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A strategy to prepare high performance starch/rubber composites: In situ modification during latex compounding process

You-Ping Wu [a,*], Qing Qi [a], Gui-Hua Liang [a], Li-Qun Zhang [a,b,*]

[a] *The Key Laboratory of Beijing City for Preparation and Processing of Novel Polymer Materials,*
Beijing University of Chemical Technology, Beijing 100029, China
[b] *The Key Laboratory for Nano Materials, Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, China*

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Abstract

Starch/styrene butadiene rubber (SBR) composites were prepared by directly mixing and co-coagulating rubber latex and starch paste, which was in situ modified by resorcinol-formaldehyde(RF) and *N*-β(aminoethyl)-γ-aminopropyl trimethoxy silane (KH792). Modified starch/SBR composite exhibited excellent comprehensive properties relative to those of the corresponding starch/SBR composite without modification. According to Environmental Scanning Electron Microscopy (ESEM), tensile fractured surfaces of various starch/SBR composites demonstrated better interfacial adhesion achieved by the modification. DMTA showed that starch/SBR composites had only one glass transition of SBR and it shifted to the lower temperature compared to that of pure SBR. The glass transition of modified starch/SBR composites shifted to the higher temperature relative to that of the unmodified one due to the improved interfacial adhesion.
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1. Introduction

Starch, obtained from renewable resources, has many advantages, such as low cost, abundant supply, and environmental amity, and it is widely used in food, paper-making, fine chemicals, packing material industry, etc. Ways to find out its other potential applications on a big scale have attracted much interest. To reduce dependence on synthetic polymers made from oil, much efforts have been made on developing starch-based materials, for example, *starch biocomposites* (Lu, Weng, & Cao, 2005; Wu, 2005), starch-based thermoplastic through blending starch and synthetic polymer, to replace synthetic polymer materials or their composites (Carvalho, Job, Alves, Curvelo, & Gandini, 2003; Chandra & Rustgi, 1997; Rouilly, Rigal, & Gilbert, 2004; Shogren, Lawton, Tiefenbacher, & Chen, 1998; Vaidya, Bhattacharya, & Zhang, 1995; Yang, Bhattacharya, & Vaidya, 1996). This area has become more and more important and promising, since the use of starch is desirable as an environmental friendly alternative to the present use of petroleum-based plastics. More recently, in the patent literature (USP, 1997, 2001, 2002, 2003), starch has been creatively used as a filler in tyre compounds in order to lower the rolling resistance and reduce the use of carbon black made from natural gas or oil resource. Goodyear Tyre Co. has utilized a new starch-based material called Bio-TRED to partially replace the conventional carbon black and silica in producing GT3 tyres to reduce the tyre weight and the rolling resistance, and simultaneously decrease the energy consumption in the production processes; the Ford company in Europe expects to use the GT3 on its fuel-stingy version of the Ford Fiesta. The use of starch in tyre compounds probably opens a new application area for starch—starch-filled rubber composites (Henri & Clarke, 2005). With anticipated low cost, light weight and good comprehensive performance, starch/rubber composites will be applied not only in rubber tyres, but also in other kinds of rubber products. However, starch particles are about 5–20 μm in the non-reinforcing filler range for rubber, and with many hydroxyl groups on its surface, starch is extremely polar, leading to low interaction with non-polar rubbers, such as styrene–butadiene rubber (SBR) and natural rubber (NR). This could not only result in the advantage of low hysteresis in tires, but could also generate the disadvantage of

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* Corresponding authors. Fax: +86 10 64433964.
E-mail addresses: wu_youping3@sohu.com (Y.-P. Wu), zhangliqunghp@yahoo.com (L.-Q. Zhang).

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low mechanical properties and consequently prevent starch/rubber composites from wide applications. To improve the mechanical properties, first, the dispersion size of starch in rubber should be evidently reduced down to the nanometer scale (Zhang & Jia, 2004); second, the interfacial interaction between starch and rubber matrix should be enhanced.

