

The Effects of Crumb Rubber on the Properties and Microstructure of Modified Starch Degradable Composites

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Modified starch (MS) degraded composites were prepared *via* a molding method with starch as a substrate and a blending process with crumb rubber (CR) and added plasticizers such as glycerol, urea, and formamide. The mechanical properties and water absorbability of the MS degraded composites were measured. The functional group variations were confirmed by Fourier transform infrared spectroscopy (FT-IR), and the changes of the functional groups were investigated with a stereoscopic microscope to analyze the microstructure of the composites. The results indicated that the addition of CR substantially improved the performances of degradable composites. When the CR content was 50 wt% of the MS, the interfacial properties of the reinforced materials and the dispersing degree of the filler were improved. Compared with the composite without additive, the tensile strength and bending strength of the composites were increased by 107% and 49.5%, respectively. The minimum water absorption ratio was reduced by 78% compared with the composite without the additive.

Keywords: Crumb rubber; Modified starch; Mechanical properties; Water absorption properties; Microstructure

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INTRODUCTION

Starch degradable composites are prepared by blending starch, fibers, and their derivatives. The degradation products are non-toxic and harmless. However, due to the fact that the performance and degradability of degradable materials cannot be taken into account at the same time, it is difficult for existing degradable composites to have excellent performance. The process of changing the water absorption and improving the comprehensive mechanical properties of the composites is of great significance to expand the limitations of the application of the materials (Pant *et al.* 2011).

Therefore, a number of researchers have investigated the enhancement and modification of films produced with starch (Singh and Adedeji 2017). Starch-based composites have attracted attention from academic and industrial researchers (Visakh 2017). Starch granules absorb moisture in humid conditions because of their hydrophilic characteristics. Its moisture content has a significant influence on the morphology, thermal, and mechanical properties (Yu *et al.* 2013). The effect of glycerol (GE) as a plasticizer on the physical properties of carboxylated styrene-butadiene rubber/cassava starch blend films was investigated (Chantawee and Riyajan 2019).

Rubber samples may differ in both particle size and in the state of the surface, which largely determines their properties and possible applications (Zhorina *et al.* 2018). LeCorre

et al. (2012) evaluated the influence of the botanic origin of starch nanocrystals on the performances of non-vulcanized natural rubber nanocomposites. Senna *et al.* (2013) modified the natural rubber matrix using electron beam irradiation and then compounded the irradiated natural rubber with starch. There are few reports on the starch/other filler hybrids rubber composites.

Crumb rubber (CR) production is more favorable than reclaimed rubber production because it is less energy-intensive and is environmentally safe. The creation of new materials based on CR, especially its composites with starch, is a promising area of research in this field.

In this paper, we intend to provide a new facile route to make rubbers reinforced modified starch degradable composites, which may be suitable for industrial applications, such as children's toys and packaging. The mechanical properties, water absorption, and interfacial compatibility of modified starch degradable composites with different proportion of CR are better than those without addition, which provides theoretical reference for further research on the properties of modified starch degradable composites.

EXPERIMENTAL

Materials

Cassava starch (Guangdong, China), used in this work has a diameter of 250 microns; it was dried at 105 °C. Glycerol (Shanghai Zhengyi Chemical Reagent Co., Ltd., Shanghai, China), is an analytical pure (AR), colorless oily liquid. Formamide (Tianjin Institute of Photosynthetic Fine Chemistry, Tianjin, China), AR, is a colorless liquid. Chlorinated paraffin 70 (Shanghai Yousuo Chemical Technology Co., Ltd., Shanghai, China) has a melting range of 95 to 120 °C, the specific gravity is 1.60 to 1.70, the chlorine content is about 70%, and the industrial grade CR (Pingqiao District, Xinyang City, Henan Province, China) is a black powder. It contained spherical particles of rubber with an average diameter around 1 μm. The density of dry CR, was 1.4 g/cm⁻³, and it contained 98 % of cis-1,4-polyisoprene.

