

Improvement in Physical Properties of MMA Grafted Coir Fibres

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Abstract

This work deals with the surface modification of Coir fibre through graft copolymerization process. Graft copolymerization of methyl methacrylate (MMA) onto coir fibre was carried out with Potassium per sulphate (PPS) as an initiator under the catalytic influence of Ferrous ammonium sulphate (FAS) in aqueous medium. Control and grafted coir fibres were subjected to evaluation of properties like tensile strength, flexural rigidity, density, water absorbance and light fastness studies. It was observed that MMA grafted coir fibre shows more resistance towards water and light fastness when compared with that of control coir fibre. Further morphological, structural changes and thermal stability of control and grafted coir fibre have also been studied by SEM and TGA techniques. For statistical significance the Analysis of variance (ANOVA) were studied and the P values obtained were less than 0.05 which revealed that the value was highly significant for the improvement of physical properties on coir fibre by graft Co- polymerization.

Keywords: Graft co-polymerisation, methyl methacrylate, catalyst, initiator, coir fibre

Introduction

Natural fibres have provided raw materials to meet the human requirements of fibres in their life. With the high-tech developments of man-made fibres, natural fibre lost much of its interest and many of the ancient natural fibres are no longer in use. However, as a result of a growing awareness of the interconnectivity of global environmental factors, the principles of sustainability, industrial ecology, eco-efficiency and green chemistry and engineering are being integrated into the development of the next generation of materials, products and processes (Mohanty et. al., 2005).

Coir fibre have many advantages, they are low density, recyclable and biodegradable. Additionally they are renewable raw materials and have relatively high strength and stiffness. Their low-density values allow producing composites that combine good mechanical properties with a low specific mass. The advantages of natural fibre composites include lightweight, low-energy production and environment friendly (Sakthivel and Ramesh, 2013). In order to improve the physical properties of natural fibre, grafting is one of the best technique. The properties of natural fibres can be modified by graft copolymerization and blending. Desirable and targeted properties can be imparted to natural

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and synthetic polymers through graft copolymerization in order to meet out the requirement of specialized applications. Grafting is a convenient and clean method for altering the properties of numerous polymer backbones. The properties of ligno cellulosic fibres can be modified by graft copolymerization with vinyl monomers under selective and controlled conditions. As vinyl monomer Methyl Methacrylate is having outstanding resistance to exterior weathering properties. In graft copolymerization, side chain grafts with functional groups are covalently attached to a main chain of a polymer backbone to form a branched copolymer. By the chemical modification of ligno cellulosic fibres through graft copolymerization with synthetic monomers, many different properties, including mechanical strength, hydrophobic character, flexural rigidity, light fastness, thermal resistance and chemical resistance can be improved (Teli and Javed, 2012).

Many companies have shifted their focus in using materials that weigh less, are durable and efficient, and have high mechanical properties. In such scenario, natural fibres are creating great demand as they come at a very low cost, are neutral to CO₂, recyclable, biodegradable, can be separated easily, and have low density and contain desirable physical properties. These features give natural fibres great advantages over traditional fibres, such as carbon or glass. In the present investigation, methyl methacrylate (MMA) was graft copolymerized onto coir fiber using PPS as initiator in the presence of FAS as catalyst to make the coir fibre more applicable in innovative products.

Materials and methods

Materials

Mechanically extracted Coir fibres were collected from Alleppey, Kerala. Monomer: Methyl Methacrylate (MMA), Initiator: Potassium per sulphate (KPS) and Catalyst: Ferrous ammonium sulphate (FAS) used were of analytical grade.

Methods

Purification of materials

The fibres were first cleaned in willowing machine and sorted using combing board. These fibres were soaked in water over night. Then it was washed with water with stirring for 8hrs and dried in hot air oven at 70⁰C.

MMA was washed with 5% NaOH solution followed by water and dried over anhydrous sodium sulphate. Catalyst ferrous ammonium sulphate was recrystallised from hot water. Initiator potassium per sulphate was used as received.

Graft Co-polymerization

Fibres were immersed in distilled water for 24 hrs prior to the reaction. The material to liquor ratio was maintained at 1:50. A known amount of the initiator, catalyst and monomer were then added to the reaction vessel maintained at required temperature. Grafting of MMA on to Coir fibre was carried out under constant stirring. At the end of the desired reaction period, the coir fibre was thoroughly washed with acetone to remove any homo polymer generated during the reaction. Fibres were then washed with distilled water and dried in a hot air oven at 70⁰C till a constant weight was obtained. Polymerization reactions were done at optimized conditions of 25% monomer, 0.75% initiator, 0.75% catalyst based on the weight of the fibre, 50⁰C of temperature and 150 minutes reaction time on to the coir fibre. Grafting yield (GY) was calculated by the equation

$$GY = \frac{(W_2 - W_1)}{W_1} \times 100 \quad (1)$$

Where, W₁ and W₂ are the weights of coir fibre and grafted fibre respectively.

Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy studies of coir fibre and grafted coir fibre was carried out on Scanning Electron Microscope (SEM) (JEOL JSM-6390 LV, Tokyo, Japan) system with an accelerating voltage of 10 KV. The SEM images are studied under 10µm magnification.

Thermo Gravimetric Analysis (TGA)

The Thermo Gravimetric Analysis (TGA) of the coir fibre was done using Mettler Toledo TGA/SDTA 851^o, Japan. The test was carried out in an inert atmosphere under nitrogen flow rate at 10ml/min and heating rate throughout the test was 10^oC/min. The weight change was recorded as a function of the heating temperature.

Tensile properties

Tensile properties of coir fibres were determined using UTM (Universal Testing Machine) Shimadzu AG-X/R. At test parameters; strain rate = 10mm/min, gripping length=5cm at atmospheric temperature.

Flexural rigidity

Flexural Rigidity of the untreated and grafted fibres was tested using the Flexural Rigidity Tester (developed by CCRI). 25 samples each of untreated and grafted fibre were tied around a PVC pipe of 2 inch diameter to attain the shape of a ring. After 24 hours, the rings were tested using the Flexural Rigidity Tester with and without load (1g) and the ring diameter and deformation of ring on loading was noted. The average radius of the ring and deformation on loading were calculated (Beever, 1970). The Flexural Rigidity was calculated using the following formula:

$$\text{Flexural Rigidity} = 0.0047. \text{ mg. } (2 \pi r)^2 (\cos^{\theta} / \tan^{\theta}) (\text{gcm}^2)$$

where,

mg = weight of load applied in grams

r = radius of the ring in cm

d = deformation of lower end of ring in cm

$$\theta = 493d/2\pi r$$

Density

Fibre density is more conveniently determined indirectly by comparing the sample with standards of known density. The commonly used technique for indirect determination of fibre density is the Sink Float method (William Weaver, 1984).

Procedure:

For this method, known densities of two liquids are taken. The liquids must be miscible and inert to the fibre being examined. One liquid must be less dense than the fibre and the other liquid must be denser. Water (density=1) and chloroform (density=1.48) were taken. A known volume of liquid which has the density lesser than the fibre were taken in beaker and fibre is immersed in it. The next liquid is added drop wise to the beaker with constant stirring. When the density of the solution precisely equals that of the fibre then the fibre will neither sink nor float but will remain suspended in the liquids. The density of the fibre is calculated as follows

$$\text{Density of the fibre (d)} = \frac{d_A V_A + d_B V_B}{V_A + V_B}$$

V- refers to volume.

A- refers to one liquid.

B - refers to other liquid.

Light fastness

Tested the light fastness of the samples using Xeno test. This is uniform specification for rating the light fastness of materials more quickly than naturally (Anitha Das Ravindranath, 2004). The test conditions as follows.

Test method: Colour fastness to light

Humidity: 30%

Temperature: 60^oC

Standard: IS2454:1985

Water absorption

The water absorption of untreated and grafted coir fibre were determined by immersing in distilled water in a beaker at room temperature for different time durations. After immersion for 24 h, the specimens were taken out from the water and all surface water was removed with a clean dry cloth or tissue paper. The specimens were weighed regularly at 24, 48, 72, 96 and 120hrs exposures. The water absorption was calculated by the weight difference. The percentage weight gain of the samples was measured at different time intervals. The water absorption of the untreated and grafted coir fibre

was determinant by using the following relationship

$$WA = (WET - DRY) / DRY \times 100$$

Where

WET= weight of sample after immersing in water

DRY= dry weight of the sample

Results and discussions

Scanning Electron Microscopy (SEM)

SEM images at magnification 1000 were taken for untreated and grafted coir fibre. On comparing the SEM images it has been found that on grafting, considerable amount of (MMA) deposited on to the coir fibre.