In order to achieve the fine dispersion of starch in rubber matrix, we developed a novel dispersion technique, compounding rubber latex with starch paste and then co-coagulating the mixture (CN, 2003; Wu, Ji, Qi, Wang, & Zhang, 2004), namely LCM (latex compounding method), which is (originated) derived from the fact that water is a very good chemical medium to dissociate the hydrogen-bonds of starch and most rubbers have a latex form. By LCM, the size of starch granules in rubber matrixes was greatly reduced to smaller than 1 μm, and the starch/rubber composites exhibited better mechanical properties relative to those (the corresponding starch/rubber composites) prepared by direct blending (Wu et al., 2004).

Although the dispersion of starch in rubber matrix is quite fine by LCM, due to the lower interfacial strength, the mechanical properties of starch/rubber composite are relatively low (Wu et al., 2004) compared with those of silica or carbon black reinforced rubber. According to the literature (Chandra & Rustgi, 1997; Vaidya et al., 1995; Yang et al., 1996), to improve the compatibility and interfacial strength of the blends of starch and polymers, polymers having functional groups, such as maleic anhydride, were usually selected to prepare the blends of starch and synthetic polymers by melt compounding. However, with rubber materials, such a method is not practical owing to the absence of maleic-grafted rubber and the strong negative influence of acid groups of maleic anhydride on the vulcanization of rubber. In addition, although the silane coupling agent is commonly used to strengthen the interfacial interaction between filler with hydroxyl groups, e.g. silica and elastomers in rubber industry, we found that the alkoxy groups of silane coupling agents did not seem to be reactive enough towards the starch and the cause needs further study. In the 1970s, Buchanan et al. (Buchanan, Doane, Russell, & Kwolek, 1975; Buchanan, Katz, Russell, & Rist, 1971; Buchanan, Kwolek, Katz, & Russell, 1971; Buchanan, 1974) tried to use RF to modify starch xanthate/rubber composites to improve interfacial strength, and the improvement was not as high as expected.

In this study, a new strategy, in situ modified starch with the combination of resorcinol-formaldehyde (RF) and *N*-β(aminoethyl)-γ-aminopropyl trimethoxy silane ($NH_2CH_2CH_2$-$NHCH_2CH_2CHSi(OCH_3)_3$, KH792) during latex compounding process, is developed to strengthen the interfacial interaction. This design is based on the following two aspects: (1) RF can crosslink starch (Kerr, 1950) and rubbers with unsaturated double bonds (Greth, 1941) in the meantime. Due to directly mixing RF solution with starch paste in the aqueous phase, crosslinking reaction between RF and the starch should occur easily. During vulcanization, RF-modified starch particles are expected to react with rubber molecules to improve adhesion. (2) Amino groups of KH792 can easily react with RF in aqueous solution and they are also chemically reactive during vulcanization (Hofman, 1967). In this report, the interfacial structure and mechanical properties of starch/SBR composites modified with RF and KH792 were investigated. It was found that modified composites exhibited excellent comprehensive properties relative to those of the corresponding starch/SBR composite without modification. The tensile strength of starch/SBR composite containing 10 phr starch with in situ modification of RF and KH792 reached up to 16.4 MPa, improved by about six times. We expect that this work should not only promote the research of developing starch into reinforcing filler for rubber, but also contribute to obtaining new insights into interface between filler and rubber.

2. Experimental part

2.1. Materials

SBR latex (St 23%) was from Qilu Petrochemical Company (China); corn starch (100% amylopectin, 12 wt.% moisture content) was from Changchun Dacheng Special Corn Modified Starch Development Co. Ltd (China), and the particle size is in the range of 5–20 μm (see Fig. 1). Other compounding agents were purchased in the market.

2.2. Perparation of in situ modified starch paste and starch/SBR composites

About 2% starch aqueous suspension was stirred at 95 °C in water bath for 0.5 h until the solution became transparent and the starch paste was obtained. Then the base-catalyzed resorcinol and formaldehyde (RF) solution (pH 9) with a mole ratio of formaldehyde to resorcinol of 3:1 was prepared and added into the starch paste instantly. The mixture was stirred at 95 °C in water bath for another 0.5 h and the RF-modified starch paste was obtained.

