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New Type of Thermoplastic Bio Composites:

Nature of the Interface on the Ultimate Properties and Water Absorption

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Abstract

A new type of thermoplastic bio composites with coir fibre derived from coconut was fabricated by means of plasma modification of polymer surface. The plasma modification is an effective and eco friendly method to create hydrophilic polymer surfaces. Plasma modified polyethylene (PE) was used as the matrix for coir fibre reinforced composites. Use of compatibilizers, chemical modification of fibre or polymer is a usual practice to improve the interfacial adhesion and to make the fibre and polymer matrix compatible. Here, plasma modification of PE was introduced as a new method to improve the compatibility. The present study involves the preparation and characterisation of plasma modified PE (PPE) and coir fibre composite. Different preparation methods were followed and the composites prepared by hot press method proved to be better. The mechanical properties of the composites were compared with unmodified PE / coir fibre composites. The newly prepared thermoplastic composites based on PPE and modified coir fibre showed lower water absorption due to better fiber/matrix interaction. We could observe different kinds of interfaces in the composites. In plasma modified one, a good wetting of fibre by the matrix eliminated the possible microvoids. Finally, it is important to add that plasma modification of polymer was found to be an effective technique to improve the compatibility between polyethylene and natural fibre.

Introduction

Thermoplastic bio composites reinforced with natural fibers have raised great attention and interest recently due to environmental awareness. Natural fibers are the best candidates to replace conventional synthetic fibers such as glass fibers, carbon fibers and aramid fibers. Natural fibers have many advantages over synthetic fibers; these include low cost, ease of availability, eco-friendly nature and high specific strength, recyclability, low energy consumption and less abrasive nature¹⁻⁵. These bio composite materials are suitably useful for aerospace, construction, sport, packaging and automotive applications⁶⁻⁷.

thermoplastic polymer as matrix and natural fibres as reinforcing fillers. The addition of reinforcing fillers into thermoplastic matrix results in improved the particular physical and mechanical properties of the composites. The factors that ascertain the physical properties and mechanical strength of composites are the extent of filler loading, size and shape of the filler, and the filler - matrix interfacial adhesion. The properties of polymer composites depend not only on the nature of filler and matrix used but also the interaction between the polymer and fibre^{3, 8}. Natural fibers are cellulosic fibers which are hydrophilic in nature. The major problem with natural fibre composites is poor compatibility between the hydrophilic natural fibre and hydrophobic polymer matrix^{9, 10}. The usual practice to improve the compatibility and interfacial adhesion in natural fibre composites are the use of compatibilizer¹¹ and chemical modification of fibres or polymers¹²⁻¹⁴. Numerous studies have been reported on this basis. The different chemical modification of natural fibre includes alkali treatment, bleaching, benzoylation, acetylation and treatments with potassium permanganate, silane coupling agent, benzyl peroxide and etc.¹⁵⁻¹⁸.

Thermoplastic bio composites are composites composed of

The modification of polymer surface by plasma is an effective and eco friendly method to create polymer surface

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hydrophilic. Plasma treatment generates wide range of reactive species in the treated system (hydroxyl, carbonyl, carboxyl, ether, amine, peroxides etc.) which undeniably depends on the surrounding medium. This also improves its surface micro-hardness and surface roughness due to the bombardment of high energy radicals and ions²⁰⁻²². The plasma modification of polyethylene surface has got great attention from scientists as well as industrialists. Quite a lot of studies have been done in the area of plasma modification of polyethylene in the last few decades. Recently Patra et al. investigated the effect of plasma treatment on the thermal, structural and wettability changes of LDPE powder using different plasma gases²³. Pandiyaraj et al. successfully improved the adhesion properties of PE film by using air plasma treatment²⁴. Theapsak et al. successfully prepared chitosan-coated polyethylene packaging films by DBD plasma treatment²⁵. Anti-bacterial treatment of polyethylene by cold plasma for medical purposes was established by Popelka et al.²⁶. Parizek et al. explored the plasma surface treatment for adhesion and growth of vascular smooth muscle cells on lowdensity polyethylene grafted with bioactive substances²⁷. Recently, Lopez et al. enhanced the printability of polyethylene through air plasma treatment²⁸. Habitually plasma modification of polyethylene (PE) is used to improve its printability, adhesion to metal^{25, 27}, bonding with other polymers²⁹ and protein absorption³⁰. This work will provide plasma modification of polymer powder that can be effectively used for natural fibre composite preparation.

