

Mechanical and interfacial properties of poly(vinyl chloride) based composites reinforced by cassava stillage residue with different surface treatments



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ABSTRACT

Cassava stillage residue (CSR), a kind of agro-industrial plant fiber, was modified by coupling agent (CA), mechanical activation (MA), and MA-assisted CA (MACA) surface treatments, respectively. The untreated and different surface treated CSRs were used to prepare plant fibers/polymer composites (PFPC) with poly(vinyl chloride) (PVC) as polymer matrix, and the properties of these CSR/PVC composites were compared. Surface treated CSR/PVC composites possessed better mechanical properties, water resistance and dimensional stability compared with the untreated CSR/PVC composite, attributing to the improvement of interfacial properties between CSR and PVC matrix. MACA-treated CSR was the best reinforcement among four types of CSRs (untreated, MA-treated, CA-treated, and MACA-treated CSRs) because MACA treatment led to the significant improvement of dispersion, interfacial adhesion and compatibility between CSR and PVC. MACA treatment could be considered as an effective and green method for enhancing reinforcement efficiency of plant fibers and the properties of PFPC.

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1. Introduction

Plant fibers, the most abundant natural biopolymers on earth, are considered to be an almost inexhaustible source of raw material for the increasing demand of environmentally friendly and biocompatible products [1]. Plant fibers/polymer composites (PFPC), prepared by thermoplastic polymer matrix reinforced with wood or other natural fibers, have received great research interest in recent years because plant fibers have the advantages of low density, low cost, nontoxicity, wide availability, easy processing, high specific mechanical properties, and especially the renewability and biodegradability [2–5]. Currently, the use of agricultural plant fibers for the production of PFPC has drawn much attention as an alternative to traditional wood fibers in plant fibers-reinforced composites [6–9]. Cassava stillage residue (CSR) is the agro-industrial solid residue generated in the still bottoms following fermentation and distillation during the production process of cassava-based bioethanol, and the main component of this residue is plant fiber [10]. A large amount of CSR is generated every year, and most of

this residue has not been efficiently used, or is even burned or discarded as waste, resulting in adverse impact on environment. So, the utilization of CSR as filler material for the production of PFPC can efficiently increase the added value of CSR and avoid environmental pollution [7,10].

Actually, the plant fibers as well as CSR exhibit a high hydrophilicity due to attraction or interaction between the hydroxyl groups of fiber components and water molecules. The interactions between fiber and water originate from the non-crystalline region and extend to the crystalline region [6]. Plant fibers with strong polarity are not well compatible with non-polar and hydrophobic polymer matrix and the interfacial tension between plant fibers and matrix is quite high, leading to weak fiber-matrix interfacial adhesion and poor mechanical properties of the composites [11–13]. In addition, for simple premixed composites, plant fibers have a tendency to form aggregates and separate from the thermoplastic polymers during processing, which provides a poor dispersion of these fibers in matrix and the inhomogeneity of blends, leading to a potential reduction as reinforcement for polymers [9,14,15]. The interfacial adhesion between plant fibers and matrix can be improved by surface modification of fibers, including heat treatment, plasma treatment, corona treatment, alkaline treatment, esterification, etherification, graft

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copolymerization, coupling agent (CA) treatment, and their combination treatments [11,16–22]. Among these methods, CA treatment is considered as a simple and effective method for increasing the interfacial interactions and compatibility between plant fibers and matrix and improving the properties of the composites [23–25]. However, the contact between CA and plant fibers is poor under solid phase conditions because of the highly-ordered and recalcitrant structure of cellulose–hemicellulose–lignin complex and high crystallinity of cellulose in plant fibers [26]. In order to improve the accessibility of plant fibers to CA, it is necessary to adopt assisted means for surface modification of plant fibers.

Mechanical activation (MA), which refers to the use of mechanical actions to change the crystalline structure and physicochemical properties of the solids carried out by high-energy milling, is considered as a simple, effective, and environmentally friendly method for the pretreatment of solid materials attributing to the use of simple and cheap equipment and the operations without the use of solvents, intermediate fusion, etc. [27–29]. The destruction of stable hydrogen bond and crystalline structure induced by MA can efficiently enhance the accessibility and reactivity of plant fibers [30]. Moreover, MA can enhance the dispersion and contact area of plant fibers in thermoplastic matrix due to the size reduction and the split of compact fiber bundles [31]. Herein, we report the MA-assisted CA (MACA) treatment for the surface modification of CSR, and the modified CSR was used as reinforcement for the preparation of PFPC with poly(vinyl chloride) (PVC) as thermoplastic matrix by hot pressing technology. Furthermore, the mechanical and interfacial properties of the PVC composites reinforced with untreated, MA-treated and CA-treated CSRs were also investigated and compared with those of MACA-treated CSR/PVC composite.