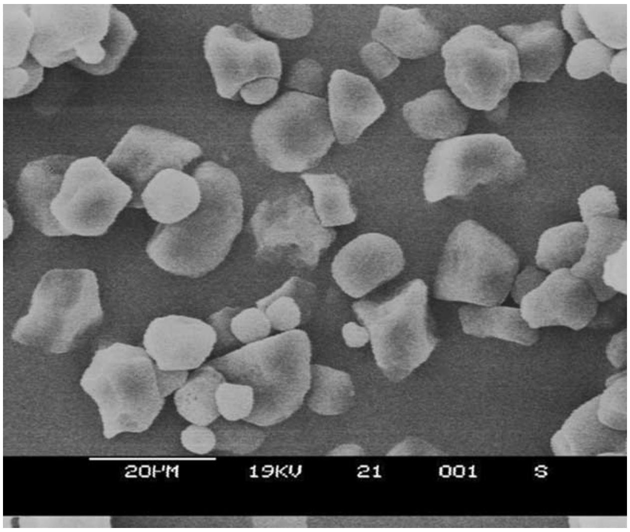

Fig. 1. SEM micrograph of starch particles.

Table 1
Compositions of starch/SBR composites (phr/100 phr rubber)

Samples	No modifier	RF	KH792	RF + KH792
Starch	10	10	10	10
Zinc oxide	3	3	3	3
Stearic acid	1.0	1.0	1.0	1.0
Accelerator CZ	1.2	1.2	1.2	1.2
Sulfur	1.8	1.8	1.8	1.8
Antioxidant 4010NA	1.0	1.0	1.0	1.0
Antioxidant RD	1.0	1.0	1.0	1.0
RF	–	1.2	–	1.2
KH792	–	–	3.0	3.0

This hot RF-modified starch paste was mixed with SBR latex and KH792 and strongly stirred for 0.5 h at room temperature, and then about 1.5 wt.% calcium chloride aqueous solution was used to co-coagulate the rubber latex and starch paste. After this the coagulum was washed several times with water and dried in an oven at 80 °C for 18 h till about 10% moisture content was reached, and then the starch/rubber blend was prepared.

The vulcanizing ingredients and other additives were incorporated into the modified starch/rubber blends with a two-roll mill at 50–60 °C by a standard procedure and the compositions are shown in Table 1. The compounds were vulcanized for t_{90} at 150 °C. The vulcanized starch/rubber compounds are designated as the starch/rubber composites.

2.3. Characterization

Scan Electron Microscopy (SEM) Morphologies were taken from the tensile fractured surface of composites using XL-30 ESEM of FEI Corp. Tan δ, as a function of the temperature of either pure SBR or starch/SBR composites, was measured on the Dynamic Mechanical Thermal Analyzer, DMTA V of Rheometrics Science Corp. in the tension mode, 1 Hz and 3 °C/min.

2.4. Mechanical tests

Mechanical tests were performed on the Electronic Tensile Machine CMT4104 according to ASTM.

3. Results and discussion

3.1. Morphology

To investigate the effect of modifiers on the dispersion of starch and interface between starch and rubber matrix, ESEM micrographs of the tensile-fractured surface of starch/SBR composites without modifiers, with RF, or with RF and KH792 are shown in Fig. 2. The surface of the composite without modifiers is relatively smooth, and some apparent craters of starch particles are left on the fracture surface of composites as seen in Fig. 2(a), which strongly suggests that the interfacial adhesion between starch and rubber is relatively weak. In Fig. 2(b), with RF modification, the surface is very rough, suggesting that the interfacial strength is improved. In Fig. 2(c), with modification of RF and KH792, no holes of starch particles are left on the surface, and starch particles are embedded in the matrix. These results demonstrate that in-situ modifiers increased the interfacial strength of starch and rubber largely.