In this study we endeavoured to fabricate a new kind of thermoplastic bio composite reinforced with coir fibre. To the best our knowledge, plasma modified PE /coir bio composites have not been reported till date. This new approach provides ample opportunity to make use of coir fibers which is one of the most important agro fibres in the southern part of India and many Asian countries for the fabrication of high performance bio composites using polyolefins such as LDPE, HDPE, and PP. We also investigate the different methods of preparation of these bio composites and their influence on the interfacial interaction, mechanical properties and water absorption characteristics as well. The water absorption studies gave valuable information on the nature of interface between coir fibre and the PE matrix in the presence and absence of plasma modification.

Materials

Polyethylene and the standard plasma-treated powder were obtained from the firm SurfaceTreat Itd, Czech Republic. The specific gravity and melting point of the polymer are 0.935g/cc, 124 °C respectively. The detailed description of plasma treatment was given in the previous publications of Spatenka et al. ^{31, 32}. Microwave discharge excited in oxygen and/or air was used for the modification. All experiments were performed in stationary oxygen under pressure 70-100 Pa and room temperature (20-23) °C. Treatment time was 60 - 600 s. PE powder for roto moulding Surpass RMS 244-U/UG (particle average diameter 300 mm).

Coir fibre was collected from local market in Kerala, India. Coir contains cellulose (36-43%), lignin (41-45%), hemicellulose (0.15-0.25%) and pectins (3-4%) together with some water-soluble materials. The fibers were thoroughly washed and chopped into 6 mm length to ensure easy mixing with polymer matrix. The chopped fibers were dried at 120 °C for 24 hrs. The dried fibres were subjected to various chemical treatments described below.

Chemical treatments for coir fiber

Alkali treatment. The dry fibre was treated with 5% of NaOH for 2 hrs to remove unwanted soluble cellulose, hemicelluloses, pectin, lignin, etc.¹⁶ from the fibre. The fibre to solution weight ratio was maintained as 1:25. After 2 hrs the fibers were washed thoroughly in distilled water to remove excess of NaOH and dried at 60 °C for 24 hrs.

Treatment with hydrogen peroxide. Coconut fibers were subjected to oxidation using 40ml of hydrogen peroxide solution in basic medium (0.05g NaOH and 18 ml of hydrogen peroxides 30%v/v for 100ml of solution) at 85°C for 2h. During this process the fibers were cooked under gradual rise of temperature. Finally the cooked fibers were removed from the mixture. Then the fibers were washed with distilled water thoroughly. The fibers were dried and chopped to 6 mm length and again dried in an air oven at temperature of 100°C for 2h. Then these fibers were designated as bleached fibers.

Preparation of the composites

Melt mixing method. The composites were prepared by melt mixing using a Hakke type plasticorder at 130 $^{\circ}$ C for 10 minutes. The speed of the rotor was maintained at 50 rpm. After mixing the sample was moulded using hydraulic press at temperature and pressure of 130 $^{\circ}$ C and 120 psi respectively.

Mechanical mixing and hot press method. PE and heated coir fibre were taken in a beaker, mixed thoroughly by means of a glass rod. After proper mixing, the mixture was kept for 24 hrs. Then it was moulded using hydraulic press. Compression mould temperature and pressure are set at 130 °C and 120 psi respectively

Characterization

Contact angle measurements were carried out in a SEO Phoenix instrument with water (triply distilled), on samples of size $1 \times 1 \times 0.2$ cm3 at room temperature. The contact angle was measured within 45-60 s of the addition of the liquid drop with an accuracy of $\pm 1^{\circ}$. The volume of the sessile drop was maintained as 5μ l in all cases using a micro syringe. Measurements were repeated ten times with different test pieces of the same sample to check the accuracy. Also contact angles were measured with definite time intervals for a single drop and the measurements were recorded as snap shots.

Surface chemical properties coir fibers and polyethylene were analyzed by Infrared spectroscopy using Perkin Elmer FTIR spectrometer spectrum R-X-1 in the mid IR rage, i.e. from 400 and 4000cm⁻¹.