2. Materials and methods

2.1. Materials

Cassava stillage residue (CSR) was kindly supplied by Guangxi State Farms Minyang Biochemical Group, INC., China. The cut CSR was comminuted and screened to prepare 40–60 mesh size (0.25–0.38 mm) particles. The comminuted CSR was then oven-dried at 105 °C for 4 h (moisture content < 3%) before use. The dried CSR was uniformly mixed with 5% w/w calcium carbonate (weight percent compared to CSR) that had been treated by 30% w/w stearic acid (weight percent compared to calcium carbonate) to improve the flowability of CSR, and this mixed CSR was designated as untreated CSR. PVC was obtained from Nanning Chemical Co., Ltd., China, and was used as polymer matrix. Aluminate coupling agent (ACA, DL-411-A) was purchased from Nanjing Unite Chemical Co., Ltd., China. All other chemical reagents were of analytical grade without further purification and were obtained commercially.

2.2. Surface treatments of CSR

The MACA surface treatment of CSR was carried out in a customized stirring ball mill driven by a commercially available drill press equipped with a speed-tuned motor [32]. A fixed amount of milling balls (300 mL, 6 mm diameter) was first added into a jacketed stainless steel chamber (1200 mL), and then 40.0 g of CSR, 0.4 g of ACA were added into the chamber. The mixture was subjected to milling at the speed of 375 rpm at a constant temperature of 80 °C. The balls were removed after the sample was milled for 25 min, then the chamber and milling balls were thoroughly cleaned and dried before the next milling experiment. The resulting sample was oven-dried at 105 °C for 2 h and then sealed for standby.

MA treatment of CSR was operated the same way as in MACA treatment, except for the non-addition of ACA.

CA treatment of CSR was performed in a GF-1100 high-speed mixer (Laizhou Huarun Chemical Machinery Factory, China). The CSR was first added to the high-speed mixer and stirred while gradually increasing the temperature. When the temperature reached 80 °C, 1% w/w ACA (weight percent compared to CSR) was added and the modification of CSR was carried out for 25 min under high-speed stirring at the speed of 1000 rpm. The CA-treated CSR was oven dried at 105 °C for 2 h and then sealed for standby.

2.3. Preparation of CSR/PVC composites

For each composite preparation experiment, PVC and 1% w/w Ca-Zn composite heat stabilizer (weight percent compared to the total weight of CSR and PVC) were first added in the GF-1100 high-speed mixer to mix uniformly, and then the CSR sample (50 wt.%, weight percent compared to the total weight of CSR and PVC) was added in the mixer. After thorough mixing, the compound was removed from the mixer. The resulting mixture was compression-molded in an XLB25-D plate vulcanizing press (Huzhou Xingli Corp., China) to produce the composite specimens in a preheated press at 190 °C under a pressure of 6 MPa for 12 min.

2.4. Mechanical properties of the composites

The stress–strain properties of the composites were measured by an Instron DNS-100 universal testing machine (Changchun Testing Machine Research Institute, China). The flexural strength was measured at a crosshead speed of 2.0 mm/min according to ASTM D790, and the tensile strength was measured at a crosshead speed of 5.0 mm/min according to ASTM D638 [33]. All these tests were performed at room temperature.

2.5. Scanning electron microscopy (SEM) analysis

Morphologies of fracture surfaces of the composite specimens were performed using an S-3400N scanning electron microscope (Hitachi, Japan). The samples were fixed on a sample bench using double-sided tape, and then a thin layer of gold was coated on the samples prior to measurement to improve the conductivity. SEM micrographs with different magnifications were obtained to observe the surface morphologies of different composites.

2.6. Water immersion test

Water absorption of the composites was determined following ASTM D570 [11]. The dried composite specimens were immersed in deionized water and maintained at 20 °C for 24 h. The water absorption (W_a) was represented as follows:

$$W_a = \frac{(W_t - W_0)}{W_0} \times 100\% \quad (1)$$

where W_0 is the initial weight of dried composite specimens and W_t is the wet weight of the composites immersed in water for 24 h.

The dimensional changes of the composites were measured by comparing the length, width and height of each specimen before and after water immersion. The changes for length (L_c), width (W_c) and height (H_c) were given by:

$$L_c = \frac{L_t - L_0}{L_0} \times 100\% \quad (3)$$

$$W_c = \frac{W_t - W_0}{W_0} \times 100\% \quad (4)$$

$$H_c = \frac{H_t - H_0}{H_0} \times 100\% \quad (5)$$

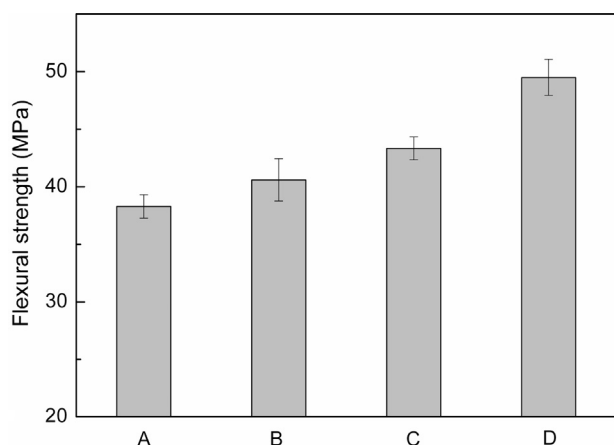


Fig. 1. Flexural strength of the composites: (A) untreated CSR/PVC composite, (B) MA-treated CSR/PVC composite, (C) CA-treated CSR/PVC composite, and (D) MACA-treated CSR/PVC composite.

where L_0 , W_0 , and H_0 are the initial length, width, and height of the dried composite specimens, respectively, and L_t , W_t , and H_t are the length, width, and height of the wet composites immersed in water for 24 h, respectively.

