



A green and efficient method for preparing acetylated cassava stillage residue and the production of all-plant fibre composites



Yanjuan Zhang^{a,b}, Tao Gan^a, Yuanwei Luo^a, Xiaohong Zhao^a, Huayu Hu^a, Zuqiang Huang^{a,*},
Aimin Huang^a, Xingzhen Qin^a

^aSchool of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, China

^bGuangxi Research Institute of Chemical Industry, Nanning 530001, China

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ABSTRACT

Cassava stillage residue (CSR), a kind of agro-industrial plant fibres, was directly acetylated and converted into thermoplastic material by mechanical activation-assisted solid phase reaction (MASPR) in a stirring ball mill without the use of organic solvent and additives. As combining mechanical activation and chemical modification in the same equipment, the destruction of hydrogen bonds and crystalline structure of CSR induced by intense milling improved the reactivity of CSR, leading to the effective acetylation of CSR. After acetylation by MASPR, the modified CSRs possessed thermoplasticity, ascribing to the introduction of acetyl groups and the destruction of high crystallinity structure of cellulose. The self-reinforced all-plant fibre composites (APFC) were successfully produced with the modified CSRs as both matrix and reinforcement by hot pressing technology. The direct acetylation of CSR and successful production of APFC suggested that MASPR was a simple, efficient and environmentally friendly method for chemical modification of agro-industrial lignocellulose biomass.

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1. Introduction

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 a main component of this residue is plant fibre [1,2]. A large amount of CSR is generated every year, and most of this residue has not been effectively used, or is even discarded as waste. The decay of so much solid residue will cause serious environmental pollution, so it is a significant issue to properly dispose the CSR. Recently, a new class of plant fibre-based biocomposites, defined as all-plant fibre composites (APFC), is prepared by using plant fibres as both the matrix and reinforcement [3,4]. Without the use of petroleum-based materials, the self-reinforced APFC are fully bio-based and fully biodegradable [5]. Besides, the interfacial adhesion is expected to be improved by using the same molecular level materials as matrix and reinforcement [6]. Thus, the effective utilization of CSR for the preparation of APFC can help to avoid environmental pollution and increase the added value of this lignocellulosic biomass. It is well known that plant fibres mainly consist of cellulose, hemicellulose and lignin. Due to the

high degree of crystallinity of cellulose and the three-dimensional net structure of lignin, plant fibres cannot be processed like thermoplastic polymers [3,7]. It has been demonstrated that plant fibres can be converted into thermally formable materials through chemical modifications, such as etherification and esterification [8,9]. As a result, the self-reinforced plant fibre composites can be prepared by hot pressing, in which the plasticized parts serve as matrix and the unplasticized parts as reinforcement. However, the conventional chemical modifications often involve the use of organic solvents [10–12], which result in high cost for solvent recycling and the reduction of the possibility for industrial scale-up. So, it is important to develop a simple, efficient and environmentally friendly method for chemical modification of plant fibres.

With the increasing concerns on environmental protection, solid phase reaction (SPR) has attracted much attention for the advantages of the simplification of reaction process and product separation without the use of solvent, specificity of reaction, high selectivity and efficiency, and saving resources, and it is considered as an efficient procedure for green chemistry [13–15]. However, the contact between reagents and plant fibres is poor under SPR conditions because of the highly-ordered and recalcitrant structure of cellulose–hemicellulose–lignin complex and high crystallinity of cellulose in plant fibres [16]. In order to improve the reactivity of plant fibres and enhance the efficiency of SPR, it is necessary to

* Corresponding author. Tel.: +86 771 3233728; fax: +86 771 3233718.

E-mail address: huangzq@gxu.edu.cn (Z. Huang).

adopt assisted means for chemical modification of plant fibres. 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, efficient 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. [17–19]. The destruction of stable hydrogen bond and crystalline structure induced by MA could effectively enhance the reactivity of plant fibres [20]. Generally, MA is used for the pretreatment of solid materials, and then the reaction of the pretreated materials is carried out in other equipment. However, during the process of MA, a part of mechanical energy can be converted into internal energy of the milled solids and thus generates many metastable active sites, which may rapidly reduce after removing the solids from the equipment of MA [21]. In order to make full use of the mechanical energy induced by MA and improve the conditions of chemical modification by SPR, we combine the MA pretreatment and chemical modification of plant fibres in the same equipment, and this MA-assisted SPR (MASPR) method can also simplify the technological process and improve the production efficiency. In this study, CSR was directly acetylated and converted into thermoplastic material by MASPR in a stirring ball mill without the use of organic solvent and additives, and then the modified CSR was used to produce APFC by hot pressing technology.

