Surface modification of recycled coir fibers with hybrid coating and its effect on the properties of ABS composites

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Keywords: r-coir fibers, ABS, compatibility, modification

Abstract

In this work, a hybrid coating (TSMA) was produced using tetraethyl orthosilicate (TEOS)/KH550/Styrene maleic anhydride copolymer (SMA) as raw materials. The coating was afterwards applied to modify recycled coir (r-coir) fibers via dip-coating. R-coir fibers reinforced ABS composites were then prepared and the reinforcing effect of fibers on the composite structure was investigated, as well. The r-coir fibers coated with TSMA were hydrolyzed in air for 3 days. The SiO2 particles produced by sol-gel reaction of TEOS were used to connect KH550 and SMA to the surface of the fibers and form an organic-inorganic ‘armor’ structure. The successful surface modification of the r-coir fibers was proved via FTIR spectroscopic study and the improvement of their decomposition temperature was evidenced by TGA. Furthermore, the homogeneous dispersion of TSMA on the surface of r-coir fibers was observed via SEM. In addition, the tensile strength of single fibers was found to increase by 36.1%. According to the results, TSMA can be successfully homogenized on the fiber surface, enabling one to repair the damaged areas and improve the tensile strength of single fibers. Besides, good compatibility between r-coir fibers and ABS was revealed by contact angle measurements. Furthermore, the bending strength and elastic modulus of TSMA-modified r-coir fibers/ABS composites were improved by 6% and 27%, respectively. Therefore, the method of plant fiber modification proposed in present work provides a reliable way for effective reuse of r-coir fibers.

1. Introduction

Plant based natural fibers are the third kind of composite reinforcing materials after glass and carbon fibers, which is due to their excellent mechanical properties and ecological value. These fibers are composed of cellulose, lignin, hemicelluloses, pectin, and waxy substances, among which cellulose accounts for as much as 70% [1]. Cellulose is a natural polymer compound with a chemical formula (C6H10O5)n, where n is the degree of polymerization and represents the number of glucose groups C6H11O5. Each repeating unit (C6H11O5) contains three hydroxyl groups that endow plants with high hydrophilicity [2], resulting in poor compatibility with a hydrophobic resin matrix. Therefore, the mechanical characteristics of composite materials will be decreased when the plant fibers are mixed with a resin matrix [3, 4]. In order to improve the compatibility between plant fibers and resin matrix, surface modification of the former ones is an essential step to maximize the mechanical properties of composites.

In the past years, due to the increasing shortage of oil resources and a series of environmental protection policies of the government, incineration and landfill are no longer suitable for handling agricultural and forestry residues [5]. Therefore, finding an alternative way for effective reuse of plant fibers is an urgent task. In this respect, plant fiber reinforced composites seem to be a suitable solution for these issues.

At present, plant fiber reinforced composites have been used in packaging and transportation, electronic appliances, fitness equipment, and other industries [6]. However, their applications are only limited to some
non-force-bearing or sub-force-bearing structural products. Recently, a lot of research has been dedicated to the pretreatment and surface modification of plant fibers with the aim of improving their compatibility with the resin matrix. In terms of pretreatment, steam explosion allows one to greatly reduce the content of hemicellulose and lignin in plant fibers, while increasing proportionally the specific surface area of cellulose. Thus, the mechanical properties of related composites can be noticeably improved [7]. Pre-heat treatment is a very environmental method. It enables one to effectively enhance the dimensional stability of the material by reducing the moisture content and the internal voids in the fibers, which increases the tensile performance to a certain extent [8]. Plasma treatment consists in using the high-energy rays to bombard the surface of the fiber, thereby causing a series of physical and chemical reactions, which reduce the crystallinity of the fiber [9, 10]. Compared with the above methods, alkali treatment can be easily controlled by the reaction time and temperature, thus becoming the most common pretreatment technique. In such a technique, destroyed hydroxyl (OH) groups react with water molecules and move out from the fiber structure. In turn, the remaining molecules create the fiber–cell–O–Na groups. This allows one to partly eliminate hemicellulose, lignin, pectin, wax and oil from the fiber surface to make the latter one cleaner and smoother [11]. Therefore, the pretreatment of fibers before the surface modification is usually implemented in an alkaline environment.