Composites Preparation

For modified starch, cassava starch was pre-mixed with 10 wt% of glycerol, 10 wt% of formamide and 20 wt% of chlorinated paraffin. Then the mixture was processed using a heated two-roll mill at a temperature of 160 °C for 15 min. A certain amount of modified starch and rubber were separately placed in a clean tray and dried with an electrothermal constant temperature blast dryer (DHC-9140A). The drying temperature was set to 90 °C, and the drying time was 4 h. The amount of rubber added was 0 wt%, 25 wt%, 50 wt%, and 75 wt% of the total mass of the starch. The raw materials of different proportions were mixed and stirred at high speed for 20 min. The self-made mold cavity was mixed and filled, placed in an XLB-400*400 plate vulcanizing machine (Shanghai Qicai Hydraulic Machinery Co., Ltd., Shanghai, China), and then pressed under approximately 8 MPa for 10 min. The temperature of molding was set to 180 °C, and the composites with a smooth surface were obtained by venting three times during molding. The die cavity size was 120 mm (long) × 100 mm (wide), and the thickness of the molding material was 6 to 10 mm (Fig. 1a). After cooling, the material was processed into the dimensions required for testing.

Methods

Mechanical property testing

The tensile strength of the composites was tested by a computer controlled electronic universal testing machine (SANS CMT6104; Meitesi Industry System Co., Ltd., Shanghai, China) according to GB/T 1040 (2006). The tensile speed was set to 2 mm/min. The bending strength of the composites was tested according to GB/T 9341 (2008), and the loading speed was set to 2 mm/min. The impact strength of the composites was tested using a domestic simple-supported beam impact testing machine (XJJ-5; Meitesi Industry System Co., Ltd., Shanghai, China) according to GB/T 1451 (2005). The size of the specimen was 100 mm x 10 mm x 10 mm (Fig.1b). All tests were conducted at room temperature, and the results were the averages of three replicates.

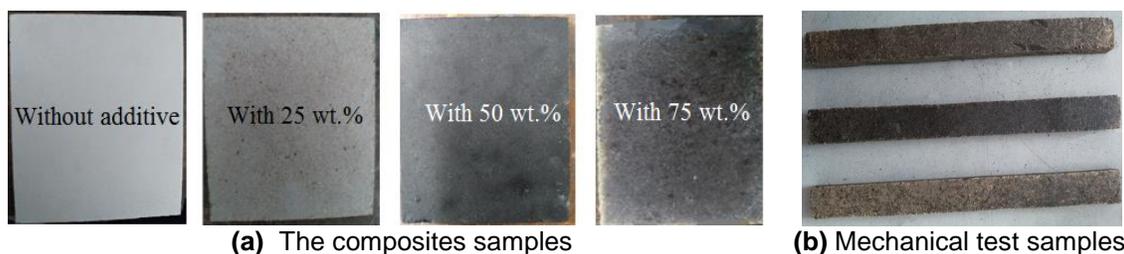


Fig. 1. Photograph images of the composites samples before test observed from digital camera

FT-IR analysis

The modified starch degradable composite powders were vacuum dried at 110 °C for 2 h. Then 0.002 g of each dried composite powder was evenly mixed with 0.2 g of KBr. The sample was prepared by pressing. The samples were scanned by the Nicolet iS-10 FT-IR (Thermo Fisher Scientific, Waltham, USA). The scanning wavenumber was recorded in a range from 4,000 to 400 cm^{-1} , and the resolution was 4 cm^{-1} with 16 scans.

Water absorption test

The water absorption of modified starch degradable composites in 24 h was determined according to the GB/T 1934.1 (2009) standard. The composites were dried at 103 ± 2 °C. After reaching a constant mass, the composites were immersed in a water tank at $\text{pH } 7 \pm 1$ at room temperature. The water surface was kept higher than the material surface, and the lower surface of the material did not contact the bottom of the tank. A distance of 10 mm was maintained between each material, which made the material expand freely. The material was soaked for 24 h (± 5 min) and then removed and dried with filter paper. The size of specimen was 50 mm x 50 mm x 10 mm. The water absorption (A ; %) was calculated using Eq. 1,

$$A (\%) = [(m - m_0) / m_0] * 100 \quad (1)$$

where m_0 and m denote the oven-dried weight (g) and weight (g) at a given immersion time (t), respectively.

Confocal microscopy

The microstructure of cross-sections of modified starch degradable composites was observed by LEXT OLS 4100 laser confocal microscopy (Olympus Ltd., Shanghai, China). The size of specimens was 10 mm x 2 mm.