Tensile properties of short coir fibre polyethylene and plasma modified polyethylene with different fibre contents were measured according to ASTMD638 using universal testing machine TINUS OLSEN H50KT at a gauge length of 60 mm and speed of 50mm/minutes. The flexure properties were measured by the three point bending method according to ASTMD790 using universal testing machine. The flexure properties were carried out at room temperature with a cross head speed of 2mm/minutes. Reported values are the average of 5 specimens.

Water absorption characteristics of the composites have been studied at room temperature. Square specimen having 2mm side length and 2mm thickness were immersed in distilled water and the percentage weight change was determined until the equilibrium values were reached. After immersion in water, samples were removed at different times, wiped with tissue paper to remove surface water and weighed with an analytical balance with 1 g resolution. The morphology of the bio composite was investigated by using a stereo microscope with deep image sharpness.

The molar absorption \mathbf{Q}_t (mol percent) of water by the composite at time t was calculated from the equation given below

$$Q_t(\%) = \frac{(w_2 - w_1)}{18 \times w_1} \times 100$$

Where W_1 is the weight of dry specimens and W_2 is the weight of the wet specimen. The molar absorption at equilibrium (infinite time) is represented by Q ∞ . The weight gains maximum moisture contents and diffusivity of such materials during immersion in distilled water was also estimated.

Results and discussion

Effect of plasma modification on the properties of PE

The surface hydrophilicity was measured using contact angle analysis for both modified and unmodified polyethylene to understand the change in polarity after plasma modification. Water contact angle measurement was one of the important techniques for analysing the change in hydrophilicity during plasma treatment^{33, 20, 23}. The measured contact angle values were given in Table1.

Table. 1. Contact angle measurements of PE and modified PE [Table. 1. here]

The wetting behaviour of the polymer surface with respect to water was analyzed, which determined the effect of plasma

modification on wetting characteristics such as work of adhesion, total surface free energy, interfacial free energy, spreading coefficient and Girifalco-Good's interaction parameter²⁸. Water is a polar liquid and polyethylene is highly non polar. Due to the polar - non polar nature of the solvent and polymer, the unmodified PE showed a higher contact angle value of 91°. From the Table 1 it is clear that plasma modification decreased the water contact angle to 79°. The work required to separate the solid and liquid is called work of adhesion (WA), which increases with interfacial interaction. In this case work of adhesion increased with plasma modification, which is an evidence for the better interfacial interaction between water and polymer surface after plasma modification. From this we can understand that the polar nature of the PE surface can be improved by plasma modification. Interfacial energy and spreading coefficient decreased with plasma modification, which implies that better wetting is possible for PPE. The degree of interaction between water and polymer surface can be predicted using Girifalco-Good's interaction parameter. The PPE showed higher value for interaction parameter compared to PE. These all indicate that the attraction of polymer surface towards water increased after plasma modification due to the increased polarity (increase in number of polar groups after plasma modification) of PPE. Previous studies showed that this plasma modification is nearly permanent for a long time $^{31, 32}$.

[Fig.1 here]

Fig. 1. FTIR spectra of untreated PE and plasma treated PE

The influence of plasma treatment on PE was studied by FTIR measurements and showed in Fig 1. The spectrum of the untreated PE is a typical polyethylene spectrum as reported³³. After plasma exposure of the pristine material, the characteristic oxygen functional groups were introduced and therefore significant changes in the measured spectrum have been observed. These changes seem to be caused by the incorporation of some polar groups by plasma treatment with the appearance of peaks at 1741 cm⁻¹ (C=O stretch in carboxylic acid) and 1168 cm⁻¹ (C=O stretch in alcohol)²⁸.

Effect of chemical treatment on coir fibres

[Fig.2 here]

Fig. 2. FTIR spectra of raw coir fibre, NAOH treated coir fibre and H_2O_2 treated coir fibre

The FTIR spectra of natural and treated coir fibers are shown in Fig. 3. All these spectra reveal a broad and intense peak at 3340 cm⁻¹ suggesting hydrogen-bonded (O-H) stretching vibration from the cellulose and lignin structure of the fibre., The band at 1728 cm⁻¹ corresponds to axial vibration of C=O (which is the characteristic band of hemicellulose, observed in the natural coir fibre) disappeared after chemical treatments. The band at 1238 cm⁻¹ is related to the vibration (C-O) of esters, ethers and phenols groups attributed mainly to a presence of waxes in the epidermal tissue³⁴ and the

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disappearance of this band in the treated fibers results from the removal of those waxes.

