre which are very popular for their strength and other advantageous properties. A varied applications of bio-composites can be found in construction, automobile, packaging and medical industry[5].

Thus, the use of agricultural waste as a filler in the polymer matrix to obtain composite material of desirable properties are becoming more and more popular among researcher. However, working with
raw natural fibre is challenging because of their hydrophilicity and in turn the incompatibility with traditional polymer matrices which are hydrophobic in nature. Because of this nature, the bonding between fibre and matrix becomes weak and affects the resultant mechanical properties of the composites. Raw fibres must undergo some kind of physical or chemical modification before being used in polymer matrix in order to get better mechanical properties [6], [7]. Because of abundance and renewability, working with wheat straw fibres as filler in polymer matrix is popular option among researchers and scientist. It is found in literature that researchers have used wheat straw and wheat straw blended with other natural fibres as a filler material to reinforce polymer matrix and have reported that wheat straw fibres are a good alternative to manufacture green composite material and its application in various domains [8], [9].

In this paper, therefore we have investigated the combined effect of organo-sulfide Si 69 coupling agent and alkali treatment on the mechanical performance of wheat straw particulate filler reinforced bio-composites.

2. Materials
Epoxy resin (SMR 2085) of epoxide number 4.93 and viscosity of 3200 cPs at 25°C has been is catalysed by triethylenetetramine (C₆H₁₈N₄) hardener of density 0.980 g/cc at 20°C and refractive index of 1.499 hardener has been used. An organo-sulfide based coupling agent Si 69 has been used in the study. Wheat straw was obtained from local agricultural field. All chemical reagents were of laboratory grade.

3. Methods

3.1 Pre-treatment of wheat straw
Wheat straw was collected from the local agricultural field in Jaipur for this research. The wheat straw fibres were converted into powder form using a standard mixer. This sample was then passed through the sieve 450-micron sieve and the portion that passed through the sieve was used as filler in the epoxy matrix. This powdered wheat straw fibres were then kept in 5% NaOH solution for 24 hours. It was then washed properly using distilled water. The washed wheat straw filler was then oven dried for 24 hours at 60°C temperature. The alkali treated wheat straw fibres were then modified with organo-sulfide coupling agent (Si 69). These modified fibres were washed again with distilled water and then oven dried for 24 hours at 60°C for 24 hours before using it in the epoxy matrix.

3.2 Fabrication of bio-composites
Milled wheat straw particulates were then used in proportions of 10% and 15% by weight of epoxy as a filler material in the epoxy matrix. The ingredients were then mixed using a mechanical stirrer (Remi motors, RQ-124A) at 500 rpm to form a uniform mixture. For further uniform distribution of the filler materials the mixture was then put in ultrasonicator for 30 minutes at room temperature. This composition was then poured into a silicon mould and was left to harden. The average hardening time was 4 hours for all samples. A, B, C,D,E,F and O are the seven different samples taken in this study. Table 1 shows the composition of this samples and the type of treatment it has been subjected to.
Table 1: Composition of Bio-composites

| Sample | Epoxy Resin | Wheat straw (phr*) | Silane treatment | NaOH treatment |
|--------|-------------|--------------------|------------------|---------------|
| O      | 100         | 0                  | No               | No            |
| A      | 100         | 10                 | No               | Yes           |
| B      | 100         | 15                 | No               | Yes           |
| C      | 100         | 10                 | Yes              | Yes           |
| D      | 100         | 15                 | Yes              | Yes           |
| E      | 100         | 10                 | No               | No            |
| F      | 100         | 15                 | No               | No            |

3.3 Mechanical testing
Mechanical strength plays an important parameter for any composite material be it flexural strength or compressive strength. For determination of mechanical properties, rectangular samples were cut from the prepared wheat straw epoxy composite in size of 50x10x4 for compression testing (as per ISO 604) and in size of 80x10x4 for flexural testing (according to ISO 178). At least 5 samples of each composition were tested using universal testing machine (UTM) of Dak Systems using 10 kN load cell.