Most of researchers give preference to esterification modification [12], coupling agent modification [13], and graft copolymerization [14]. Meanwhile, these methods are quite harmful to the fragile plant fibers and easily damage their structure. This issue can, however, be solved via surface coating modification that has become a popular modification technology at present. Especially, organic–inorganic hybrid coatings prepared by anhydrous sol-gel process exhibit the high wear resistance and outstanding hardness of inorganic materials as well as the toughness of organic ones. Thus, the method has the advantages of continuous processing, size controllability, and economy [15]. However, the reports considering the application of surface coatings to plant fibers are still sparse. In particular, Praveen et al [16] used plasma pretreatment to increase the effective concentration of the fluoroalkyl functional siloxane networks sprayed on the coir fibers, which enabled them to obtain an extremely hydrophobic sol-gel coating on the fiber surface with improved average breaking force, breaking strength, elastic modulus, and elongation at break.

Furthermore, when producing plant fiber–reinforced composites, one commonly uses the matrix of polyvinyl chloride [17], polyethylene [18], or polypropylene [19]. On the contrary, the plant fiber–reinforced composites on ABS matrix that have excellent physical and mechanical properties have rarely been reported. For instance, Ma et al [20] prepared wood–plastic composites based on ABS and bamboo fibers, and found that both the alkali treatment of the bamboo fibers and the inclusion of the SMA copolymer improved the interactions between the bamboo fibers and ABS matrix. In this work, the r-coir fiber reinforced ABS composites were prepared by melt compounding. In order to improve the compatibility between r-coir fibers and ABS, the former ones underwent modification through the production of a TEOS/KH550/SMA hybrid coating. The practicality of TEOS and KH550 was shown in our previous study [21] by the example of coating inorganic layers on PET fibers. At the same time, SMA was selected as compatibilizer to make fibers compatible with ABS matrix. The SiO₂ particles produced by a sol-gel reaction of TEOS were used to connect KH550 and SMA to the fiber surface and form an organic–inorganic ‘armor’ structure atop. In addition, modified r-coir fibers and unmodified r-coir fibers–reinforced ABS composites were also prepared for the comparative analysis.

2. Experimental

2.1. Materials

R-coir fibers were recycled from waste coconut palm mattresses. The ABS, with the trade name of PA-747, was provided as pellets by Chi Mei Corp. (Jhunan, Taiwan, China). Its density and melt flow index (MFI) were 1.03 g cm⁻³ and 1.2 g/10 min, respectively. SMA with a density of 1.12 g cm⁻³ and maleic anhydride content over 16% was purchased from Jiaxing Huawen Chemical Co., Ltd (Jiaxing, China). P-toluene sulfonic acid (PTSA) was provided by Shanghai Naicheng Biological Technology Co., Ltd (Shanghai, China). TEOS was produced by Shanghai Xilong Biochemical Technology Co., Ltd (Shanghai, China). KH550 was fabricated by Beijing Huaweiruike Chemical Co., Ltd (Beijing, China).

2.2. Surface modification of R-Coir fibers

The synthesis of the hybrid coating was carried out according to the previous work [21]. The solution A was prepared by adding SMA powder into the boiling xylene solution until it dissolved completely. The solution B was obtained by mixing PTSA, TEOS, and xylene at a mass ratio of 0.01:1:20 and stirring for 2 h at room temperature. The solution C was then produced by mixing KH550 and xylene at a mass ratio of 0.5:20. Then, solutions A, B and C were mixed together at 130 °C for 1 h to obtain the final hybrid coating labeled as TSMA.
The r-coir fibers were washed in a mixed solution of water and acetone (with a volume ratio 1:1) for 2 h and then rinsed 4 to 5 times with deionized water before drying at 80 °C. In addition, the fibers were treated with NaOH solution (with a 4 wt% sodium content) for an hour at 80 °C and afterwards rinsed 4 to 5 times with deionized water. The samples were dried at 80 °C and labeled as coir fibers (CF). After that, CF were coated with pure SMA and TSMA through the dipping method and subjected to air drying at room temperature for 3 days. The water vapor from the air was conducive to the hydrolysis reaction of TEOS in the r-coir fibers impregnated with TSMA modifier, leading to the production of SiO2/SMA/KH550 modified layers on the fiber surface. The entire process can be described by the reactions shown in figures 1 and 2 [22]:

![Reaction equations for TSMA modified r-coir fibers.](image)
2.3. Preparation of R-coir fiber/ABS composites

The r-coir fibers and ABS were mixed and homogenized with respect to the mass ratio of 10:90 in an internal mixer with a rotation speed of 60 rad s$^{-1}$ at 180 °C for 8 min. The 4-mm-thick sheets were compression molded at 180 °C for 8 min and then air-cooled for 3 min under constant pressure before being removed from the mold.