Effect of method of preparation of thermoplastic biocomposites

Different methods were used to prepare PPE as well as PE coir fibre composites such as melt mixing and hot press as described in the experimental part. In order to optimize the preparation method, the mechanical properties of the composites were analyzed. Tensile properties of composites prepared by melt mixing method were given in Fig 3(a) and that of composites prepared by hand mixing method was given in Fig 3(b).

[Fig.3 here]

Fig. 3. Stress strain plot of PPE bio composites and PE bio composites with 10 phr coir fibre prepared by a) melt mixing method b) hand mixing method

Table 2. Tensile strength of biocomposites at 10 phr of coir fibre loading

[Table 2. here]

Unmodified polyethylene based composites showed better properties when prepared by melt mixing method. During melt mixing high temperature and high shear were applied, which could improve the dispersion of coir fibre in the PE matrix. But in the case of composite based on plasma modified PE, hand mixing method found to be more suitable. PPE composite prepared by hand mixing method showed higher value for tensile strength and modulus (Table 2.). This could be due to the high temperature and high shear applied during melt mixing, which allowed the functional groups to be destroyed from the plasma modified polyethylene surface. The functional groups such as hydroxyl, carboxyl, etc were present on the surface of polyethylene as a result of plasma modification. So the interaction between coir fibre and polymer matrix decreased during this process at higher temperature. And also some of the polymer chains may undergo crosslinking reaction because of the radical formation during melting. That too reduces the dispersion of fibre in the polymer matrix. Thus for further studies hand mixing method was followed to prepared PPE coir composites. The Fig. 4 represents schematic illustration of different preparation methods of bio composites.

[Fig.4 here]

Fig. 4. Schematic representation of preparation methods of biocomposites

Effect of chemical treatment of coir fibre on the properties of bio composites

[Fig.5 here]

Fig. 5. Stress strain plot of bio composites with varying amount of coir fibre a) PE and b) PPE

Stress strain behaviour of thermoplastic bio composites prepared from PE and PPE is shown in Fig. 5. The plasma modification did not alter the stress strain behaviour of PE but a small reduction in the tensile strength was observed. This could be due to the chain scission came about during plasma treatment²⁰. The addition of coir fibre completely modifies the stress strain behaviour of the system. The thermoplastic biocomposites were not showing any plastic deformation because of the presence of rigid coir fibres³⁶. The modulus of the system tremendously increased with the addition of fibre in both cases. But the tensile strength of the PE biocomposite is lower than the neat polyethylene. This is mainly due to the lack of proper interfacial adhesion between the polymer matrix and coir fibre and inefficient dispersion of fibre. Tensile strength of the composites increased with the amount of coir fibre added into it. Fig. 5(b) describes the stress - strain behaviour of thermoplastic bio composites prepared from PPE. In this case the biocomposite with 5 phr coir fibre showed higher tensile strength which is higher than that of neat polymer and further addition of fibre decreases the tensile strength. This means that there is interaction between the coir fibre and PPE matrix which improves the interfacial adhesion.

Effect of chemical treatment of coir fibre on the properties of bio composites

[Fig.6 here]

Fig. 6. Stress strain plot of bleached coir fibre composites with varying amount of coir fibre a) PE and b) PPE

Stress strain behaviour of thermoplastic bio composites prepared by bleached coir fibre is shown in Fig.6. The biocomposite with bleached fibres were also showing the same trend for stress strain plot. But the tensile properties such as tensile strength and tensile modulus were increased. Bleaching with hydrogen peroxide improves the quality and the aspect ratio of the coir fibre by partially removing the lignin and hemicelluloses³⁴. That might be the reason for the improvement in tensile properties of biocomposite with bleached fibre. In this case also the composite with 5 phr fibre were showing better properties and higher loading of fibre show a small decrease in the tensile strength as well as tensile modulus. PPETr biocomposites has been showed better properties compared to that of PETr biocomposites. The maximum tensile strength and modulus was shown by composite with 5 phr loading of treated coir fibre. At this composition there may be good interfacial adhesion between the fibres and matrix that could be further explained from morphology and water absorption studies. The increased aspect ratio of coir fibre after bleaching helped to improve the dispersion and also the partial removal of lignin and hemicellulose from the surface made cellulose more interactive with the plasma modified PE matrix. The interphases of three different types of biocomposites are represented schematically in Fig.7a illustrates the untreated PE coir fibre interphase in which no interaction between the nonpolar matrix and polar cellulosic fibre is observed. So this