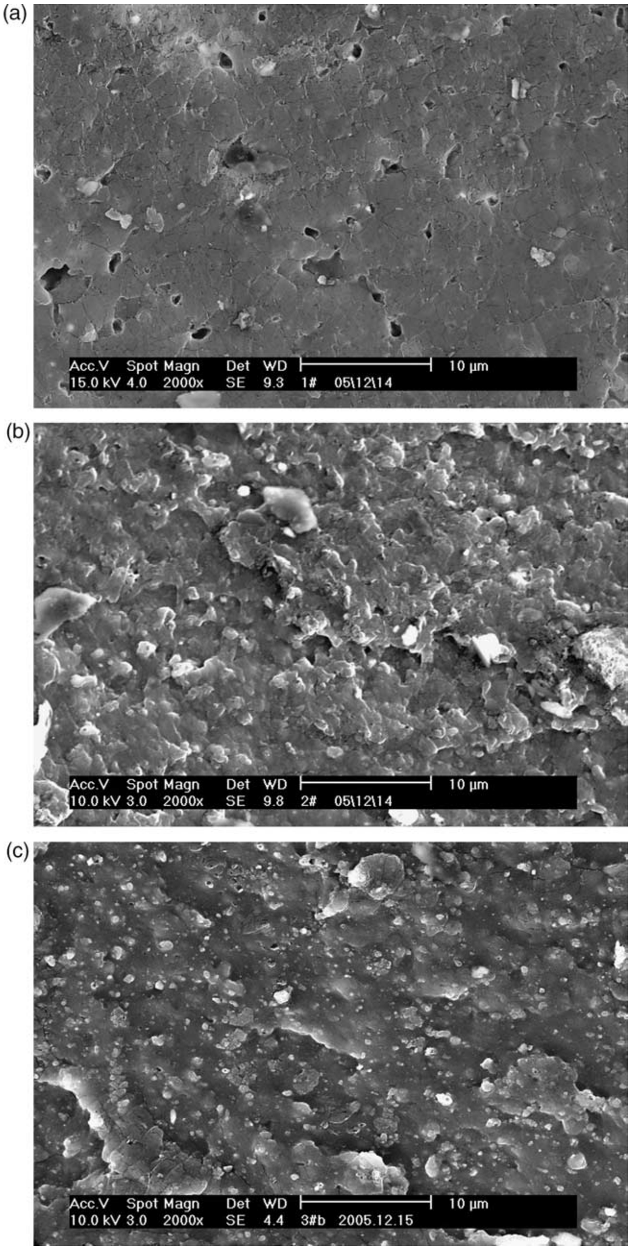

Fig. 2. SEM micrographs of the tensile fractured surface of starch/SBR composites: (a) no modifier; (b) modification with RF; (c) modification with RF and KH792.

3.2. The mechanical properties of SBR/starch composites

The mechanical properties of starch/SBR composites without or with modifiers are shown in Table 2 and the

Table 2
Effect of different loading of RF on mechanical properties of starch/SBR composites

Samples	No modifier	RF	KH792	RF+KH792
Shore A hardness	50	57	52	55
Stress at 300%, MPa	1.4	2.6	2.1	2.9
Tensile strength, MPa	2.7	11.1	4.6	16.4
Elongation at break, %	581	748	575	768
Tear strength, kN/m	13.4	24.1	19.4	27.0

