Characterization of Sisal/Polypropylene Composites Treated with Plasma

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ABSTRACT

In this study, sisal/polypropylene composites were experimentally investigated for their flexural, thermal and water absorption characteristics. The effect of oxygen (O), argon (Ar) and ammonia (NH_3) plasmas on the surface of the sisal fibre as well as the effect of the sisal fibre content on the above mentioned properties was studied. The composite laminates (4 mm thick) were processed by hand lay-up technique by using a compression moulding machine, with the mould temperature of 165°C and the pressure of 6.89×10^2 kPa for 15 minutes. Specimen preparation and testing were carried out as per ASTM standards. Flexural data obtained showed that the plasma-treated sisal fibre-reinforced polypropylene offered superior flexural properties compared to untreated laminates, which indicated better adhesion between the sisal fibre and the untreated polypropylene matrix. Thermal investigations revealed that the sisal/polypropylene composite had its thermal stability in between that of the fibre and the matrix. Furthermore, the water absorption studies indicated that plasma treatment decreased the water uptake of the laminates, thereby leading to better fibre-matrix adhesion. Morphological studies were carried out by using SEM to complement the results.

INTRODUCTION

In recent years, there has been an ever-growing demand for lignocellulosic fibres, also called natural, plant or vegetable fibres. Among them sisal, flax, hemp, jute and other bast fibres are a group of environmentally friendly reinforcement in composites from a wide variety of thermoplastics matrices, including polypropylene, polyethylene, polystyrene and polyvinyl chloride. These natural fibres are very popular as reinforcements due to some of their unique characteristics, such as biodegradability, renewability, low cost, availability, density, reduced health hazard, no damage to processing equipment and reasonable stiffness and strength. Among natural fibres, the sisal (*Agave sisalana*) fibre removed from the leaves of the sisal plant is categorized as a hard fibre, with length between 1 to 1.5 meter and thickness about 0.1 to 0.3 mm [1]. It is composed of cellulose (78%), hemicellulose (10%), lignin (8%), wax (2%) and ash (1%) [2]. At 20° microfibrillar angle, the sisal fibre has much higher strength and good specific properties than other natural fibres due to its low density [3]. These exceptional mechanical properties of sisal fibres have consequently increased the enthusiasm to use sisal fibres in a variety of industrial applications, such as automo-

tive, aviation, construction, packaging etc. However, there are some drawbacks associated with its application along with polymeric matrices. Natural materials which are hydrophilic in nature, with the increase in hydroxyl groups, tend to absorb moisture from the atmosphere and become wet, thereby leading to poor interfacial adhesion. Furthermore, the difference between the properties of highly polar natural fibres and the less or non-polar polymeric counterpart also causes low interfacial adhesion. Conversely, Adriana et al. [4] have observed in their study that plasma-treated high-density polyethylene (HDPE) and untreated sisal fibre composites recorded higher tensile strength values compared to the plasma-exposed sisal and the untreated HDPE. As such, these dissimilar materials exhibit poor stress transfer from the matrix to the reinforced fibres resulting in poor mechanical properties [5]. Furthermore, the structure and properties of fibres play a vital role on the manufacturing processes. Many properties, like the shrinkage, adhesion, wettability, static charge generation, pilling, soil resistance etc. are governed by the surface characteristics of the fibres which can induce desired functionality to the substrate [6]. A great deal of work on surface modification has been carried out by using conventional wet-processing techniques such as chemical modification, addition of compatibilizers or plasma treatment to improve the adhesion. Favaro et al. [7], in their studies on sisal fibre-reinforced recycled high-density polyethylene composites, have chemically modified sisal fibres and the polyethylene (PE) matrix to improve their compatibility. Sisal fibres were mercerized and acetylated, whereas the PE matrix was oxidized. The obtained results demonstrated that the composites prepared with modified sisal fibres and the unmodified polyethylene showed improved mechanical properties, but no benefits were obtained by the modified PE. Joseph et al. [8] investigated the effect of fibre content and chemical treatments on thermal properties of sisal/polypropylene (PP) composites and have reported that the treated fibres show superior properties compared to the untreated system. Kalaprasad et al. [3] studied the effect of fibre length and chemical modifications on sisal/glass hybrid low-density polyethylene composites by varying fibre lengths in the range of 1-10 mm. Fibre-matrix adhesion characteristics with several fibre chemical modifications were found to be successful in improving the interfacial adhesion. Of all the surface modification techniques, plasma treatment is a clean and dry technology which offers many advantages as it is considered environmentally friendly and economical, due to the reduced treatment time and the reduction of chemicals used compared to the other chemical processes [4,6,9,10]. Plasma consists of reactive species like the ions, electrons as well as neutral species, which makes it a unique medium for surface modification. It is often referred to as the fourth state of matter [11]. When polymer surfaces are exposed to plasma, different effects are often observed, such as modification of the chemical composition, etching, surface cleaning etc. Plasma treatment can bring changes to the surface topography without altering the bulk properties. Kafi et al. [12] in their study on jute fibres found that the plasma treatment of jute induced some changes in the surface chemistry and topography which were accompanied by the improvement in the final composite materials. Hua et al. [5] in their analysis with Ar- and O_2-RF-plasma treatments have reported that both plasmas create HC=O, O-C=O and O-CO-O functionalities on cellulose substrates. Furthermore, Ar-plasma was associated with the cleavage of C1-C2 linkages while O_2-plasma was associated with more intense C-O-C bonds splitting mechanism. However, prolonged exposure to plasma has shown to decrease the adhesion characteristics [9] leading to measurable changes in the mechanical properties. Furthermore, there are still other disadvantages, such as the degradation induced by moisture absorption, causing a swelling. Owing to the swelling process, the fibre-matrix interface is weakened which leads to the mechanical degradation of composites. Additionally, thermal analysis is a useful technique to quantify the amount of moisture and volatiles present in composite laminates [13]. Furthermore, with respect to cellulosic materials, the degradation that sets in at around 200°C determines the thermal stability of the materials. As such, in this study, the effect of plasma treatment on sisal fibres and the influence of the fibre content