kind of composites showed sharp interphase that was the reason for poor mechanical properties. The interphase of plasma modified PE and coir fibre is given in Fig. 7b. The presence of polar functional groups on modified PE facilitates more interaction between the fibre and matrix. In the third case, coir fibres were bleached and so most of the lignin and hemicelluloses were removed during bleaching therefore more hydroxyl groups were available for the interaction.

[Fig.7 here]

Fig. 7. Schematic representation of biocomposite interphases

[Fig.8 here]

Fig. 8. Tensile strength Vs Amount of filler of all composites

[Fig.9 here]

Fig. 9. Tensile modulus Vs Amount of filler of all composites

Fig. 8 and 9 describe the tensile strength and tensile modulus of all bio composites with varying amount of coir fibre respectively. The tensile strength was increased by around 100% in the case of PPETr biocomposite where as it was only 10% for PETr biocomposite than neat polymer. Even though the tensile moduli increased to a great extend for both cases, PPETr biocomposites showed higher modulus than PETr biocomposites. The composite prepared from PPE and bleached fibres showed the best properties. This is because of the interaction between the polar groups on the polymer surface and hydroxyl groups of the cellulose fibre. This new biocomposite showed better interfacial adhesion, good dispersion of fibres and proper wetting of fibers. As a result of the high degree of interfacial interaction, the stress transfer from the matrix to the reinforcement is very efficient. The good interfacial adhesion and proper wetting of fibre was further confirmed from the morphological analysis. In all the compositions 5 phr fibre loading showed better properties and at higher loadings agglomeration of fibers adversely affect the mechanical properties. But compared to other samples, the unusual trend observed in the 10 phr loaded samples is within the statistical error.

[Fig.10 here]

Fig. 10. Flexural modulus Vs Amount of filler of all composites

The variation of the flexural modulus of both raw and treated coir reinforced PE biocomposites at different fiber loading is shown in Fig. 10. The flexural modulus of coir fiber reinforced composites increased with the fiber loading^{-37,38}. Since the coir fiber is of higher modulus, higher fiber concentration demands higher stress for the same deformation. So the incorporation of the coir fiber into the soft polyethylene matrix resulted in increase of the modulus. The flexural modulus of PPETr biocomposites was the highest. This is because treated fiber composite provides evidence of homogeneous distribution of the fiber particles into the matrix and better fibre –matrix interaction.

[Fig.11 here]

Fig. 11. Microscopic images of biocomposites with untreated coir fibre a) PE and b) PPE

[Fig.12 here]

Fig. 12. Microscopic images of biocomposites with treated coir fibre a) PE and b) PPE

Morphology

Morphology of the fractured composites surface was studied by using a stereo microscope. The Fig. 11a and Fig. 11b illustrate the images of PE biocomposite and PPE biocomposite respectively. In figure 11a a visible gap is clearly observed between the fibre and matrix, which can be attributed to the poor interfacial adhesion between PE and coir fibre. But in the case of PPE biocomposite there is no micro voids and we can see nice wetting of polymer matrix on the fibre surface (Fig. 11b). All these observations can be evidence for good interfacial adhesion between PPE matrix and coir fibre, which can be evidenced in the improvement in mechanical properties. The strong adhesion and fibre wetting was the result of the formation of polar interactions between the plasma modified polymer surface and cellulosic fibres. The morphology of biocomposites prepared by treated coir fibres also showed the same behaviour (Fig. 12). Morphology reveals that good wetting of coir fibre was observed by PPE matrix where as we can clearly see the interface in the case of PE biocomposite. A good fibre/ matrix interfacial adhesion was established in PPE coir fibre composite in place of PE coir fibre composite.

Water absorption behaviour of bio composites

The study of water absorption characteristics is significant in the case of natural fibre composites, due to their intense sensitivity to water, which affects the performance of the material. Water absorption studies of PE and PPE based bio composites were conducted at room temperature. The water uptake evolution by the composites as a function of time at various filler loading is given in Fig. 13.