Thus, the percentage hygroscopic dimensional change (volumetric change, V_c) could be calculated by the following equations [34]:

$$V_c = \left(\left(1 + \frac{L_c}{100} \right) \left(1 + \frac{W_c}{100} \right) \left(1 + \frac{H_c}{100} \right) - 1 \right) \times 100\% \quad (6)$$

In addition, the flexural and tensile strength of the soaked composites were also measured to investigate the effect of water immersion on the mechanical properties of the composites.

2.7. Statistical analysis

All tests were replicated three times, and the results were calculated and analyzed by Microsoft Excel (2007). The curves were obtained by drawing with using OriginPro 7.5.

3. Results and discussion

3.1. Mechanical properties of the composites

In most composites, effective wetting and uniform dispersion of all components in a given matrix and strong interfacial adhesion between the phases are required to obtain a composite with satisfactory mechanical properties [17,35]. For the plant fibers reinforced composites, mechanical properties can directly reflect the interfacial properties between thermoplastic matrix and fibers [11]. PVC possesses good mechanical properties (the flexural and tensile strength of pure PVC used in this study were 91 and 53 MPa, respectively), but the inherent defects such as poor thermal stability, aging resistance and processing performance limit its application in many fields. The use of plant fibers as reinforcement can overcome these disadvantages of PVC, but poor interfacial interaction between hydrophilic plant fibers and hydrophobic PVC can lead to the decrease in mechanical properties. So, surface treatment is necessary to improve the interfacial properties between CSR and PVC matrix, resulting in the enhancement of the properties of CSR/PVC composites [36–38]. The effect of surface treatment of CSR on the flexural strength of the composites is given in Fig. 1, which shows that the flexural strength of the composites reinforced by MA-treated, CA-treated and MACA-treated CSRs increased by 6.1%, 13.2% and 29.3% in comparison with that of the untreated CSR reinforced composite, respectively. Correspondingly, Fig. 2 presents the

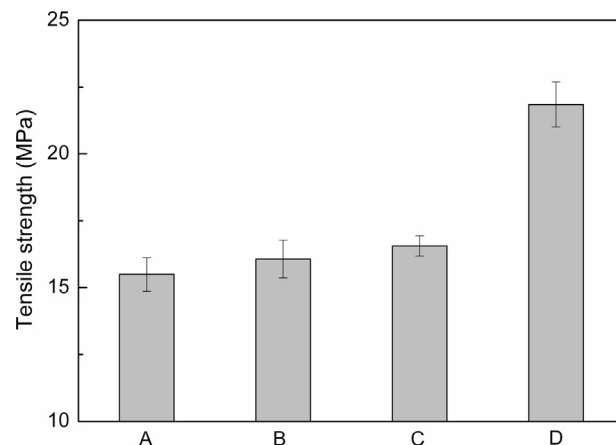


Fig. 2. Tensile strength of the composites: (A) untreated CSR/PVC composite, (B) MA-treated CSR/PVC composite, (C) CA-treated CSR/PVC composite, and (D) MACA-treated CSR/PVC composite.

effect of surface treatment of CSR on the tensile strength of the composites, showing that the tensile strength of MA-treated, CA-treated and MACA-treated CSRs reinforced composites increased by 3.7%, 6.9% and 41.1% compared to that of the untreated CSR reinforced composite, respectively. These indicate that MA and CA treatments had a positive effect on the mechanical properties of the composites, and MACA treatment significantly improved the mechanical properties of the composites.

MA could induce the decrease in particle size and ordered structure, increase in specific surface area, and split of fiber bundles, which helped to improve the dispersion of CSR in PVC matrix and the penetration of PVC in CSR and thus enhanced the interfacial bonding [31]. So, the slight increment in mechanical properties of the MA-treated CSR/PVC composite was just attributed to the structural changes of CSR induced by ball milling. Generally, CA is used for the surface modification of plant fibers in composite applications. For the modification of CSR using ACA, the condensation reaction between ACA and hydroxyl groups of the CSR fibers is illustrated in Fig. 3. The hydrophobicity of plant fibers would increase and hence improve the compatibility between the fibers and thermoplastic matrix [36,39,40]. However, the recalcitrant structure of cellulose–hemicellulose–lignin complex and high crystallinity of cellulose in CSR make ACA difficult to fully contact and react with CSR, and common CA treatment is unlikely to obtain good surface modification of CSR. Therefore, the mechanical properties of the CA-treated CSR reinforced composite were enhanced in comparison with the untreated CSR reinforced composite, but the increment was not satisfactory. When subjected to intense milling, the strong hydrogen bonding and stable crystalline structure of CSR can be significantly destroyed, leading to the increase of activated hydroxyl groups in CSR. As a result, the condensation reaction between ACA and CSR could efficiently take place with combining MA and CA modification in the same equipment, leading to better hydrophobicity of CSR and improving the compatibility between CSR and PVC matrix. In addition, the structural changes of CSR were also induced by MA, contributing to the increase of the effective contact area between CSR and matrix. These can improve the interfacial adhesion and mechanical interlocking bonds between CSR and PVC, which make it feasible for stress transfer to take place from the thermoplastic matrix to the CSR, resulting in the increase of the mechanical properties of the composites [41]. Therefore, the MACA-treated CSR/PVC composite possessed the best mechanical properties among the composites reinforced by these three surface treatments of CSR.