RESULTS AND DISCUSSION

Mechanical Properties of Modified Starch Degradable Composites

Table 1 shows the mechanical properties of modified starch degradable composites with different proportions of crumb rubber (CR). The mechanical properties of modified starch degradable composites were improved by adding an appropriate amount of CR. With the increased CR content, the tensile strength and impact strength of modified starch degradable composites first increased but then decreased. The impact strength of the composites increased continuously with increasing CR up to a level of 50%. The maximum tensile strength and bending strength of the composites with 50% CR were 2.41 MPa and 3.24 MPa, respectively, which were higher than those of the composites without the additive. The tensile strength (1.16 MPa) and bending strength (2.17 MPa) of the composites were increased by 107% and 49.5%, respectively relative to the unfilled starch. These increases in tensile and flexural strength may be attributed to the transformation of the modified starch particles in composites from a crystalline structure into an amorphous structure. This structural transformation makes the rubber disperse well in modified starch and enhances its interaction with modified starch, which also improves the mechanical properties of composites (Mondragon *et al.* 2009). Also, the addition of chlorinated paraffin, glycerin, and formamide enhanced the bonding strength between CR and starch. Rubber exhibits polar groups at a certain heating temperature, and elasticity properties of rubber improve the sample's impact strength (Yokesahachart and Yoksan 2011). The polar covalent bonds in the molecular structure of the additives were beneficial to the uniform diffusion of rubber in modified starch during hot pressing, which improved the composite materials (Pichaiyut *et al.* 2016). The internal cohesion, tensile strength, and flexural strength of the composites with rubber were considerably improved. However, when the content of rubber is too high, local agglomeration of the rubber will occur in the composites. The poor interfacial compatibility between CR and modified starch leads to the decrease of the strength of the composites (Bootklad and Kaewtatip 2007).

Table 1. Mechanical Properties of Modified Starch Degradable Composites with Different Proportions of Crumb Rubber

Mechanical Properties	Without additive	With 25 wt%	With 50 wt%	With 75 wt%
Tensile strength (MPa)	1.17	1.18	2.41	0.67
Bending strength (MPa)	2.17	2.42	3.24	1.20
Impact strength / (kJ·m ⁻²)	0.56	0.66	1.27	2.40

FT-IR Spectra of Modified Starch Degradable Composites

After starch is chemically modified, new chemical groups form chemical bonds with the hydroxyl groups in the starch (Shen *et al.* 2016). These chemical bonds have specific absorption peaks for continuous wavelength infrared light (Swain *et al.* 2017). Therefore, infrared spectroscopy is an important way to detect the changes in the chemical structure of polymers.

Because there are many hydroxyl groups in a starch glucose unit, the hydroxyl groups had free and associative peaks at 3600 cm⁻¹ and 3200 cm⁻¹. The free peaks were sharp, and the associative peaks were broad; as such, the infrared spectrum of starch showed a wide associative peak from 3200 to 3600 cm⁻¹ and a stretching vibration peak at

2930 cm^{-1} (Dang and Yoksan 2015). There was a C-O bond stretching vibration peak in the chelating aldehyde group at 1647 cm^{-1} . There was an asymmetric C-O-C stretching vibration peak, secondary alcohol C-O stretching vibration peak, primary alcohol C-O stretching vibration peak, and pyran ring vibration peak at 1154 cm^{-1} and 1022 cm^{-1} (Goriparthi *et al.* 2012). Rubber contains trace organic amino acid structures, so there were C=O stretching vibration peaks at 1743 cm^{-1} and characteristic peaks of amide I and II bands at 1640 cm^{-1} and 1540 cm^{-1} (Swain *et al.* 2017). Figure 2 shows that the absorption peaks of FT-IR spectra were enhanced and weakened when CR was added to the composites. The FT-IR spectra of composites showed both CR and starch peaks, which indicates that there was a close bond between modified starch and natural rubber. The hydroxyl peaks of the composites with CR changed at 3600 cm^{-1} and 3200 cm^{-1} . This change was due to the large degree of substitution of CR, which could replace a large number of hydroxyl groups and destroy the formation of hydrogen bonds. The hydroxyl peaks changed, and the peak area became smaller in the following order: 50 wt% > 25 wt% > 75 wt%. These results indicate that the composites with 50 wt% modified starch have good interfacial compatibility, which is consistent with the results of the mechanical properties test.