on the flexural, thermal and moisture absorption are reported. Sisal fibres were treated with oxygen, argon and ammonia plasma. The purpose of using these three gases was to find the conditions that yield the best results and to establish optimum conditions.

EXPERIMENT

Materials and Methods

Sisal fibres were purchased from local sources. These fibres were approximately 1-1.5 m in length. The longer length made it easier to perform the plasma treatment on the fibres. Typical chemical compositions of sisal fibres are shown in Table 1 [2]. The plasma-treated fibres were then cut into 30 mm long pieces by using hand shears. Only the central part of the fibre has been used as reinforcement. A 1 mm thick polypropylene film with a melting temperature of 160°C was used as a matrix in this study.

Table 1. Composition and density of sisal fibres [2]

Cellulose (%)	Hemicellulose (%)	Lignin (%)	Pectin (%)	Wax (%)	Density (g/cm³)
67.0-78.0	10.0-14.2	8.0-11.0	10.0	2.0	1.45

Fibre surface modification

Plasma treatment was used to functionalize the surface of sisal fibres under selected plasma conditions. Glowischarge atmospheric plasma treatment was carried out with a Hydro Pneo Vac Technologies plasma device (HPVT – PS, India), equipped with an aluminium-type electrode, with the system frequency of 60 kHz. The sisal fibres were treated with oxygen of high purity, argon and ammonia; these gases were used as a plasma medium in the plasma chambers. Plasma cleaning of the chamber walls was carried out with respective gases, at 80 W, with the pressure of 9×10^{-2} kPa for the duration of 5 minutes before treating the test specimens. The prepared sisal fibres were then arranged on a rectangular specimen holder (51 x 55 cm) and placed between two electrodes charged at 60 W, at a pressure of 9×10^{-2} kPa, and treated for 10 minutes. After the treatment the samples were stored and sealed for composite preparation.

Fabrication of composites

The composite laminates were fabricated by hand lay-up method. The sisal fibres were cut into 30 mm long pieces and evenly dispersed during manufacturing. The laminate plates were fabricated by using 4 mm thick spacer between the press plates with the fibre content of 15%, 25% and 35%. 1 mm thick polypropylene films were used as the matrix. Laminates were cured in a hot-plate press for 15 minutes at 165°C with the pressure of 6.89×10^{2} kPa. Each of the laminates was then slowly cooled to room temperature while still under pressure.

Mechanical Properties

Flexural testing

Flexural strength and flexural modulus were determined by using the three-point bending method as per American Society for Testing and Materials (ASTM) standard D790, with the span length 16 times the thickness and the crosshead speed of 1.3 mm/min, by using an Instron testing machine (Model 3369). All tests were conducted at 27±2°C and 65±2% relative humidity, allowing prior specimen conditioning for 24 hours.