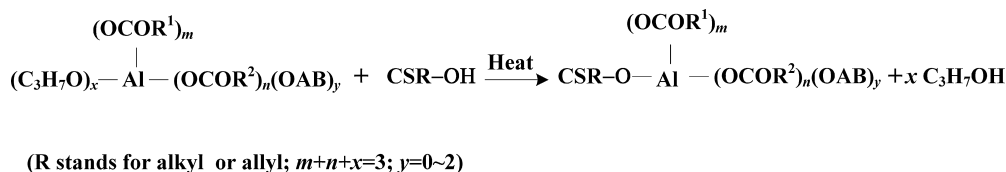


Fig. 3. Condensation reaction between ACA and CSR fibers.

Table 1

Water absorption and dimensional changes of the composites reinforced by untreated and different surface treated CSRs.

Sample	Water absorption ^a (%)	Dimensional change ^a (%)
Untreated CSR/PVC composite	3.58 ± 0.06	2.43 ± 0.03
MA-treated CSR/PVC composite	3.15 ± 0.04	1.67 ± 0.06
CA-treated CSR/PVC composite	2.68 ± 0.02	0.89 ± 0.03
MACA-treated CSR/PVC composite	0.84 ± 0.02	0.02 ± 0.00

^a Data represent the mean ± standard deviation.

3.2. Fracture morphologies of the composites

As shown in Fig. 4, SEM was used to examine the fracture surfaces of CSR/PVC composites and directly observe the dispersion and interface bonding of CSRs in the PVC matrix. The SEM images of untreated CSR/PVC composite in Fig. 4a1 and a2 show rough fracture surface and many gaps between CSR and PVC. This poor adhesion is due to the formation of hydrogen bonds between CSRs as well as large difference in surface energies between CSR and PVC matrix. After MA treatment, the structural changes of CSR could help to spread out the CSR particles uniformly in the matrix, leading to the improvement of mechanical interlocking bonds between plant fibers and polymer matrix (Fig. 4b1 and b2). However, the interfacial bonding and wettability were also poor because of the strong hydrophilicity of CSR, and MA treatment could not enhance the compatibility between CSR and PVC matrix. As can be observed from the fracture surface of CA-treated CSR/PVC composite in Fig. 4c1 and c2, the interfacial adhesion between CSR fibers and matrix is better than untreated CSR/PVC composite, ascribing to the increase in hydrophobicity of CSR by CA modification. But the fibers were pulled out from the matrix, which gave rise to the holes in composite and the aggregation of some fibers, leading to poor distribution of CSR in matrix. As shown in Fig. 4d1 and d2, the fracture surface of the composite reinforced by MACA-treated CSR is compact and smooth with little gaps, and the fiber-matrix interface is indistinct, indicating the better compatibility between CSR and PVC matrix attributed to the increase in the hydrophobicity of CSR by MACA treatment. In addition, the destruction of the compact and stable structure of CSR led to the enhancement of the dispersion of CSR in PVC matrix, which thus improved the interfacial adhesion between fibers and polymer matrix. Undoubtedly, the significant increase of compatibility and interfacial adhesion between fillers and matrix induced by MACA treatment could effectively improve the properties of NFPC.

3.3. Water absorption and dimensional changes of the composites

The water absorption of the composites reinforced by untreated and different surface treated CSRs and the corresponding dimensional changes of the composites are shown in Table 1. Without any treatment of CSR, the interaction and wettability between CSR and PVC matrix were poor. Such features created some defects and cracks in which more water could penetrate and fill the voids left by the non-wetted fibers in the untreated CSR/PVC composite, and the dimensional change was obvious. After MA treatment, the destruction of CSR structure improved the dispersion of CSR in

PVC matrix and penetration of PVC in CSR, leading to the enhancement of the mechanical interlocking bonds and interfacial adhesion between CSR and PVC and the reduction of defects and cracks in composite, which thus decreased the water absorption capability and increased the dimensional stability of MA-treated CSR/PVC composite. The decrease in water absorption and dimensional change of CA-treated CSR/PVC composite demonstrates that the CSR treated by CA improved the water resistance and dimensional stability of the composite. CSR surface nature was modified from hydrophilic to hydrophobic with CA treatment for better performance of the water resistance, which increased the compatibility and interfacial bonding between CSR and PVC matrix, leading to the improvement of the dimensional stability of the composite. For MACA-treated CSR, the destruction of highly-ordered and tight crystalline structure of CSR induced by MA resulted in the increase of amorphous phase and activated free OH groups, which made CSR more accessible to CA and improved the coupling reaction between ACA and hydroxyl groups of the CSR fibers. This coupling reaction led to the increase in hydrophobicity of CSR and improved the compatibility between CSR and PVC matrix, and MA could also result in the increase of effective surface area, fiber dispersion and interfacial adhesion. As expected, the MACA-treated CSR/PVC composite possessed the best water resistance and dimensional stability.