2.4. Characterization

The morphology of TSMA modifier and modified r-coir fibers, as well as the bending sections of r-coir fibers/ABS composites, were examined through scanning electron microscopy (SEM, S-3400N, Hitachi, Tokyo, Japan).

To confirm the successful manufacture of modifier and identify the surface modification of the r-coir fibers, Fourier transform infrared (FTIR) spectroscopy was applied. For this, samples were loaded on potassium bromide tablets and analyzed in attenuated total reflectance mode in the wavenumber range of 400–4000 cm$^{-1}$ using a FTIR spectrometer (Nicolet iS50, Polaris Long life IR source, Thermo Electron, USA) at a resolution of 0.09 cm$^{-1}$.

Figure 2. Reaction scheme for TSMA modified coir fibers.
The thermal stability of unmodified and TSMA-modified r-coir fibers was tested by thermogravimetric analysis (TGA, 7820A-MS5978B thermo-analyzer NETZSCH Co., Germany) under dynamic nitrogen atmosphere. Samples were heated from room temperature to 800 °C at a heating rate of 10 °C min⁻¹.

The contact angles of r-coir fibers relative to water were measured using a contact angle meter (OCA20, Dataphysics Company, Esslingen, Germany). Prior to experiments, the r-coir fibers were pressed with an infrared tablet press into smooth and flat sheet samples; each specimen was probed five times to take the average value.

The tensile strength of single fibers was assessed by means of a XQ-1 universal testing machine (Shanghai) in accordance with GB/T 14337 standard. The flexural properties of ABS and r-coir fibers/ABS composites were evaluated conforming to GB/T9341-2008 standard, using a WSM-20KN universal testing machine (Changchun).

3. Results and discussion

3.1. FTIR

The FTIR spectra of SMA and TSMA modifiers are shown in figure 3. In both spectra, the peaks at 1780 cm⁻¹ are attributed to the stretching vibration of C=O bonds [23]. In turn, the emergence of bands at 700 cm⁻¹ is assigned to the characteristic vibration of a monosubstituted benzene ring.

The bands at 1400 cm⁻¹ are associated with asymmetrical C–N stretching vibrations, whereas the signature at 1602 cm⁻¹ corresponds to the N–H bending in secondary amine [24]. Combining the reaction mechanism from figure 1 with the infrared spectrum of TSMA, it can be concluded that the maleic anhydride in SMA has reacted with the amine group in KH550 to form an imino group (amide) close to the carbonyl unit, which is peptide bond [25]. Therefore, the appearance of these bands confirms the successive formation of TSMA.

Through the comparison of the standard spectrum, it is found that the bands at 758 cm⁻¹ and 1078 cm⁻¹ are due to symmetrical and asymmetrical stretching vibrations of Si–O–Si bonds, which prove that KH550 hydrolysis products have reacted with TEOS ones to form strong silicon-oxygen bonds. This indicates the presence of organic-inorganic hybrid modified layers in the produced composites.

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Figure 3. FTIR spectra of SMA and TSMA modifiers.
Meanwhile, there are also the bands at 1704 cm$^{-1}$ caused by C=O stretching vibrations of the amide [27]. Therefore, these FTIR results confirm the surface modification of r-coir fibers.

### 3.2. Microstructure of SMA-and TSMA-modified R-Coir fibers

Figure 5 shows the surface morphologies of r-coir fibers. It is clear from figure 5(a) that there were the grooves and gullies on the surface of unmodified r-coir fibers, as well as a small amount of cuticles composed of wax and
The surface of the r-coir fibers modified with SMA in figure 5(b) was laminated with SMA molecular layers that were scaly and easy to separate. Compared to the SMA-modified r-coir fibers, the surfaces of TSMA-modified r-coir fibers in figures 5(c), (d) were covered with uniform layers, and there was basically no gap between the layers and the fibers. These results are due to the capillary force emerging after the fibers are dipped into TSMA. This force, in turn, yielded the coating self-assembly on the surface of r-coir fibers to form the uniform and completely modified layers. According to the combination mechanism, these layers were composed of strong silicon-oxygen bonds and SMA molecules in restricted positions. SiO2 not only inhibited the agglomeration of SMA molecules, but also provided a nucleating agent for the crystallization of SMA, which allowed the SMA molecules to be uniformly dispersed across the fiber surface and react with superficial hydroxyl groups.