At least five specimens were tested for each type. Flexural modulus (E_f) and flexural strength ($σ_f$) were calculated by using the following equations:

$$E_f = \frac{mL^3}{4bd^3}$$
$$σ_f = \frac{3PL}{2bd^2}$$

(1),

where *L* is the span between the two supports; *P* is the maximum load in N; *b* is the width of the sample in mm; *d* is the thickness of the sample in mm; and *m* is the slope of the load displacement curve.

Impact strength

The impact behaviour of a composite laminate is related to the overall toughness of the composite and is defined as its ability to resist damage under applied stress. Figure 3 shows the variation of work of rupture of plasma for the treated and the untreated sisal/polypropylene reinforced epoxy composites. Impact tests were carried out on unnotched test specimens according to ASTM D256. The impact tests were carried out at room temperature with an impact speed of 4ms-1 and incident energy of 4 J.

Thermogravimetric analysis (TGA)

The thermal stability of samples was assessed by Q50 series T. A. Instrument's apparatus. The test specimens of 5 mg were placed in a platinum pan, heated from 20°C to 700°C at a heating rate of 10°C/min in a nitrogen atmosphere with a flow rate of 60 ml/min to avoid unwanted oxidation.

Moisture absorption

Moisture absorption studies were carried out with rectangular-shaped test specimens measuring 76.2 mm x 25.4 mm x 4 mm as per ASTM D570. All the test specimens were dried in an oven at 105-110°C for 1 hour. Then the specimens were weighed with a digital analytical balance with a ±0.001 mg sensitivity. Following this the specimens were fully immersed in distilled water at room temperature for 24 hours. After 24 hours of immersion the specimens were removed from water, wiped dry with a piece of cloth and weighed again with the same balance. The moisture content was calculated from the difference in weight before and after immersion.

RESULTS AND DISCUSSION

Flexural tests

Flexural strength is the capability of a material to bear bending forces applied to its longitudinal axis [14]. The stresses induced due to the flexural load are a combination of tensile, shear and compressive stresses. The composite laminate in flexural testing was loaded by using a three-point bend test until the specimen deflected and ruptured at the outer surface [5,9]. Flexural properties were calculated and reported in terms of the maximum stress and strain that occur at the outside surface of the test specimen. The flexural strength and flexural modulus of the untreated sisal/polypropylene composites and those treated by plasma gases (oxygen, argon and ammonia) with various fibre content percentages are shown in Table 2 and separate charts for flexural strength and flexural modulus are depicted in Figures 1 and 2.

Table 2. Flexural strength and flexural modulus of treated and untreated composite laminates

Test specimen	Laminate thickness (mm)	Weight fraction (%)	Flexural strength (MPa)	Flexural modulus (GPa)	Flexural strain at max. flexural stress (%)
Untreated	4	15	63.26	4.05	2.81
	4	25	82.21	4.71	3.45
	4	35	44.08	1.98	3.51
Oxygen plasma-treated	4	15	110.49	6.66	2.93
	4	25	118.70	6.85	3.23
	4	35	57.29	3.60	2.78
Ammonia plasma-treated	4	15	87.36	4.78	3.72
	4	25	108.31	7.17	2.59
	4	35	55.30	2.38	4.59
Argon plasma-treated	4	15	71.79	3.25	3.97
	4	25	81.55	5.75	2.67
	4	35	54.70	2.05	6.09

Flexural behaviour of untreated specimens

It can be noted that the flexural strength and the flexural modulus of the untreated test specimens were lower compared to the plasma-treated specimens. Among the untreated specimens with three different fibre content percentages, the flexural strength was highest for those with 25% fibre content and lowest for those with 35% fibre content, implying that the flexural properties improved with the increase in the fibre weight fraction from 15% to 25%; beyond this, the properties deteriorated drastically. The lower flexural strength and flexural modulus with respect to the 15% fibre content could be attributed to a lack of reinforcing fibres to share the load, whereas the poor behaviour of 35% fibre content laminate could be attributed to poor wetting of the sisal fibre reinforcements by the matrix. As such, the matrix has not been able to transfer the stress completely to the fibres leading to their poor behaviour.