3.4. Mechanical properties of the composites after water immersion

Flexural strength is the ability of the material to withstand bending forces applied perpendicularly to its longitudinal axis. The stresses induced due to the flexural load are a combination of compressive and tensile stresses [6]. Higher flexural strength of the fibers-reinforced composites is due to the better interfacial interaction and adhesion between fibers and matrix [40]. Therefore, flexural strength was a critical index for investigating the effect of water immersion on the mechanical properties of the CSR/PVC composites. The flexural strength of untreated and different treated CSR/PVC composites before and after water immersion is illustrated in Fig. 5. After water immersion, the flexural strength of the composites reinforced by untreated, MA-treated, CA-treated and MACA-treated CSRs decreased by 46.9%, 14.8%, 6.8% and 0.5% compared with that of the composites before water immersion, respectively. Moreover, the tensile strength of the soaked composites was also measured, which is presented in Fig. 6. It shows that the tensile strength of untreated, MA-treated, CA-treated and MACA-treated CSRs reinforced composites decreased by 40.4%, 20.3%, 12.0% and 1.2% compared with that of the composites before water immersion, respectively. The changes in flexural and tensile strength of the composites before and after water immersion are consistent with the results of water absorption and dimensional changes. The results show that water could easily enter into the interior of the composite with poor interaction between fiber and matrix, leading to sharp decrease in flexural and tensile strength of the untreated CSR/PVC composite after water immersion. MA and CA treatments of CSR improved the interfacial bonding between CSR and matrix, and water did not easily enter into the composites, so the reduction of flexural and tensile strength of

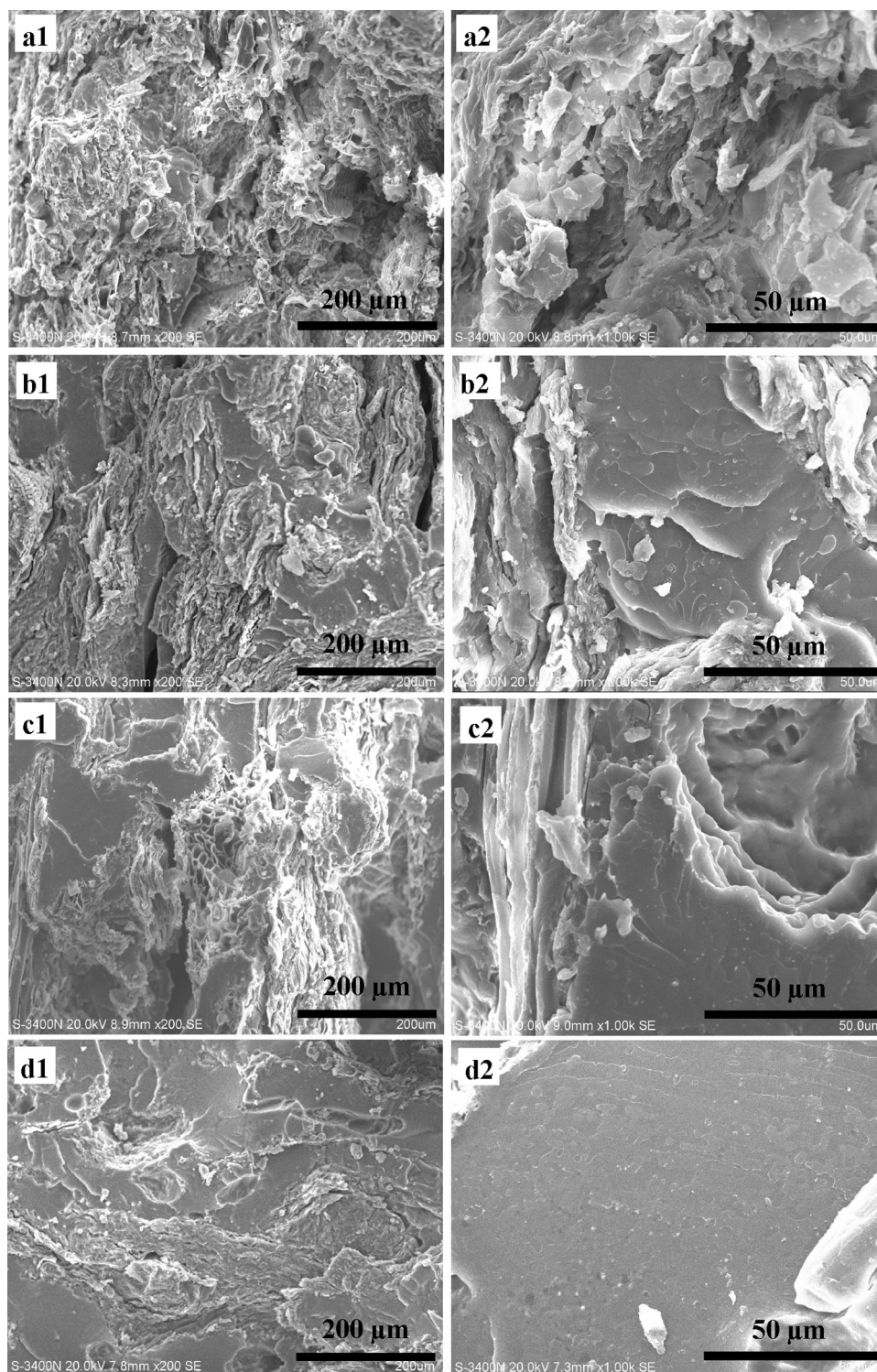


Fig. 4. SEM micrographs of the composites: (a1, a2) untreated CSR/PVC composite, (b1, b2) MA-treated CSR/PVC composite, (c1, c2) CA-treated CSR/PVC composite, and (d1, d2) MACA-treated CSR/PVC composite.