2. Materials and methods

2.1. Materials

CSR was kindly supplied by Guangxi State Farms Minyang Biochemical Group, INC. (Nanning, China). The sun-dried CSR was comminuted and further oven-dried at 105 °C for 4 h before use. The dried CSR was designated as original CSR. The components of CSR were crude fibre (35.5 wt.%), crude fat (4.3 wt.%), crude protein (2.6 wt.%), ash (7.2 wt.%) and nitrogen-free extract (50.4 wt.%, mainly low molecular compounds). All chemical reagents were of analytical grade without further purification and were obtained commercially. Deionized water was used throughout the work.

2.2. Acetylation of CSR by MASPR

The chemical modification of CSR was performed in a customized stirring ball mill driven by a commercially available drill press equipped with a speed-tuned motor [22]. A fixed amount of milling balls (500 mL, 5 mm diameter) was first added into a jacketed stainless steel chamber (1200 mL), and then 20.0 g of CSR, 60.0 g of acetic anhydride and 6.0 g of catalyst (ZnCl_2) were added into the chamber. The mixture was subjected to milling at the speed of 375 rpm and reacted at a constant temperature of 80 °C by circulating the thermostatic water in the jacket of chamber. When the mixture was milled for different desired reaction time, the balls were removed from the resulting sample, which was then purified through repeated washing-filtration processes with water to remove inorganic salts and with absolute alcohol to remove residues of acetic anhydride and by-products, respectively. Finally, the modified CSR was oven-dried at 60 °C until reached constant weight.

2.3. Determination of weight gain

Due to the complexity of CSR with containing macromolecular and low molecular compounds, the extent of acetylation was measured by percentage weight gain after the chemical modification.

The weight gain (W) of modified CSR was calculated by using the following equation [23]:

$$W = \frac{m_2 - m_1}{m_1} \times 100\% \quad (1)$$

where m_1 is the dry weight of original CSR, and m_2 is the dry weight of modified CSR.

2.4. Activation grade measurement

Activation grade (A_g) is defined as the degree of nonwettability between water and solids, and the higher A_g value indicates the better hydrophobicity of the solids. The A_g of CSR samples was measured according to our previous work [24].

2.5. Preparation of APFC

The modified CSR samples were first comminuted by a high-speed pulverizer (Tianjin Taisite Instrument Co. Ltd., China), and then they were put in the molds with liquid paraffin as lubricant. These CSR particles were compression-molded in an XLB25-D plate vulcanizing press (Huzhou Xingli Corp., China) to produce APFC specimens in a preheated press at 120 °C under a pressure of 8 MPa for 5 min.

2.6. Mechanical properties of APFC

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 and flexural modulus were measured at a crosshead speed of 2.0 mm/min according to ASTM D790, and the tensile strength and elongation at break were measured at a crosshead speed of 2.0 mm/min according to ASTM D638 [25]. All these tests were performed at room temperature.

2.7. Characterization

Fourier transform infrared spectroscopy (FTIR) spectra of the samples were acquired on an 8400S Fourier transform infrared spectrometer (Shimadzu, Japan) using the KBr disk technique. For FTIR measurement, the samples were mixed with anhydrous KBr and then compressed into thin disk-shaped pellets. The spectra were obtained with a resolution of 4 cm^{-1} and a wavenumber range of 4000–400 cm^{-1} .

X-ray diffractometry (XRD) patterns were recorded on a D/MAX 2500 V diffractometer (Rigaku, Japan) using Cu $K\alpha$ radiation ($\lambda = 0.154 \text{ nm}$) at 40 kV and 30 mA. The scattering angle (2θ) was varied from 10° to 40° with a step width of 0.02°.

Differential scanning calorimetry (DSC) curves of the samples were determined using a DSCQ20 analyzer (TA Instruments, USA) under nitrogen atmosphere with a heating rate of 10 °C/min.

Morphologies of the samples 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 the samples were coated with a thin layer of gold prior to examination to improve the conductivity. SEM micrographs with different magnifications were obtained to observe the surface morphologies of different samples.