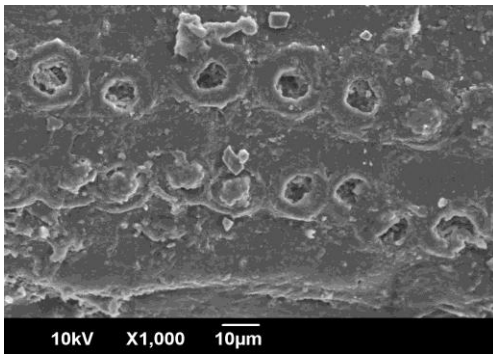


Figure 1(a). SEM image of Untreated Coir Fibre

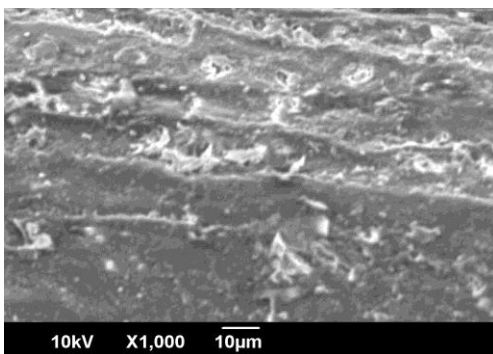


Figure 1(b). SEM image of MMA grafted Coir

In Fig. 1(a), lots of pits are clearly observed. These have resulted from the leaching of coir fibre due to the purification process prior to the grafting process. In Fig. 1(b), the surface becomes more or less uniform and the pits are covered owing to deposition of PMMA grafts

along the direction of fibre axis. This surface modification increases the strength of grafted fibres compared with untreated fibres (Khullar et.al., 2008).

Thermo gravimetric analysis (TGA)

Thermal behavior of control coir and grafted coir fibre were examined by a study of their TGA thermograms. It is observed that initial and final decomposition temperature of control coir fibre are 80°C and 450°C where as in the case of grafted coir fibre the initial and final decomposition temperatures are 90°C and 670°C respectively Fig.2 (a & b). It is quite evident that the thermal stability of grafted fibre is higher than that of control fibre. (Jayaraj et al., 2014).

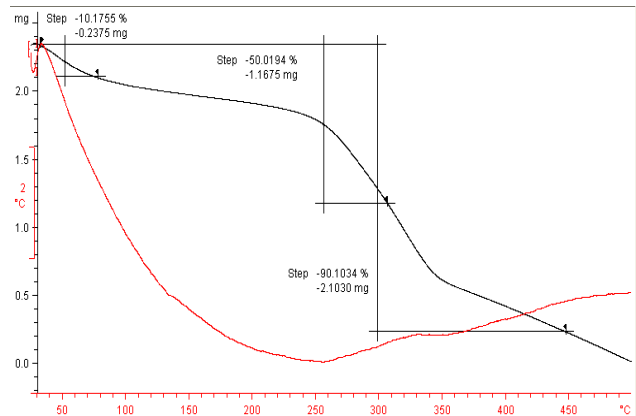


Figure 2(a). TGA data of Control coir fibre

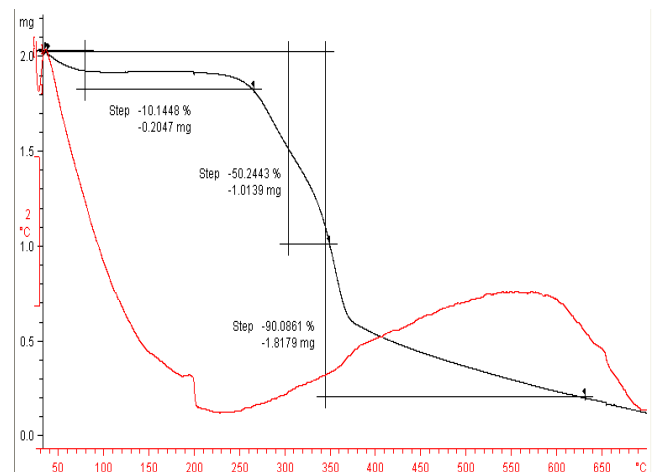


Figure 2(b). TGA data of Grafted coir fibre

Tensile Properties

The tensile properties of control and grafted coir fibre were determined by taking a minimum of 50 fibres. It clearly shows that (fig 3) there is an appreciable improvement in the tensile properties of coir fibre due to grafting. There is an improvement of 71.29% in the breaking stress of grafted fibres compared to the ungrafted one. The increase in breaking stress is from 213.08 N/mm² to 365 N/mm² for control and grafted fibres respectively. The increase in breaking stress of grafted coir fibre may be due to the orderly arrangement of PMMA units on the cellulosic backbone of the coir fibre.

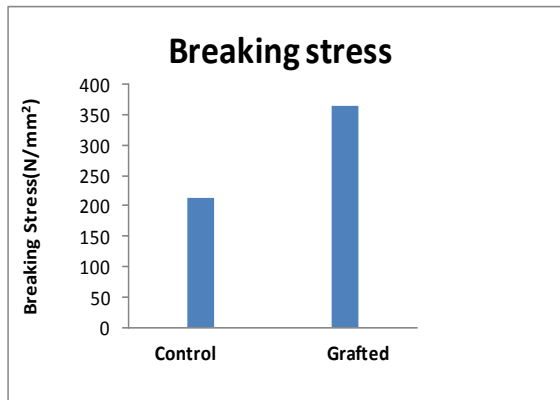


Figure 3. Breaking stress of control and grafted coir fibre

Flexural rigidity

Flexural rigidity test indirectly measures the degree of softness by evaluating the flexural rigidity of the fibre, when subjected to deformation. The grafting was found to be capable of imparting softness to the coir fibre. Apart from improved sensory perception in the feel of the fibre, the flexural rigidity test confirmed the softness. FR values obtained were 1.37 gcm² for untreated fibre and 0.85 gcm² for grafted fibre. Almost 38 % reduction in flexural rigidity of the fibre was observed after grafting even with improvement of 71.30% of tensile stress. Reduction in flexural rigidity is directly proportional to the improvement in softness. The result can be interpreted as a bar diagram as shown in fig 4.