MA-treated or CA-treated CSR/PVC composite was less than that of the untreated CSR/PVC composite. In addition, CA treatment increased the hydrophobicity of CSR, which avoided the attraction and interaction between the hydroxyl groups of CSR and water molecules, leading to better water resistance of CA-treated CSR/PVC composite. As a result, the decrease of flexural and tensile strength of CA-treated CSR/PVC composite was less than that of MA-treated CSR/PVC composite. Undoubtedly, MACA treatment

of CSR significantly increased the interfacial adhesion and compatibility between fibers and matrix, and it was difficult for water to enter into the composite, which in turn resulted in higher resistance to deflection and better efficiency for energy transfer [42]. So, there were almost no changes in flexural and tensile strength of MACA-treated CSR/PVC composite before and after water immersion, indicating an excellent performance in mechanical properties and water resistance.

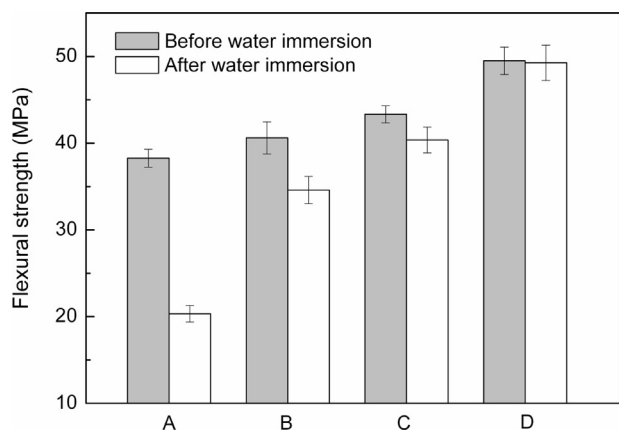


Fig. 5. Flexural strength of the composites before and after water immersion: (A) untreated CSR/PVC composite, (B) MA-treated CSR/PVC composite, (C) CA-treated CSR/PVC composite, and (D) MACA-treated CSR/PVC composite.

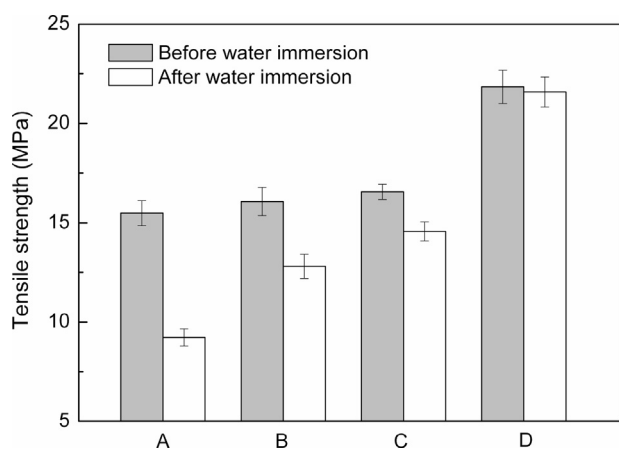


Fig. 6. Tensile strength of the composites before and after water immersion: (A) untreated CSR/PVC composite, (B) MA-treated CSR/PVC composite, (C) CA-treated CSR/PVC composite, and (D) MACA-treated CSR/PVC composite.

4. Conclusion

The influence of different surface treatments of plant fibers on the mechanical and interfacial properties of PPFC has been studied. Four types of CSRs (untreated, MA-treated, CA-treated, and MACA-treated CSRs) were used to reinforced the PVC-based composites. It was demonstrated that surface treatments of CSR had a positive effect on enhancing the properties of the composites. MA treatment destroyed the compact and stable structure of CSR, resulting in the improvement of the dispersion of CSR in PVC matrix and the penetration of PVC in CSR, which could enhance the mechanical interlocking bonds and interfacial adhesion between fibers and polymer matrix. For CA treatment, the condensation reaction between ACA and CSR fibers increased the hydrophobicity of CSR, which thus enhanced the compatibility and interfacial bonding between CSR and PVC matrix. MACA treatment changed the structure of CSR and enhanced the coupling reaction, leading to the significant increase of dispersion, interfacial interaction and compatibility between CSR and PVC matrix. Therefore, the improvement of interfacial properties between CSR and PVC matrix induced by surface treatments enhanced the mechanical properties, water resistance and dimensional stability of the composites, and MACA-treated CSR/PVC composite possessed the best properties compared with the composites reinforced by untreated, MA-treated and CA-treated CSRs. This study suggested that MACA treatment was an efficient and environmentally friendly method

for enhancing reinforcement efficiency of plant fibers and the properties of PPFC.