3. Results and discussion

3.1. Synthesis and properties of acetylated CSR

CSR consists of complex components, including macromolecular and low molecular compounds. Chemical modification of CSR

is not only the acetylation of plant fibre, but also the acetylation of other components. Because of the chemical heterogeneity of CSR, it is difficult to measure the substituting degree of acetylated CSR by means of calculating the degree of substitution of cellulose derivatives [3]. Instead, the extent of acetylation can be quantified by the percentage weight gain after the modification, and a higher weight gain means higher extent of acetylation. Plant fibre is a main component of CSR, and it is unable to react with acetic anhydride before being preactivated due to the recalcitrant structure of cellulose–hemicellulose–lignin complex and high crystallinity of cellulose in CSR [26]. When subjected to intense milling, the strong inter- and intramolecular hydrogen bonding and stable crystalline structure of plant fibre can be significantly destroyed, leading to the increase of activated hydroxyl groups, which thus enhance the reactivity of plant fibre [1]. In addition, the metastable active sites in CSR induced by milling can rapidly react with acetic anhydride, benefiting from combining MA and reaction in the same equipment. Furthermore, intense milling greatly improves the contact between CSR and acetic anhydride under solid phase, which can significantly enhance the reactivity of all components of CSR. Simultaneously, the hydrophobicity (evaluated by A_g) of modified CSR would increase, attributing to the decrease of hydroxyl groups on the surface of CSR and the increase of insoluble low molecular compounds after acetylation [24,27]. The effect of milling time on the weight gain and A_g of modified CSRs is presented in Fig. 1. With the assistance of MA, acetylated CSRs were successfully prepared by SPR. The extent of acetylation and hydrophobicity of modified CSRs increased as the increase of milling time, and reached the maximum values at 2.0 h. However, further increase of milling time had negative effect on the weight gain and A_g of modified CSR. This is because that when the acetylation came to a certain extent, the degradation rate of acetylated CSR was faster than acetylation rate, leading to the decrease of weight gain and hydrophobicity.

Fig. 2 illustrates the FTIR spectra of original CSR and the modified CSRs with different milling time. All the FTIR spectra of the samples show two main absorption regions, presenting at low wavelengths in 1800–700 cm^{-1} and higher wavelengths in 3500–2700 cm^{-1} , which are consistent with the typical spectra of plant cellulose [28]. Compared with the original CSR, it can be seen that the modified CSRs have an obvious new absorption peak at 1740 cm^{-1} , which is assigned to C=O stretching vibration of –COCH₃. This indicates that acetic anhydride had reacted with CSR to form acetylated CSR. Furthermore, the absorption band at 1740 cm^{-1} gradually increases with the milling time, which is consistent with the increasing trend of weight gain. This proves that the increase in weight gain of modified CSRs was attributed to

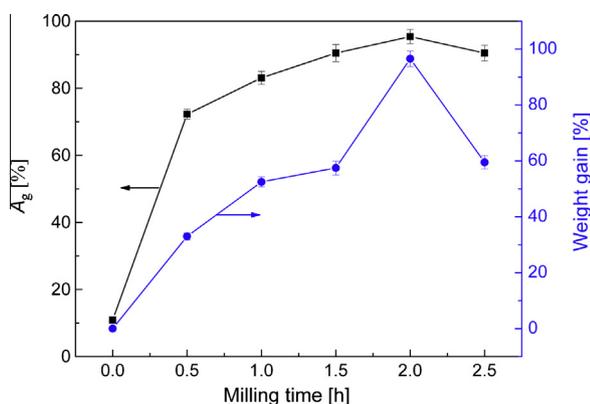


Fig. 1. Effect of milling time on weight gain and A_g of the modified CSRs. Means of three replicates \pm standard deviation.