Flexural behaviour of plasma-treated specimens

It can be seen that the plasma-treated sisal/polypropylene composites have much higher flexural strength and flexural modulus than the untreated sisal polypropylene composites, irrespective of the type of plasma gas used. Among the three plasma gases used for treatment, the flexural properties of composite laminates treated with oxygen gas showed significant improvements compared to ammonia and argon plasma-treated specimens.

From Figures 1 and 2 it can be inferred that with the increase in fibre content from 15% to 25% weight fraction, there is an increase in flexural strength and flexural modulus. This trend is observed for both the treated and the untreated sisal fibre composites, where these values are highest at 25% fibre weight fraction. However, the flexural strength of the 15%, 25% and 35% fibre weight fraction composite laminates improved by approximately 74%, 43% and 29% respectively with oxygen plasma, 38%, 31% and 25% respectively with ammonia plasma and 12%, 2% and 22% respectively with argon plasma treatment compared to the untreated composite laminates, whereas the flexural modulus was 66%, 45% and 81% respectively with oxygen plasma, 19%, 51% and 20% respectively with ammonia plasma and -18%, 22% and 3% respectively with argon plasma treatment compared to the untreated composite laminates. The above results could be attributed to poor adhesion at the fibre-matrix interface [9].
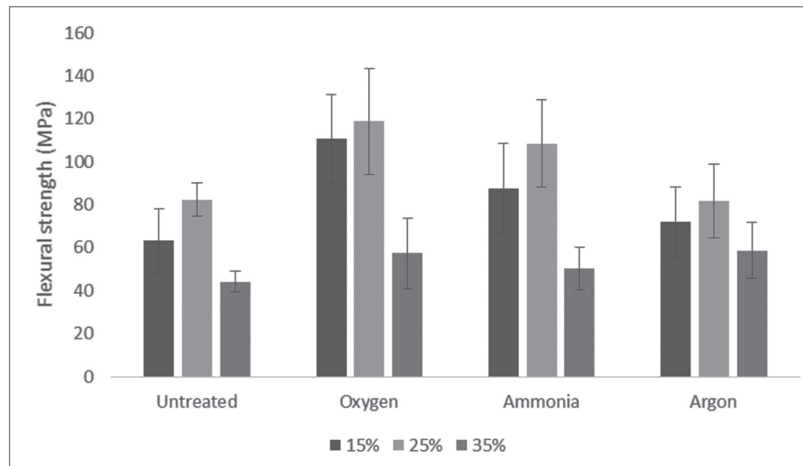
Figure 1. Effect of plasma treatment process on flexural strength
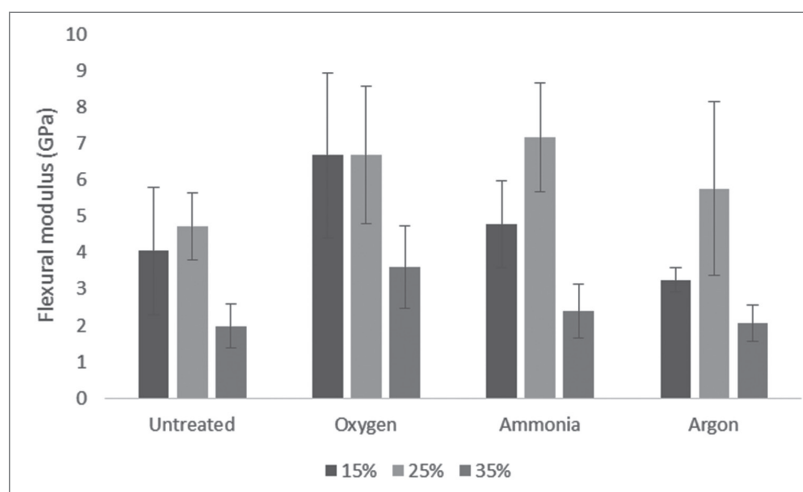