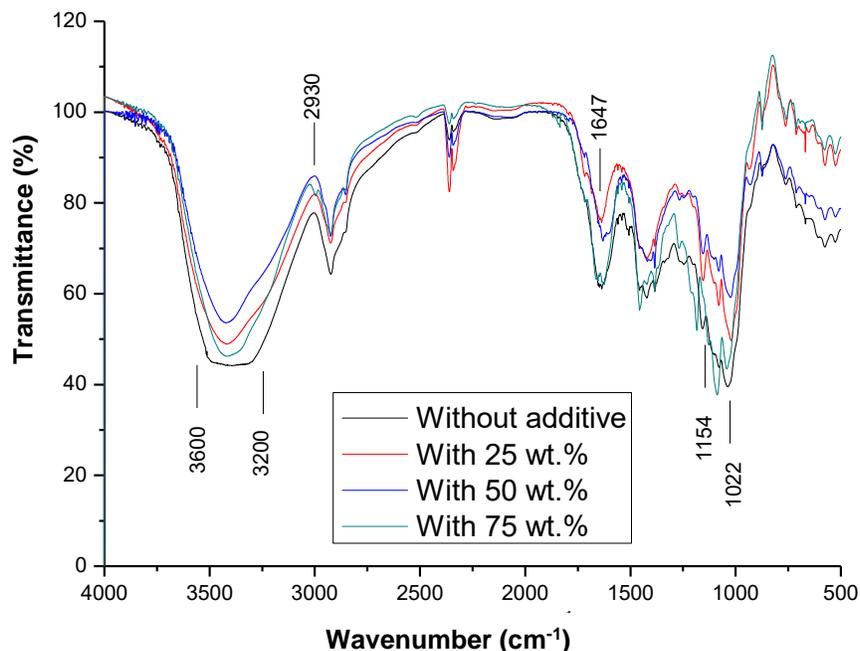


Fig. 2. FT-IR spectra of modified starch degradable composites

The Effect of Different CR Contents on the Water Absorption of Composites

The results from the 24 h interval water absorptions showed that the water absorption values of MS filled with CR were greatly reduced compared with the samples without the CR addition (Fig. 3). The water absorption of the composites with 50 wt% CR addition was 78% lower than that of the composites without the addition (Smith *et al.* 1997). In the process of molding, starch was gelatinized and treated at a high temperature, which resulted in unstable chemical bonds in the starch molecules and was conducive to breaking. With the breaking of these chemical bonds, the crystalline region in the starch granules changed from the original closely arranged state to a loose state. When this change occurs, the loose state is conducive to the entry of water molecules, and thus has a very

strong water absorption (Khanna and Tester 2006). Therefore, the water absorptivity of the samples without additive reached 274.6% in 24 h. With the addition of different proportions of CR, the compatibility of the two phases in glycerol and chlorinated paraffin plasticized composites may be improved. This improvement makes the interaction force between the components of glycerol plasticized composites maximize and effectively prevents water molecules from entering the composites. In addition, the water absorption of the composites is mainly provided by starch. The addition of natural rubber reduces the proportion of starch content, and the water absorption decreases greatly (Morrison *et al.* 1993). The composite with 50 wt% water absorption rate is the smallest, which may be due to the better interfacial compatibility of the composite and the closer bonding between the internal molecules of the material, which can effectively hinder the diffusion of water molecules and lead to the best waterproof performance (Tester *et al.* 2004).