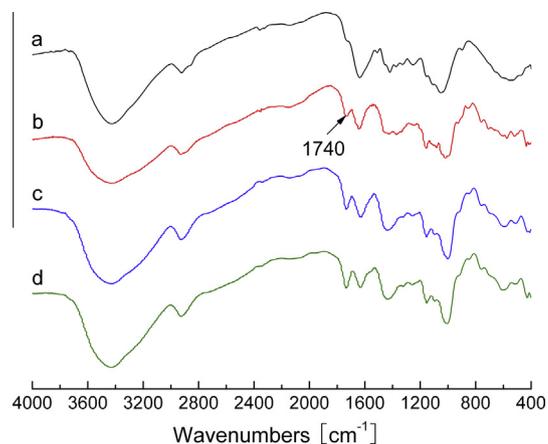


Fig. 2. FTIR spectra of (a) original CSR and the modified CSRs with different milling time: (b) 0.5 h, (c) 1.0 h, and (d) 2.0 h.

the introduction of acetyl. The absorption peak at about 3400 cm^{-1} is attributed to stretching vibration of hydroxyl groups, which was not obviously weaker after the process of MASPR. This may due to the presence of unreacted free and activated hydroxyl groups in modified CSRs, which could contribute to the increase in the strength of –OH absorption peak [1,20].

As can be seen from the XRD patterns of different CSR samples in Fig. 3, the diffraction intensities of modified CSRs are weaker than that of original CSR, and the broadening of diffraction peaks is also took place after the process of MASPR. These reveal that MA significantly disrupted the inter- and intramolecular hydrogen bonds in cellulose and caused the destruction of macromolecular chains and crystalline structure, the variation of crystallite size and an increase in amorphous phase [29]. When subjected to intense milling, the destruction of stable hydrogen bonds and crystal structure of cellulose could result in the generation of active and free hydroxy groups, which help to increase the reactivity of CSR. In addition, the introduction of acetyl also contributed to the amorphization of modified CSRs, leading to the decrease in diffraction intensity after acetylation. As a result, compared with the MA-pretreated CSRs without acetylation, the decrease in crystallinity of MASPR-modified CSRs was more remarkable after the same milling time [1].

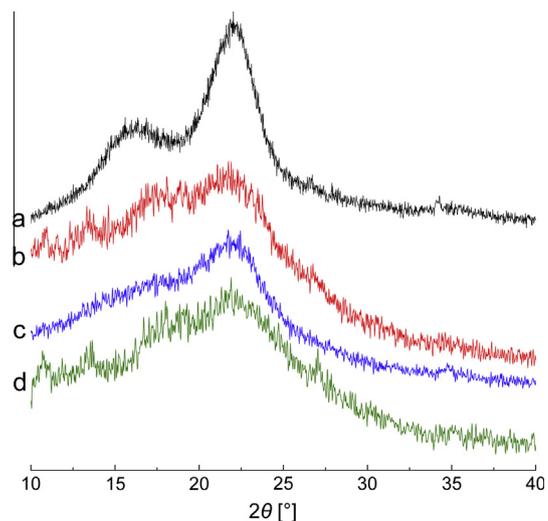


Fig. 3. XRD patterns of (a) original CSR and the modified CSRs with different milling time: (b) 0.5 h, (c) 1.0 h, and (d) 2.0 h.

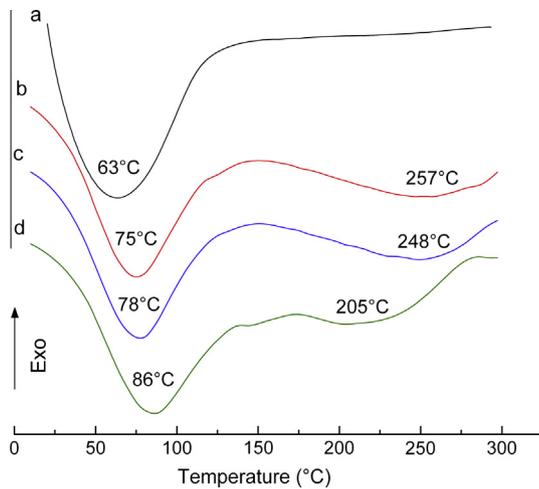


Fig. 4. DSC thermograms of (a) original CSR and the modified CSRs with different milling time: (b) 0.5 h, (c) 1.0 h, and (d) 2.0 h.