Figure 2. Effect of plasma treatment process on flexural modulus

Impact test

Impact behaviour of the unnotched plasma-treated and the untreated sisal/polypropylene composite laminates is represented in Figure 3. It can be observed that plasma treatment significantly increases the unnotched impact toughness of composites. The highest impact toughness values are associated with the argon-treated sisal fibre composites. This data also substantiates the earlier conclusion that the exposure of sisal fibres to plasma might induce significant surface decomposition and surface cross-linking reaction mechanisms which obviously will limit the molecular interaction on both oxygen- and ammonia-treated sisal fibres/polypropylene interface. Furthermore, the impact strength increases with the increase in fibre weight fraction, but at 35% fibre content the strength goes down, because, as the fibre weight increases in the composite, it tends to decrease the matrix component, thereby impairing the stress transfer.
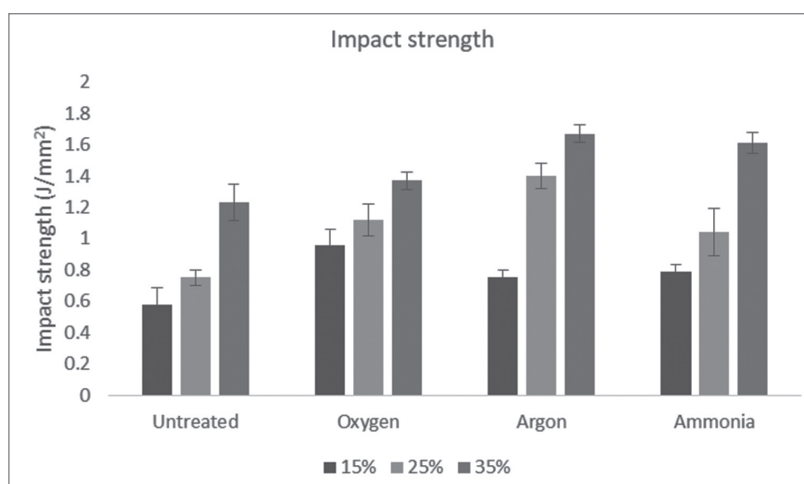
Figure 3. Impact strength of treated and untreated sisal/polypropylene laminates with 15%, 25% and 35% fibre content

Thermogravimetric analysis

The thermal stability of the sisal fibres, the neat polypropylene and the untreated sisal/polypropylene rein-forced composites were examined with thermogravimetric analysis (TGA). The temperature at which considerable weight loss starts to take place is taken as a basis to assess the thermal stability. Thermal stability parameters, such as the initial degradation temperature, the final degradation temperature and the residual char content are presented in Table 3. The investigation was carried out in the temperature range of 20°C-700°C. The TGA curves of the sisal fibres, the neat polypropylene and the untreated sisal/polypropylene composite laminates containing 15%, 25% and 35% fibre weight fraction are shown in Figure 4. From the curves it can be observed that the sisal fibre degradation after dehydration occurs in the temperature range of 60°C-200°C. With the further increase in the temperature to about 350°C, most of the cellulose is decomposed, whereas polypropylene was decomposed at a higher temperature than the sisal fibres, at around 430°C. The TGA curves of the untreated sisal/polypropylene composites reveals that in all the three laminates (15%, 25 % and 35%) the fibres degrade before the virgin polypropylene, thus indicating that the thermal stability of a composite is higher than that of a fibre and lower than that of a matrix [8]. At around 700°C the specimens with 35% weight fraction possess the highest char residue because of the higher cellulose content.

Table 3. Thermal properties of sisal fibres, polypropylene and untreated sisal/polypropylene laminates with 15%, 25% and 35% fibre content

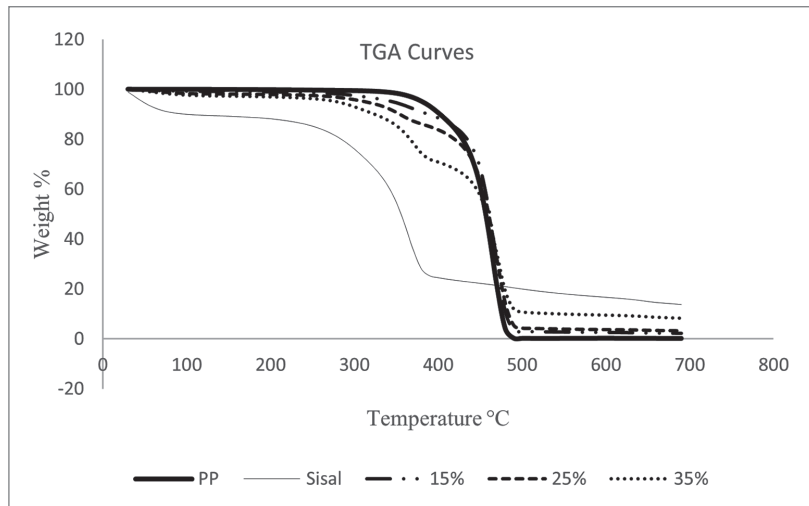|	Degradation temperature (°C)		
Composites	Initial degradation temperature	Final degradation temperature	Char residue (%)
Sisal fibre	230	390	13.79
Neat PP	350	490	0.18
15% Laminate	310	480	2.23
25% Laminate	300	470	3.23
35% Laminate	280	470	8.28