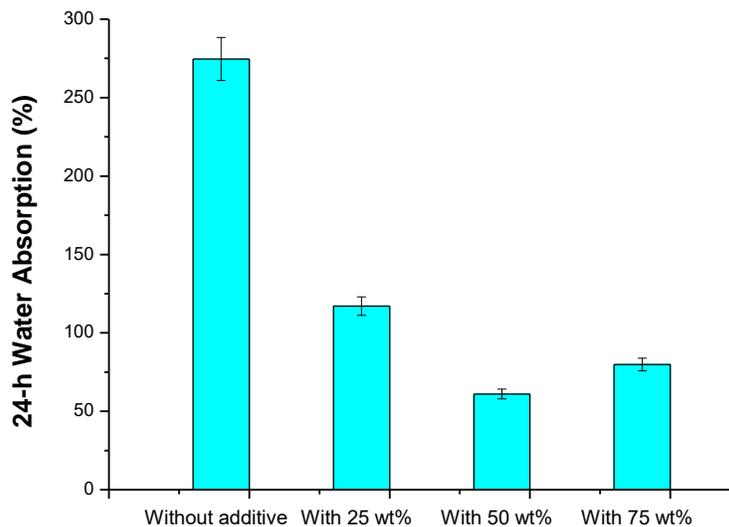


Fig. 3. Water absorption rate of modified starch degradable composites

Microstructure of Modified Starch Degradable Composites

Figure 4 shows the cross-sectional structure of modified starch degradable composites with different CR content. Figure 4(a) shows that the modified starch degradable composites without the additive had large particle size and a smooth cross-sectional structure. The fiber structure was distributed in layers, and the lamellar structure can easily absorb water. Figure 4(b) illustrates that the cross-sectional microstructures of the composites with 25 wt% CR form a two-phase interface compared to the composites without the additive, which indicates that the dispersibility and compatibility of the CR in the composites were not good (Rajisha *et al.* 2014). Figure 4(c) is the cross-sectional microstructure of composite material with 50 wt%. As shown, the particle size of modified starch decreased, and the interface between modified starch and rubber became blurred. These changes are due to the surface polar hydroxyl groups of starch being consumed and the polarity of particles being reduced after modification, which improved the dispersion of CR, improved the compatibility, and produced strong interfacial bonding (Coativy *et al.* 2015). The finer the particles were, the better the mechanical properties were as well. Figure 4(d) shows that the high content of rubber leads to a larger proportion of the rubber agglomerating. In addition, the total contact area between starch and rubber was greatly reduced and cannot be fully combined, which lead to an optimal impact resistance.

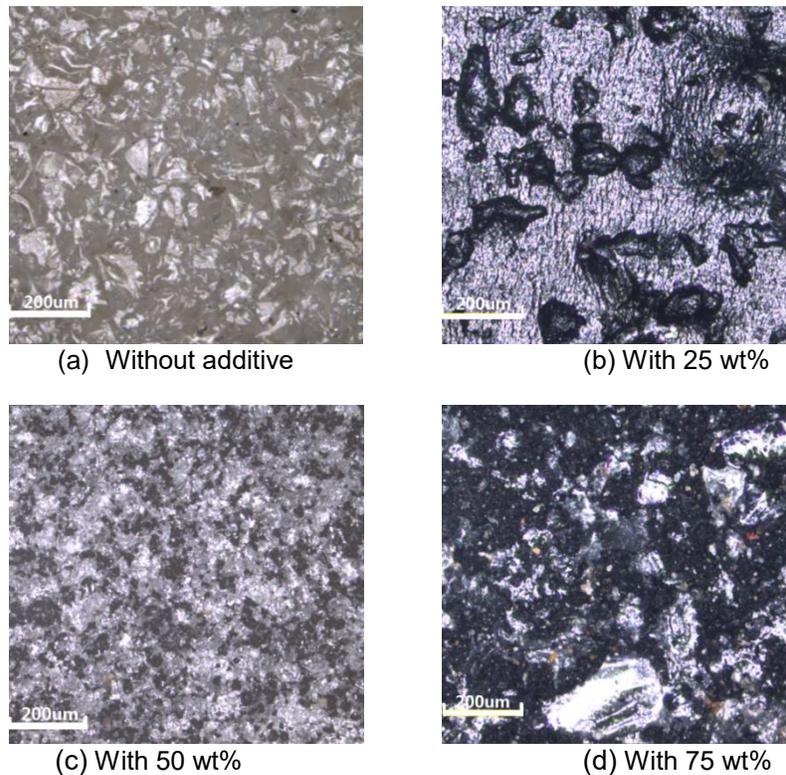


Fig. 4. The microstructure of composites filled with CR and (a) without additive, (b) with 25 wt%, (c) with 50 wt%, and (d) with 75 wt%

CONCLUSIONS

The modified starch composites containing varying contents of crumb rubber (CR) was successfully prepared. This study revealed that the incorporation of CR helped to overcome the brittleness of the blend and improved the flexibility of the starch composites. The mechanical properties of modified starch degradable composites were improved by adding an appropriate amount of CR. The flexural strength of the composites increased continuously with increasing CR up to a level of 50%. The absorption peaks of FT-IR spectra were enhanced and weakened when CR was added to the composites. The water absorption of the composites with 50 wt% CR addition is 78% lower than that of the composites without the additive. The particle size of modified starch decreased, which improved the dispersion of CR, improved the compatibility, and produced strong interfacial bonding.

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