3.4 Optical microscopy
Moticam 5.0 MP optical microscope has been used to observe the prepared samples. A magnification of 500x was used to see the morphology of the composite samples prepared. All the fractured samples are grinded using coarser grinder paper to finer grinder paper and then it was polished using diamond paste in the polisher to get a smooth surface to observe under the microscope.

4. Result and discussion

4.1 Mechanical properties
Figure 1 and 2 show compressive strengths and flexural strengths of the bio-composites respectively. At least five samples of each compositions were tested. It was observed that pure epoxy samples have the highest compressive and flexural strength of 45.83 MPa and 58.78 MPa respectively. This could be attributed to the fact that wheat straw fillers being hydrophilic in nature, interfacial compatibility with hydrophobic epoxy matrix would be limited. However, it was observed that effect of alkali treatment could improve both compressive and flexural strength for both fibre loading (10 phr and 15 phr). The strengths were further enhanced on treatment with organo-sulfide coupling agent, indicating a synergistic effect. The much-improved dispersion of the bio-fibres and the interaction between the fibre and epoxy matrix are in good agreements with the optical micrographs as shown in figure 3. The results could be attributed to the fact that effect of alkali treatment could remove the undesirable components such as waxes and gums, thereby facilitating resin impregnation and better fibre wetting. This in turn resulted into improved mechanical properties. The effect of coupling agent could be attributed to improved interfacial compatibility between filler and epoxy matrix, thereby, resulting into enhanced mechanical strength. It was also observed from fig.1 and fig.2 that incorporation of 10 phr filler could result into optimized mechanical properties, beyond which there were reduction in mechanical strengths. This could possibly be attributed to non-uniform dispersion wheat straw fillers at higher (15 phr) loading.
4.2 Optical microscopy
Optical micrographs of the fractured surfaces of all the samples taken in this study are shown in fig. 3. The figure (g) represents the fractured surface of pure epoxy sample. No voids can be observed and the surface morphology is smooth and very uniform. Micrographs (e) and (f) represents the samples prepared from raw straw and epoxy. It is clearly visible from these micrographs that there is neither proper dispersion of the bio-fibres in the polymer matrix nor proper interaction between fibre and matrix. Moreover, voids and cracks can be found in these composites. With the alkali treatment there is improvement of the interaction between fibre and matrix as observed in micrographs (a) and (b). It is because alkali treatments remove the outer layer from the wheat straw and makes the surface of the bio-fibres rough, helps in better bonding between the polymer matrix and fibre. It is also evident that the use of coupling agent resulted in enhanced fibre/matrix interfacial compatibility (micrographs c and d) which could prevent major crack formation and development of voids. Micrographs show that all the specimens failed in brittle manner. These observations are in very good agreement with the results obtained from mechanical tests.
5. Conclusions

A range of bio-composites were developed using agri-residue based fillers (wheat straw) as reinforcements within epoxy matrix. The fillers were treated with alkali solution and then with organo-sulfide coupling agent. Although there were reductions in mechanical properties (compressive strength and flexural strength) on the incorporation of wheat straw particulate fillers compared to the pure epoxy samples but the properties were found to be enhanced on treatment with alkali solution and further enhanced by organo-sulfide coupling agent treatment. Results also indicated an optimized filler loading (10 phr) both for compressive and flexural strengths. With the increase of loading of wheat straw, there was reduction in the mechanical strengths. The fact that chemical treatments (both alkali and silane treatment) play a significant role in improving the mechanical properties because of improvement of interfacial compatibility between fibre and polymer matrix is also backed by optical micrographs showing the surface morphology of the fractured samples. Major crack formation and voids were found restricted in the coupling agent treated samples and were in good agreements with

Figure 3. Micrographs of fractured samples (a) A (b) B (c) C (d) D (e) E (f) F (g) O
the results obtained from mechanical tests. Over all the mechanical strength of the double treated fibre specimen showed significant improvement over single treated fibres and raw fibre epoxy composite.

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