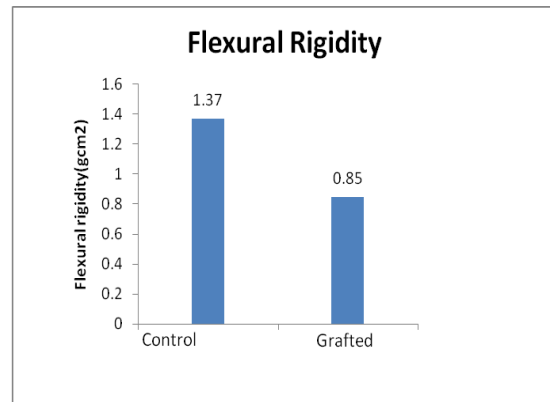


Figure 4. Flexural rigidity of control and grafted coir fibre

Density

Density of the coir fibre may vary by change in diameter. The value seems to be 0.67-1.3g/cm³. Using Sink float method density of the control and grafted coir fibres were 1.3 and 1.1g/cm³ respectively (fig 5). Density of the coir fibre slightly decreases as a result of grafting. This may be due to the leaching of the extractives from coir fibre during the process of grafting. Tensile properties of the grafted fibres were increased even with the reduction in density and flexural rigidity.

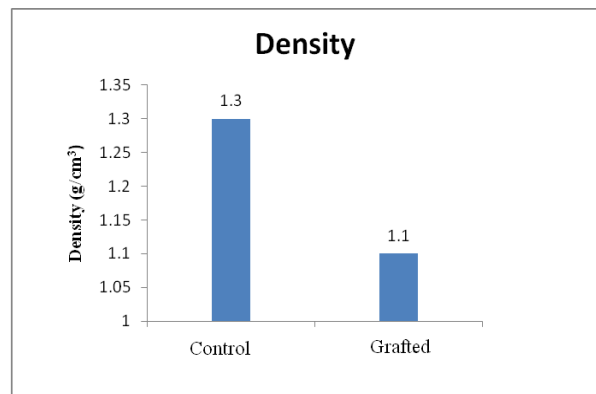


Figure 5. Density of control and grafted coir fibre

Water absorption

Water absorption of control and grafted coir fibres were determined by the method as mentioned above. Water absorption values are

found to be 81% and 66% for control and grafted fibre (fig 6). It is found that 15% reduction in water absorption value of grafted fibre is due to the blockage of active sites on polymeric backbone by grafted MMA, thereby increasing the hydrophobic nature of the fibre.

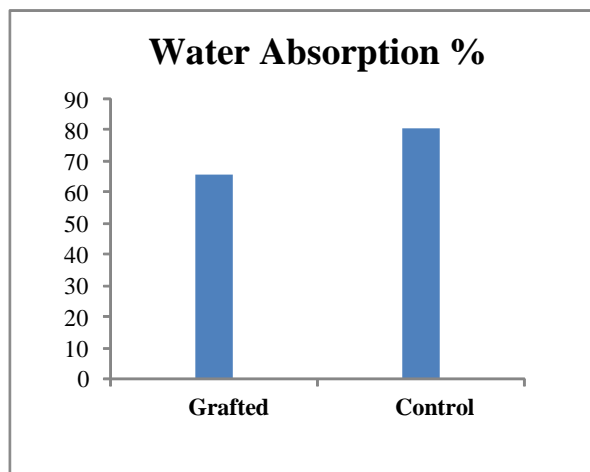


Figure 6. Water absorption of control and grafted coir fibre

Light fastness

Control and grafted fibre were subjected to Xeno test which rated the control fibre as Grade II and the grafted fibre rated as Grade III to IV. This shows that grafting enables improvement in light fastness property compared to control fibre.

Conclusion

Surface modification of Coir fibre through graft copolymerization has been confirmed by FTIR, SEM and TGA. Thermal stability of MMA graft copolymerized fibres has been found that higher than that of untreated Coir fibre. Enhancement in softness, hydrophobic character, light fastness and density of MMA graft Coir fibre has also been observed. All these properties of surface modified fibres could help in their applications especially in the synthesis of natural fibre reinforced composites for their better end use.

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