Figure 4. TGA curves of sisal fibres, polypropylene, untreated sisal/polypropylene laminates with 15%, 25% and 35% fibre content

Water absorption

Figure 5 shows the water absorption behaviour of various treated sisal/polypropylene composites with 15%, 25% and 35% fibre content. It is observed that the sisal fibre-reinforced laminates absorb water. The water uptake increased with the increase in fibre percentage. With different plasma treatments the water uptake also varies. The treated laminates show lower water absorption levels, which can be attributed to the surface modification which has induced chain scission leading to the formation of free radicals. These free radicals have improved the adhesion between sisal fibres and the polypropylene resin, rendering the sisal fibres hydrophobic and in turn leading to a better stress transfer at the fibre-matrix interface.
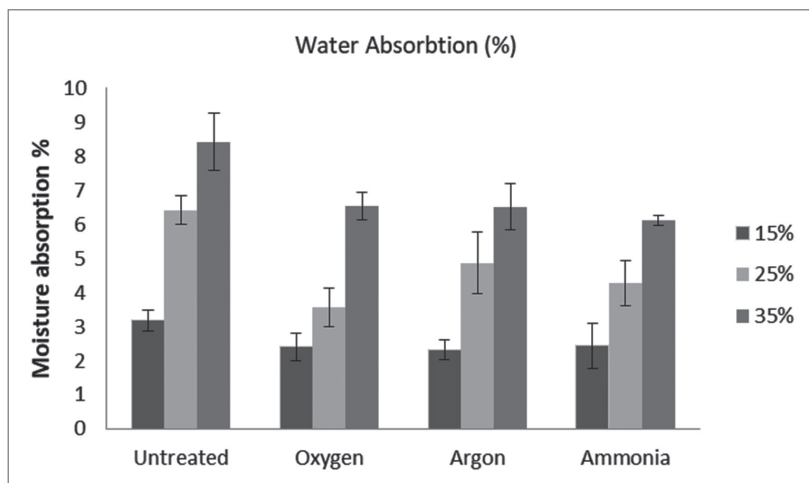

Figure 5. Water absorption behaviour of treated and untreated sisal/polypropylene composites

SEM micrograph

The SEM analysis photomicrographs of the treated and the untreated sisal/polypropylene composites are shown in Figure 6. The samples were fractured in flexural testing prior to the observation with scanning electron microscopy (SEM). In the micrographs of the untreated sisal/polypropylene composite presented in Figure 6(a) it is possible to observe a clear fibre pulled out without any matrix adhered to the fibre surface, suggestive of non-existence of phase adherence, with further local stress whitening regions indi-

cating excessive matrix straining leading to poor stress transfer to the reinforcement. However, the oxygen plasma-treated specimen presented in Figure 6(b) shows an increase in adhesion between the phases, and the sisal fibres revealed globular protrusions or patches with the matrix adhered at a few places with some observable micropores [15]. From the argon- and ammonia-treated specimens viewed in Figure 6(c) and 6(d) it was observed that the adhesion was nonhomogeneous, with the specimen presenting regions of non-adherence, fibre damage, fibrillation and cracks. All of that can be attributed to poor mechanical properties of composites treated with argon and ammonia plasma.
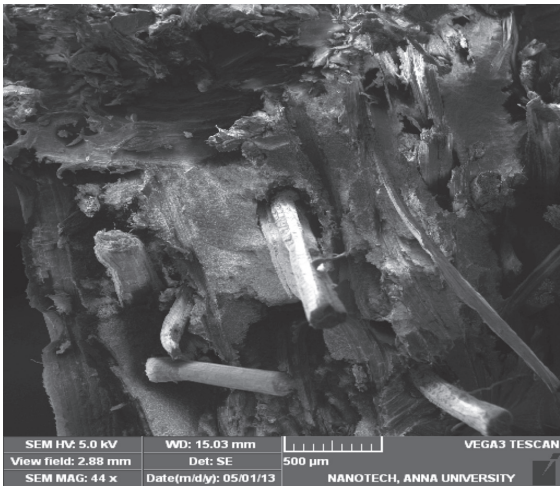