DSC curves of the samples are presented in Fig. 4, which shows the changes in thermal properties of the CSRs before and after modification. The DSC curve of original CSR shows an endotherm of dehydration in which the peak is centered at 63 °C. But this peak shifts to 75, 78 and 86 °C after milled for 0.5, 1.0 and 2.0 h, respectively. During the process of MASPR, the hydrogen bonds in CSR were destroyed to generate free hydroxyl groups, which easily reacted with acetic anhydride. The introduction of acetyl could prevent the formation of inter- and intramolecular hydrogen bonding in the components of CSR, but the hydrogen bonding between water and carbonyl groups of acetylated CSR or unreacted free hydroxyl groups was formed. So, the interaction between water and acetylated CSR was stronger as the increase of milling time and extent of acetylation, resulting in the increase of dehydration temperature [20,30]. In the DSC curves of the modified CSRs with the milling time of 0.5, 1.0 and 2.0 h, another endothermic peak can be observed at about 257, 248 and 205 °C, respectively, which belong to the melting of acetylated CSRs. But this peak cannot be found in the DSC curve of original CSR. Because of the strong hydrogen bonding and stable crystal structure, the original CSR cannot be melted but just decomposed under high temperature. After acetylation by MASPR, the introduction of acetyl and the destruction of hydrogen bonds could weaken the intermolecular force and improve the movement of molecular chain in CSR, resulting in the melting of acetylated CSRs, which were converted into thermoplastic materials. It can be also observed that the melting peaks are weak and wide, resulting from the complex components

and a large amount of amorphous phase in modified CSRs. The temperature for the melting of acetylated CSRs decreased with the increase in weight gain, which is consistent with the FTIR result.

3.2. Preparation and properties of APFC

After acetylation by MASPR, the modified CSRs can be used to directly produce the self-reinforced APFC by hot pressing, in which the thermoplastic acetylated parts serve as matrix and the non-acetylated parts as reinforcement. Most of the components in CSR could be acetylated to produce thermoplastic substances, leading to complete and effective utilization of this agro-industrial solid residue. The effect of milling time on the mechanical properties of APFC is illustrated in Fig. 5. Clearly, the tensile strength, elongation at break, flexural strength and flexural modulus of the thermally formed sheets showed significant relationships with the milling time, and longer milling time mainly resulted in better mechanical properties. It can be also observed that the optimum milling time was 2.0 h for the mechanical properties of APFC, which is consistent with that for the extent of acetylation and hydrophobicity of modified CSRs. With the milling time of 2.0 h, MA remarkably enhanced the reaction between acetic anhydride and CSR, and the modified CSR with the best thermoplasticity was obtained, leading to the superior mechanical properties of the APFC prepared by this modified CSR. Furthermore, during the process of MASPR, intense milling could destroy the CSR particles repeatedly, leading to the split and fracture of the compact fibre bundles, the decrease in particle size and ordered structure, and the increase in specific surface [1]. These changes in the structure of CSR particles induced by MA provided better dispersion and interfacial bonding between acetylated and non-acetylated parts, which help to improve the mechanical properties of APFC.

SEM images with different magnifications are provided in Fig. 6, which shows the morphological development of fractured surfaces of the APFC produced by the modified CSRs with different milling time. After the hot pressing process, the composites were successfully produced by the modified CSRs, and the fibre bundles are hardly observed, confirming that the modified CSRs possessed thermoplasticity and could be molded by hot press. It can be observed that the fractured surface of the APFC prepared with the 0.5 h modified CSR has obvious cracks and some fibre texture. In comparison, the typical lignocellulose texture completely disappeared and plastic deformation predominated in the compact fractured surface of the APFC prepared with the 2.0 h modified CSR, attributing to the complete destruction of fibre bundles by intense milling and the increase in extent of acetylation and thermoplasticity of modified CSR. Moreover, the APFC prepared by the 2.0 h modified CSR with highly acetylated CSR as thermoplastic matrix

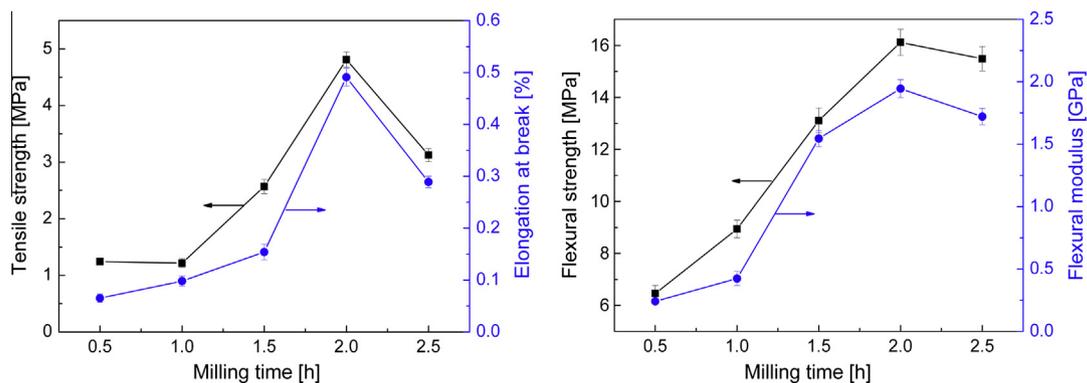


Fig. 5. Effect of milling time on the mechanical properties of APFC. Means of three replicates \pm standard deviation.