[Fig.13 here]

Fig. 13. $Q_tVs t^{2s}$ Plot of bio composite with varying amount of fibre a) PE UTr, b) PPE UTr, c) PE Tr and d) PPE Tr.

The polyethylene matrix did not absorb any water given that it is a nonpolar / hydrophobic material. We can understand from the Fig. 13 that neat PPE sheet has slightly higher water absorption behaviour than PE due to the polar functional groups introduced on the surface of polyethylene chain. Interestingly as shown earlier the water contact angle was lower for PPE samples. It is obvious from the figure that amount of water absorbed by the composites increased with the addition of coir fibre in all the cases as we expected. The water absorption of thermoplastic natural fibre composite happens, mainly due to the presence of hydroxyl groups in the

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cellulose fibre, several porous tubular structures associated with lignocellulosic fibers and also the micro voids in the composites because of the lack of interfacial adhesion³⁹. So the water absorption increased with the amount of fibre in the composites increased in all the cases. Interestingly, as expected the chemically treated coir fibre reinforced composites showed much lower water absorption compared to the raw ones. This is due to the fact that after treatment the number of hydroxyl groups, responsible for the water absorption are reducing. In the beginning, all the bio composite samples showed a very quick increase in percentage of water absorption. As the time of immersion increased, the absorption curve reached a maximum value and attains the equilibrium point. The time to reach equilibrium value and the amount of water absorbed were not same for all the bio composites. Compared to other bio composites PPETr composites showed lower percentage of water absorption and reached the equilibrium at shorter time of immersion. From this we can understand that PPETr bio composites possess higher resistance to water absorption.

[Fig.14 here]

Fig. 14. Amount of water absorbed vs amount of coir fibre plot of the bio composites

Fig. 14 describes the Q∞, molar absorption at equilibrium (infinite time) of all biocomposites. It is very clear from the figure that PPETr biocomposites show the lower absorption of water at any filler loading. PEUTr composites show the higher absorption of water. Even though neat PPE was showing small absorption than neat PE, the water absorption was very less in PPE biocomposite compared to PE biocomposites irrespective of the fibre loading. This is because a considerable amount of accessible OH groups, those are responsible for water absorption disappeared to become bonded to the polar groups on the plasma modified PE surface. And also the lack of micro voids present in the composite due to better polymer fibre interaction will help to reduce the water absorption⁴. This can be well explained from the microscopic images of the composites. The coir fibers were effectively wetted by PPE matrix which can not be seen in PE coir fibre biocomposites. Chemical treatment of coir fibre substantially reduces the water absorption of both PE composites and PPE composites. The percentage reduction of water uptake due to plasma modification polymer and chemical treatment fibre ware estimated given in Tables 3 and 4. It is clear from the tables that the plasma modification of PE has great effect on the water absorption characteristics of the biocomposites. More than 40% of reduction was observed in all the cases irrespective of the amount of coir fibre and nature of the fibre.

Table 3. Percentage of reduction in water absorption due to plasma modification of PE

[Table 3 here]

Table 4. Percentage of reduction in water absorption due to chemical treatment of coir fibre

[Table 4 here]

Conclusions

A new kind of thermoplastic bio composite reinforced with coir fibre can be successfully fabricated by means of plasma modified thermoplastic polymer with improved properties. The preparation method we adopted was mechanical mixing and hot press method, which is simple, energy saving and more cost effective than other methods like melt mixing. Plasma treatment modifies the surface of powder polymer surface to become more hydrophilic by imparting functional groups on it. This could improve the compatibility between the polymer matrix and natural fibre. The new biocomposites showed higher mechanical properties in terms of tensile and Plasma modified flexural properties. polvethylene biocomposites with treated fibres at 5 phr loading showed the best properties. The increase in tensile strength was 100 % whereas that of PE treated fibre biocomposite was only 10%. The lower water absorption characteristics of the new biocomposites disclose that there is good wetting of the polymer on the natural fibre. The morphology confirms that good wetting of fibre was obtained by plasma modified polyethylene matrix which is very essential to have good interfacial adhesion.