Based on the SEM images and the reaction mechanism of TSMA-modified r-coir fibers, the ideal surface modification of fiber layers could be visualized as shown in figure 6. As shown in figure 6(c), the silver and purple balls in the figure refer to as Si atoms and amine groups, respectively, whereas the green network is the modifier structure formed by Si-O-Si. The SiO2 layers with amine groups as a result of the reaction between KH550 and TEOS hydrolysis products create dense inorganic layers on the surface of r-coir fibers. In turn, the reaction of the amine groups with SMA limits the location of latter ones on the fiber surface and constrains their intermolecular agglomeration.

3.3. Tensile testing of single fibers

Tensile testing of single fibers was performed to characterize their mechanical properties and the corresponding data are given in figure 7. The values of tensile strength of unmodified r-coir fiber, SMA-modified r-coir fiber, and TSMA-modified r-coir fiber were found to be 5.70, 6.35, and 7.76 MPa, respectively. An obviously better tensile strength of the modified r-coir fiber was because of the presence of superficial hydroxyl groups, which...
reacted with the anhydride in SMA and bonded together, making the SMA molecular layers cover the fiber surface. In addition, the hydrolysis of TEOS obstructed the agglomeration of SMA molecules, improving the uniformity of the coating network and finally enhancing stress transfer ability. This phenomenon was referred to as the ‘surround effect’ of the hybrid coating [28]. From the perspective of r-coir fiber structure, damages and defects on the surface of the r-coir fibers decreased the strength of the latter ones. However, the coating network formed due to the hydrolysis of TEOS endowed the r-coir fiber with a smooth surface and a reduced amount of stress concentration points [29]. Finally, for the above reasons, TSMA modification could strengthen the tensile strength of monofilaments and improve the compatibility between the fiber and the matrix at the same time.

3.4. TG Analysis

In order to investigate the influence of coating on the thermal properties of r-coir fibers, thermogravimetric measurements were conducted under dynamic nitrogen atmosphere at the heating rate of 10 °C min⁻¹. Samples were heated from ambient temperature to 400 °C. Regarding the weight loss behavior of r-coir fibers, their TG curves (figure 8) could be conventionally divided into the two stages. The first degradation process representing water loss covered the temperature range of 50 °C–200 °C whereas the second step associated with cellulose degradation was between 200 and 400 °C. Since the main problem during the process was associated with cellulose degradation, in this work, attention was further paid to a second stage. According to the TGA plots, the initial decomposition temperatures of unmodified and TSMA-modified r-coir fibers were 274 °C and 283 °C, respectively. An increase in the decomposition temperature by 9 °C in case of TSMA-modified r-coir fibers indicated an increase in their thermal stability over the unmodified ones. The modification-induced improvement of thermal stability was attributed to the thermal insulation effect of modified layers due to the introduction of SiO₂ granules. The thermal conductivities of SiO₂ and r-coir fibers were found to be 7.6 W m⁻¹·k⁻¹ and 0.15 W m⁻¹·k⁻¹, respectively. This means that the heat was preferentially transferred and dispersed along the path formed by silica, so that the heating and degradation of the fibers were delayed. The coating of the modifier effectively enhanced the thermal decomposition temperature of the r-coir fibers, further improving the performance of the natural fibers in the processing of composite materials.

3.5. Wettability of unmodified and modified R-coir fibers

The most common method to characterize the wettability of a solid is to determine the contact angle \( \theta \) of the liquid on its surface. However, the polarity of the solid surface affects the spreading ability of the liquid. In this respect, the effect of the modifier on the polarity of the fiber surface in present study was reflected by measuring the contact angle of deionized water at 20 °C.