Figure 6. (a) SEM photography of fracture surface of untreated sisal fiber 25% mass fraction composite
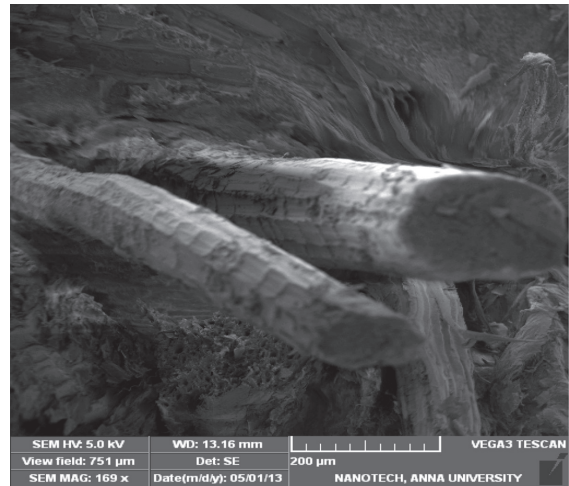

Figure 6. (b) SEM photography of fracture surface oxygen treated sisal fiber 15% mass fraction composite
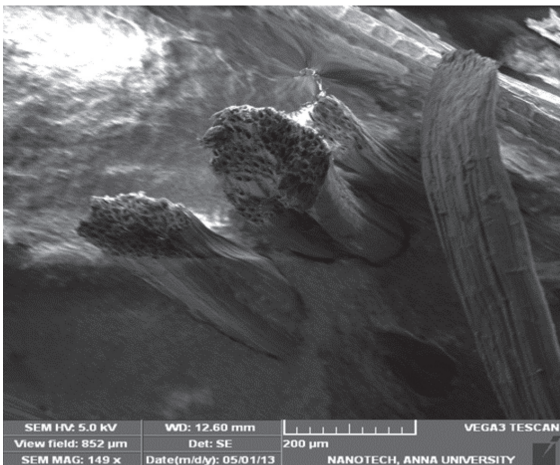

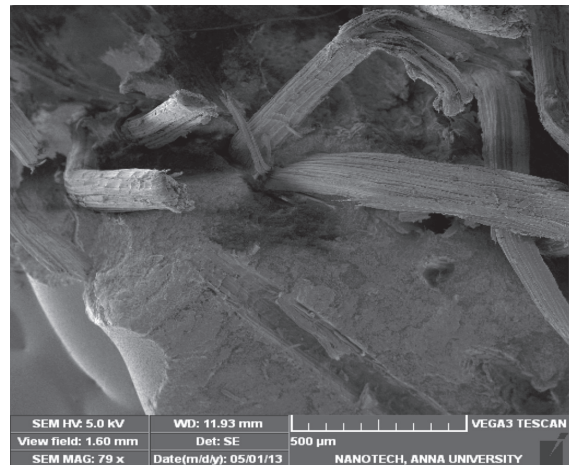Figure 6. (c) SEM photography of fracture surface of argon treated sisal fiber 35% mass fraction composite

Figure 6. (d) SEM photography of fracture surface of ammonia treated sisal fiber 25% mass fraction composite

CONCLUSION

Sisal/polypropylene composites reinforced with untreated and plasma-treated sisal fibres were fabricated by hand lay-up techniques. Sisal fibres were treated with oxygen, ammonia and argon plasma in selected plasma conditions. The flexural, impact, thermal and water absorption characteristics and the morphology of the fractured specimen were studied. It was observed that the oxygen plasma treatment was very effective in improving the adhesion as observed by other researchers [9]. SEM photomicrographs demonstrate the interfacial adhesion between the oxygen plasma-treated sisal fibres and the unmodified polypropylene.

The treatment of sisal fibres with ammonia and argon plasma was not as effective as with oxygen plasma, which explains the poor flexural properties of its composites. Thermogravimetric investigation was carried out to study the thermal stability of sisal/polypropylene composites with reference to the fibre content. It was found that most of the cellulose in the sisal fibres was decomposed at around 350°C, well before the polypropylene decomposition started, which occurred at 430°C. It was also observed that the sisal/polypropylene composite had its thermal stability in between that of the fibre and the matrix, due to the poor fibre-matrix adhesion [7]. The water absorption studies showed that the treatment decreases the water uptake of the plasma-treated laminates, thereby leading to better fibre-matrix adhesion [16].

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