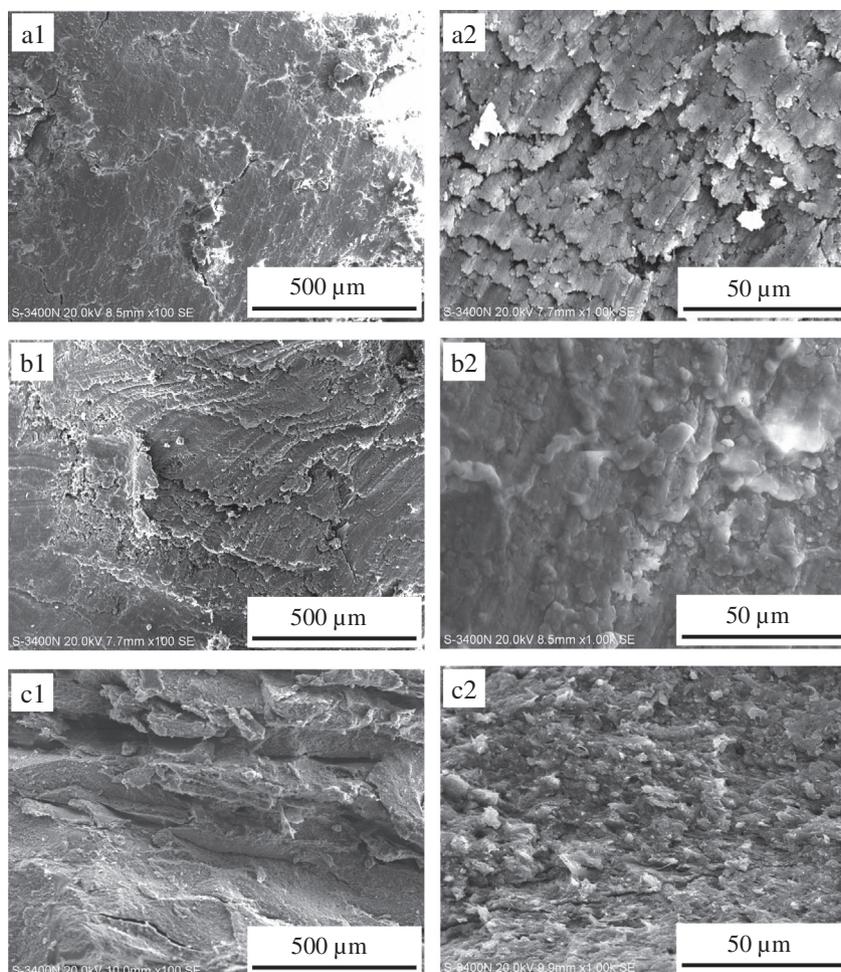


Fig. 6. SEM micrographs of fractured surfaces of the APFC prepared by the modified CSRs with different milling time: (a1, a2) 0.5 h, (b1, b2) 1.0 h, and (c1, c2) 2.0 h.

and completely destroyed CSR fibre as reinforcement possessed good interfacial adhesion, resulting in significant improvement of the mechanical properties.

4. Conclusion

It was shown that CSR has been directly acetylated by MASPR in a stirring ball mill and the self-reinforced APFC were successfully produced with modified CSRs by hot pressing technology. With combining MA and chemical modification in the same equipment, acetic anhydride could easily react with CSR because of the increase in reactivity of CSR, attributing to the breakage of hydrogen bonds, the destruction of crystalline structure and the improved contact between CSR and acetic anhydride induced by intense milling. In addition, it has been proved that acetylation was an effective method to convert agro-industrial plant fibres into thermally formable materials that could be processed using conventional techniques in plastics industry. Hopefully, this simple, efficient and green method can provide a broad range of potential applications in the effective utilization of agro-industrial lignocellulose biomass.

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