Figure 9 displays the contact angles obtained for the fibers without modification and those with SMA and TSMA modifiers. According to the results, unmodified fibers possess the hydrophilic property. This is owing to the ability of the hydroxy-terminated groups on the molecular chains of r-coir fibers to form hydrogen bonding with water molecules. Besides, the wax and oil were removed from the fiber surface by alkali treatment, while the number of hydroxy-terminated groups generated by the breakage of some molecular chains on the fiber increased, thus enhancing the hydrophilicity of the fibers. In turn, the contact angles of the SMA- and TSMA-
modified fibers increased from 69.50° to 90.25° and 83.75°, respectively, meaning that the hydrophilicity of the fibers was drastically reduced. It can be inferred that the hydroxy-terminated groups on the fiber surface were covered by the modifier, which were mainly non-polar molecular chains consisting of \(-\text{CH}_2\text{CH}\) links. Thus, the modified r-coir fiber surface exhibited the peculiarities of the modifier, namely a change from polar to non-polar characteristics. Furthermore, the smaller contact angle of TSMA-modified r-coir fibers was mainly due to the addition of TEOS. In particular, a large amount of hydroxyl groups in SiO2 introduced through the sol-gel reaction endowed fibers with hydrophilicity and affected the hydrophobic effect of SMA to some extent.

3.6. Interface compatibility of composite materials

The bending properties of ABS and r-coir fibers/ABS composites are shown in figure 10. The r-coir fibers exerted a significant strengthening effect on ABS, resulting in a dramatic increase in the bending strength and bending modulus of the composites. In particular, these parameters for the pure ABS material were 62.5 MPa and 1991 MPa, respectively. After filling the SMA modified r-coir fibers, the flexural strength and flexural modulus reached the values of 70.7 MPa and 2190 MPa, respectively. This proved that the SMA modifier effectively improved the compatibility between the fiber and the matrix. The highest bending strength and modulus were achieved in the TSMA-modified r-coir fiber-reinforced ABS composite, being 9 and 698 MPa higher than those of the pure ABS, reaching 71.2 and 2689 MPa. This means that SMA partially played a modifying role and a special organic-inorganic ‘armor’ structure of the coating allowed the fiber to withstand more stress and deformation.

Fractured surfaces of different r-coir fibers/ABS composites were analyzed using SEM. The micrographs of the specimens with untreated r-coir fibers are shown in figure 11 (a). According to the SEM images, the r-coir fibers remained smooth and unbroken, which indicates that it does not provide good reinforcement when the composite is fractured. Moreover, noticeable gaps between the fibers and the ABS matrix could be observed. This phenomenon of phase separation illustrates that the untreated r-coir fibers had poor compatibility with the ABS matrix. Meanwhile, after SMA modification, the voids between the fiber and the matrix were significantly

![Figure 9](image1.png)

**Figure 9.** The contact angles images of r-coir fibers before and after modification: (a) unmodified r-coir fibers, (b) SMA-modified r-coir fibers, and (c) TSMA-modified r-coir fibers.

![Figure 10](image2.png)

**Figure 10.** Bending properties of different ABS composites ((a) ABS, ABS composite filled with (b) unmodified r-coir fibers, (c) SMA-modified r-coir fibers, and (d) TSMA-modified r-coir fibers).
increased in Figure 11(b). This is due to the fact that the SMA-modified r-coir fibers were partially coated with non-polar groups and the interfacial compatibility between the fibers and the ABS matrix could be thereby improved. Besides, the increased fiber/matrix adhesion provided an increase in stress transfer between fibers and ABS [30]. Figure 11(c) depicts the cross-sections of TSMA-modified r-coir fibers-filled ABS composites, where the fibers and the matrix basically appear as a whole, meaning that their interfacial compatibility was improved. Therefore, using TSMA as the compatibility agent enabled one to improve the interfacial compatibility between the fibers and ABS.

4. Conclusions

In summary, uniform and homogeneous TSMA hybrid coating layers were successfully formed on the surface of the r-coir fibers. The TSMA layers allowed one to increase the single-fiber strength by 36.1% and improve the bending strength and modulus of the r-coir fibers/ABS composite by 6% and 27% respectively, as compared to unmodified r-coir fibers-filled composites. The analysis of fractured surfaces of the composites and their contact angles proved the improvement of compatibility between r-coir fibers and ABS. Thus, this work provides an alternative method for effective recycling of r-coir fibers and further improvement of ABS mechanical properties.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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