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References

- [1] J.K. Pandey, S.H. Ahn, C.S. Lee, A.K. Mohanty, M. Misra, Recent advances in the application of natural fiber based composites, *Macromol. Mater. Eng.* 295 (2010) 975–989.
- [2] M.J. John, S. Thomas, Biofibres and biocomposites, *Carbohydr. Polym.* 71 (2008) 343–364.
- [3] S.N. Monteiro, F.P.D. Lopes, A.S. Ferreira, D.C.O. Nascimento, Natural-fiber polymer-matrix composites: cheaper, tougher, and environmentally friendly, *JOM* 61 (2009) 17–22.
- [4] K.G. Satyanarayana, G.G.C. Arizaga, F. Wypych, Biodegradable composites based on lignocellulosic fibers—overview, *Prog. Polym. Sci.* 34 (2009) 982–1021.
- [5] O. Faruk, A.K. Bledzki, H. Fink, M. Sain, Biocomposites reinforced with natural fibers: 2000–2010, *Prog. Polym. Sci.* 37 (2012) 1552–1596.
- [6] A.K. Bledzki, A.A. Mamun, A. Jaszkiwicz, K. Erdmann, Polypropylene composites with enzyme modified abaca fibre, *Compos. Sci. Technol.* 70 (2010) 854–860.
- [7] Z. Wang, E. Wang, S. Zhang, Z. Wang, Y. Ren, Effects of cross-linking on mechanical and physical properties of agricultural residues/recycled thermoplastics composites, *Ind. Crops Prod.* 29 (2009) 133–138.
- [8] A. Ashori, A. Nourbakhsh, Bio-based composites from waste agricultural residues, *Waste Manage.* 30 (2010) 680–684.
- [9] F. Yan-Hong, L. Yi-Jie, X. Bai-Ping, Z. Da-Wei, Q. Jin-Ping, H. He-Zhi, Effect of fiber morphology on rheological properties of plant fiber reinforced poly(butylene succinate) composites, *Compos. Part B* 44 (2013) 193–199.
- [10] Z. Liao, Z. Huang, H. Hu, Y. Zhang, Y. Tan, Microscopic structure and properties changes of cassava stillage residue pretreated by mechanical activation, *Bioresour. Technol.* 102 (2011) 7953–7958.
- [11] S. Kaewkuk, W. Sutapun, K. Jarukumjorn, Effects of interfacial modification and fiber content on physical properties of sisal fiber/polypropylene composites, *Compos. Part B* 45 (2013) 544–549.
- [12] K. Magniez, A.S. Voda, A.A. Kafi, A. Fichini, Q. Guo, B.L. Fox, Overcoming interfacial affinity issues in natural fiber reinforced polylactide biocomposites by surface adsorption of amphiphilic block copolymers, *ACS Appl. Mater. Interfaces* 5 (2013) 276–283.
- [13] A. Dong, Y. Yu, J. Yuan, Q. Wang, X. Fan, Hydrophobic modification of jute fiber used for composite reinforcement via laccase-mediated grafting, *Appl. Surf. Sci.* 301 (2014) 418–427.
- [14] D.R. Mulinari, H.J.C. Voorwald, M.O.H. Cioffi, M.L.C.P. Silva, S.M. Luz, Preparation and properties of HDPE/sugarcane bagasse cellulose composites obtained for thermokinetic mixer, *Carbohydr. Polym.* 75 (2009) 317–321.
- [15] W. Liao, H. Tien, S. Hsiao, S. Li, Y. Wang, Y. Huang, S. Yang, C.M. Ma, Y. Wu, Effects of multiwalled carbon nanotubes functionalization on the morphology and mechanical and thermal properties of carbon fiber/vinyl ester composites, *ACS Appl. Mater. Interfaces* 5 (2013) 3975–3982.
- [16] G.W. Beckermann, K.L. Pickering, Engineering and evaluation of hemp fibre reinforced polypropylene composites: fibre treatment and matrix modification, *Compos. Part A* 39 (2008) 979–988.
- [17] C. Wu, Preparation, characterization and biodegradability of crosslinked tea plant-fibre-reinforced polyhydroxyalkanoate composites, *Polym. Degrad. Stab.* 98 (2013) 1473–1480.
- [18] M.M. Kabir, H. Wang, K.T. Lau, F. Cardona, Chemical treatments on plant-based natural fibre reinforced polymer composites: an overview, *Compos. Part B* 43 (2012) 2883–2892.
- [19] M.S. Ferreira, M.N. Sartori, R.R. Oliveira, O. Guven, E.A.B. Moura, Short vegetal-fiber reinforced HDPE-study of electron-beam radiation treatment effects on mechanical and morphological properties, *Appl. Surf. Sci.* 310 (2014) 325–330.
- [20] A.K. Bledzki, S. Reihmane, J. Gassan, Properties and modification methods for vegetable fibers for natural fiber composites, *J. Appl. Polym. Sci.* 59 (1996) 1329–1336.
- [21] A.K. Bledzki, J. Gassan, Composites reinforced with cellulose based fibres, *Prog. Polym. Sci.* 24 (1999) 221–274.
- [22] S.J. Eichhorn, C.A. Baillie, N. Zafeiropoulos, L.Y. Mwaikambo, M.P. Ansell, A. Dufresne, K.M. Entwistle, P.J. Herrera-Franco, G.C. Escamilla, M.H.L. Groom, C. Hill, T.G. Rials, P.M. Wild, Review current international research into cellulosic fibres and composites, *J. Mater. Sci.* 36 (2001) 2107–2131.
- [23] J. Lu, P. Askeland, L.T. Drzal, Surface modification of microfibrillated cellulose for epoxy composite applications, *Polymer* 49 (2008) 1285–1296.