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References

- 1 O. Faruka, A. K. Bledzkia, H-P. Fink, M. Sain, Prog. in Poly. Sci., 2012, **37**, 1552–1596
- 2 W. Paul, J. Ivens, I. Verpoest, Compos. Sci. Technol., 2003, 63,1259-1264.
- 3 S. D. Nabi, J. P. Jog, Adv. Polym. Tech., 1999, 18, 351-363.
- 4 M. N. Islam, Md. M. Haque, Md. M. Huque, *Ind. Eng. Chem. Res.*, 2009, **48**, 10491–10497.
- 5 P. Sudhakara, D. Jagadeesh, Y. Wang, C. Venkata Prasad, A.P. Kamala Devi,G. Balakrishnan, B.S. Kim, J.I. Song, *Carbohydr. Polym.*, 2013, **98**, 1002–1010.
- 6 H. James, D. Houston. *Jom*, 2006, **58**, 80-86.
- 7 Ashori, A., Bioresour. Technol., 2008, 99, 4661–4667.
- 8 M. Sain, P. Suhara, S. Law, A. Bouilloux, J. Reinf. Plast. Compos., 2005, 24, 121-130.
- 9 S. Taj, M. A. Munawar, S. Khan,. *Proceedings-Pakistan* Academy of Sciences, 2007, **44**, 129.
- 10 R. Shanks, Woodhead Publishing (2014): 66.
- 11 Y. Xie, C. A. Hill, Z. Xiao, H. Militz, C. Mai, *Composites Part A*, 2010, **41**, 806-819.
- 12 M. M. Kabir, H. Wang, K. T. Lau, F. Cardona, *Composites Part B*, 2012, **43**, 2883-2892.
- 13 M. J. John, R. D. Anandjiwala, Polym. Compos., 2008, 29, 187.
- 14 M. Pommet, J. Juntaro, J. Y. Heng, A. Mantalaris, A. F. Lee, K. Wilson, A. Bismarck, *Biomacromolecul`es*, 2008, 9,1643-1651.
- 15 C. Qin, N. Soykeabkaew, N. Xiuyuan, T. Peijs, *Carbohydr. Polym.*, 2008, **71**,458–67.

- 16 X. Li, L. G. Tabil, S. Panigrahi, *Polym. Environ.*, 2007, **15**, 25–33.
- 17 S. A. Paul, K. Joseph, G. Mathew, L. A. Pothen, S., *Compos: Part A*, 2010, **41**, 1380–7.
- 18 S. Sapieha, P. Allard, Y. H. Zang, J. Appl. Polym. Sci., 1990, **41**, 2039–48.
- 19 M. Quitzau, M. Wolter, H. Kersten, *Plasma Process. Polym.*, 2009, **6**, S392 -S396.
- 20 J. Lai, B. Sunderland, J. Xue, S.Yan, W. Zhao, M. Folkard, Appl. Surf. Sci., 2006, 252, 3375-9.
- 21 J. P. Y. Ho, N. J. Nosworthy, M. M. M. Bilek, B. K. Gan, D. R. McKenzie, P. K. Chu, *Plasma Process. Polym.*, 2007, **4**, 583.
- 22 L. Chvatalova, R. Cermak, A. Mracek, O. Grulich, A .Vesel, P. Ponizil, *Eur. Polym. J.* 2012, **48**, 866.
- 23 N. Patra, J. Hladik, M. Pavlatova, J. Militky, L. Martinova, *Polym. Degrad. Stab.*, 2013, **98**, 1489.
- 24 K. A. Vijayalakshmi, M. Mekala, C. P. Yoganand, K. N. Pandiyaraj, Int. J. Phys. Sci., 2012, 7, 2264.
- 25 S. Theapsak, A. Watthanaphanit, R. Rujiravanit, ACS Appl. Mater. Interfaces., 2012, 4, 2474.
- 26 Novak, A. Popelka, I. Krupa, I. Chodak, I. Janigova, T. Nedelcev, M. Spirkova, A. Kleinova, Vacuum, 2012, 86, 2089.
- 27 M. Parizek, N. Kasalkova, L. Bacakova, P. Slepicka, V. Lisa, M. Blazkova, V. Svorcik. *Int. J. Mol. Sci.*, 2009, **10**, 4352.
- 28 Lopez-Garcia, F. Bilek, M. Lehocky, I. Junkar, M. Mozetic, M. Sowe, Vacuum, 2013, 95, () 43.
- 29 S. J. Hardman, L. R. Hutchings, N. Clarke, S. M. Kimani, L. L. E. Mears, E. F. Smith, J. R. P. Webster, R. L. Thompson, *Langmuir*, 2012, 28, 5125.
- 30 N. Vandencasteele, F.Reniers, J. Electron Spectrosc. Relat. Phenomena, 2010, **178**, 394.
- 31 J. Hladik, P. Spatenka, L. Aubrecht, J. Pichal, *Czechoslovak J. Phy.*, 2006, 56, 1120-1125.
- 32 P. Spatenka, J. Hladik, A. Kolouch, A. Pfitzmann, P. Knoth, In Society of Vacuum Coaters 48 th Annual Technical Conference Proceedings, 2005, 540-543
- 33 Lei, L. Yang, Y. Zhan, Y. Wang, T. Ye, Y. Li, H. Deng, B. Li, Colloids Surf. B. Biointerfaces, 2014, 114, 60.
- 34 A. I. S. Brígida, V. M. A. Calado, L. R. B. Gonçalves, M. A. Z. Coelho, *Carbohydr. Polym.*, 2010, **79**, 832-838.
- 35 S. Guruvenket, G. M. Rao, M. Komath, A. M. Raichur. Appl. Surf. Sci., 2004, 236, 278-284.
- 36 J. V. Gulmine, P. R. Janissek, H. M. Heise, L. Akcelrud, Polymer Testing, 2002, 21, 557-563.
- 37 H. S. Yang, H. J. Kim, H. J. Park, B. J. Lee, T. S. Hwang, *Compos. Struct.*, 2006, **72**, 429–437.
- 38 M. M. Haque, M. Hasan, M. S. Islam, M. E. Ali, *Bioresour. Technol.*, 2009, **100**, 4903-4906.
- 39 C. Chanakan, H. Sarocha, Jongjit, K. Joseph, Compos. Part B:Eng., 2009, 40, 633–637.