- [24] A.K. Bledzki, A.A. Mamun, J. Volk, Barley husk and coconut shell reinforced polypropylene composites: the effect of fibre physical, chemical and surface properties, *Compos. Sci. Technol.* 70 (2010) 840–846.
- [25] T. Lu, M. Jiang, Z. Jiang, D. Hui, Z. Wang, Z. Zhou, Effect of surface modification of bamboo cellulose fibers on mechanical properties of cellulose/epoxy composites, *Compos. Part B* 51 (2013) 28–34.
- [26] A.T.W.M. Hendriks, G. Zeeman, Pretreatments to enhance the digestibility of lignocellulosic biomass, *Bioresour. Technol.* 100 (2009) 10–18.
- [27] P. Baláž, E. Dutková, Fine milling in applied mechanochemistry, *Miner. Eng.* 22 (2009) 681–694.
- [28] C. Sasikumar, D.S. Rao, S. Srikanth, N.K. Mukhopadhyay, S.P. Mehrotra, Dissolution studies of mechanically activated Manavalakurichi ilmenite with HCl and H₂SO₄, *Hydrometallurgy* 88 (2007) 154–169.
- [29] C. Chen, Y. Shen, A. Yeh, Physico-chemical characteristics of media-milled corn starch, *J. Agric. Food Chem.* 58 (2010) 9083–9091.
- [30] Z. Huang, X. Liang, H. Hu, L. Gao, Y. Chen, Z. Tong, Influence of mechanical activation on the graft copolymerization of sugarcane bagasse and acrylic acid, *Polym. Degrad. Stab.* 94 (2009) 1737–1745.
- [31] Z. Huang, N. Wang, Y. Zhang, H. Hu, Y. Luo, Effect of mechanical activation pretreatment on the properties of sugarcane bagasse/poly(vinyl chloride) composites, *Compos. Part A* 43 (2012) 114–120.
- [32] Z. Huang, X. Xie, Y. Chen, J. Lu, Z. Tong, Ball-milling treatment effect on physico-chemical properties and features for cassava and maize starches, *C. R. Chimie* 11 (2008) 73–79.
- [33] S.M. Luz, J.D. Tio, G.J.M. Rocha, A.R. Gonçalves, Jr. A.P.D. Arco, Cellulose and cellulignin from sugarcane bagasse reinforced polypropylene composites: effect of acetylation on mechanical and thermal properties, *Compos. Part A* 39 (2008) 1362–1369.
- [34] Y. Wei, N. Silikas, Z. Zhang, D.C. Watts, The relationship between cyclic hygroscopic dimensional changes and water sorption/desorption of self-adhering and new resin-matrix composites, *Dent. Mater.* 29 (2013) 218–226.
- [35] H. Jiang, D.P. Kamdem, Characterization of the surface and the interphase of PVC-copper amine-treated wood composites, *Appl. Surf. Sci.* 256 (2010) 4559–4563.
- [36] Y. Zheng, D. Cao, D. Wang, J. Chen, Study on the interface modification of bagasse fibre and the mechanical properties of its composite with PVC, *Compos. Part A* 38 (2007) 20–25.
- [37] D. Hammiche, A. Boukerrou, H. Djidjelli, Y. Corre, Y. Grohens, I. Pillin, Hydrothermal ageing of alfa fiber reinforced polyvinylchloride composites, *Constr. Build. Mater.* 47 (2013) 293–300.
- [38] N. Bakar, C.Y. Chee, L.C. Abdullah, C.T. Ratnam, N. Azowa, Effect of methyl methacrylate grafted kenaf on mechanical properties of polyvinyl chloride/ethylene vinyl acetate composites, *Compos. Part A* 63 (2014) 45–50.
- [39] J.G. Gwon, S.Y. Lee, S.J. Chun, G.H. Doh, J.H. Kim, Effects of chemical treatments of hybrid fillers on the physical and thermal properties of wood plastic composites, *Compos. Part A* 41 (2010) 1491–1497.
- [40] P.A. Sreekumar, S.P. Thomas, J.M. Saiter, K. Joseph, G. Unnikrishnan, S. Thomas, Effect of fiber surface modification on the mechanical and water absorption characteristics of sisal/polyester composites fabricated by resin transfer molding, *Compos. Part A* 40 (2009) 1777–1784.
- [41] P. Threepopnatkul, N. Kaerkitcha, N. Athipongarporn, Effect of surface treatment on performance of pineapple leaf fiber-polycarbonate composites, *Compos. Part B* 40 (2009) 628–632.
- [42] C.R. Reddy, A.P. Sardashti, L.C. Simon, Preparation and characterization of polypropylene-wheat straw-clay composites, *Compos. Sci. Technol.* 70 (2010) 1674–1680.