	PE	PPE
Contact angle (°C)	91±2	79± 2
Work of adhesion $W_A = (1 + \cos\theta)\gamma_1 (mJ/m^2)$	71.09	88.54
Surface energy (J)	21.3	31.9
Spreading Coefficient	74.50	57.06
Interfacial energy (mJ/m ²) $\gamma_{sl} = \gamma_{s+} \gamma_l - W_A$	23	16.16
Interaction Parameter $\phi = [(1 + \cos\theta)\gamma_1]/2 (\gamma_s \gamma_1)^{1/2}$	0.90	0.92

Table. 1. Contact angle measurements of PE and modified PE

 γ_s surface free energy of solid, γ_1 surface free energy of liquid, γ_{sl} – interfacial free energy between solid and liquid

Table 2	Tensile	strength	of bioco	mposites	at 10	phr o	of coir	fibre	loading
1 4010 2.	1 UIISIIC	Suchgui		mpositos	at 10	pm v		nore	iouunis

	Melt mixed		Hand mixed		
	PE	PPE	PE	PPE	
TS(MPa)	12.82 ±1.02	11.93 ± 0.86	10.61 ± 1.3	13.67 ±1.8	
YM (MPa)	765 ±56	689±47	585±85	1045 ±59	
EB (%)	13.44 ±0.25	9.26± 0.38	13.2 ±0.34	14.33 ±0.32	

Table 3. Percentage of reduction in water absorption due to plasma modification of PE

Amount of coir fibre (phr)	Untreated coir fibre (%)	Treated fibre (%)
5	40	46
10	46	41
15	59	50
20	39	53

Table 4. Percentage of reduction in water absorption due to chemical treatment of coir fibre

Amount of coir fibre (phr)	PE (%)	PPE (%)
5	19.73	19.79
10	23.5	15.44
15	38.94	26.5
20	33.33	41.16



136x106mm (96 x 96 DPI)



279x215mm (150 x 150 DPI)



132x67mm (96 x 96 DPI)



246x148mm (96 x 96 DPI)



128x64mm (96 x 96 DPI)



132x66mm (96 x 96 DPI)



141x54mm (96 x 96 DPI)



115x96mm (96 x 96 DPI)



118x95mm (96 x 96 DPI)



169x138mm (96 x 96 DPI)



152x125mm (96 x 96 DPI)



132x106mm (96 x 96 DPI)



129x111mm (96 x 96 DPI)



100x77mm (96 x 96 DPI)