corresponding stress–strain curves are presented in Fig. 3. Compared with starch/SBR without modifiers, the starch/SBR composites modified by RF, KH792, or RF and KH792 exhibited higher hardness, stress at 300%, tensile strength and tear strength as expected. In addition, the order of stress at 300%, tensile strength and tear strength is RF and KH792 > RF > KH792. That is, RF is more effective than KH792 in improving properties of starch/SBR composite, and this should be attributed to the reason that RF could crosslink starch and SBR simultaneously, and thus improve adhesion between starch and SBR, whereas the hydrogen bonds between KH792 and starch might only improve interfacial strength to some extent. It is worthy to note that insitu modification using RF together with KH792 is the best method and it can enhance the tensile strength of composite by six times, and the tensile strength reaches up to 16.4 MPa, even higher than that of N330 carbon black reinforced SBR at 10 phr level (5.6 MPa) (Zhang, Wang, Wang, Sui, & Yu, 2000), strongly indicating that starch possesses the potential as reinforcing filler for rubber. This exceptional reinforcing effect of starch modified with RF and KH792 should be assumed to result from excellent interfacial strength between starch and rubber. The possible explanation is as follows: in the base-catalyzed resorcinol and formaldehyde solution (pH 9), the mole amount of formaldehyde is three times that of resorcinol, and RF and excess formaldehyde could react with the hydroxyl groups of starch to crosslink starch paste as expected. In addition, part of excess formaldehyde may react with the primary amino groups of KH792 and then react with RF-modified starch in aqueous phase during the latex compounding process. During the vulcanization process, RF and part of amino groups of KH792 could participate in the vulcanizing reaction to crosslink SBR. Both RF and KH792 act as the bridge function between SBR and starch. Due to the complexity of reactions, the exact reactions among RF, KH792 and starch need to be investigated further.

3.3. DMTA measurements

To further investigate the interfacial interactions in starch/rubber composite with modification of RF and KH792, DMTA measurements of pure SBR and starch/SBR composite with insitu modification of RF and KH792 were performed, and the tan δ spectra are shown in Fig. 4. From Fig. 4, it is seen that starch/SBR composite with 10 phr starch displays a single glass transition, corresponding to SBR. According to literature (de Graaf, Karman, & Janssen, 2003), the glass transition temperature of waxy maize (99% amylopectin) is about 158 °C. Since water is an excellent plasticizer for starch, the glass transition of starch is known to vary considerably with the amount of water (Bindzus et al., 2002). In the starch/SBR composite, the amount of water in starch is about 10%, and in the meantime, based on the fact that the starch exhibited excellent reinforcement for SBR, glass transition of starch should be over 30 °C at least. However, starch/SBR composite (in Fig. 4) with 10 phr starch does not show any glass transition of starch in the temperature range of 0–150 °C. This phenomenon is not expected because of phase separation observed in the above ESEM photographs. One reason may be due to the low concentration of starch (only 10 phr starch). To testify this hypothesis, starch/SBR composite containing 30 phr starch was also selected for DMTA measurement. The tan δ curve is also shown in Fig. 4. Surprisingly, for starch/SBR composite containing 30 phr starch, no glass transition of starch appears between 0 and 150 °C, either. This observation is totally different from that of starch/EPMA (ethylene-propylene-*g*-maleic anhydride) blends, which revealed two distinct glass transitions (Vaidya et al., 1995).

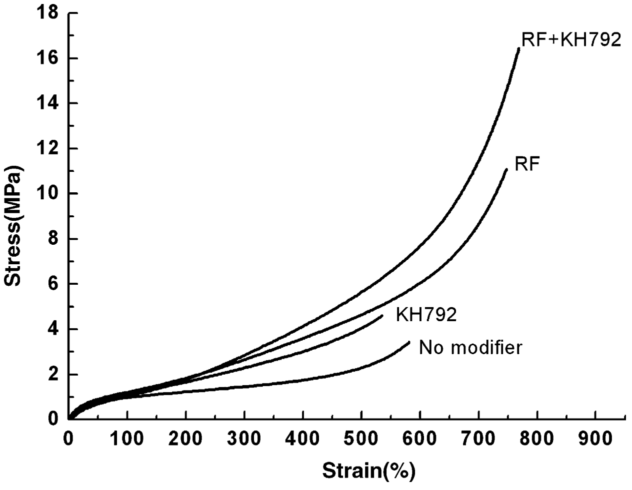

Fig. 3. Stress–strain curves of starch/SBR composites with different modifiers.

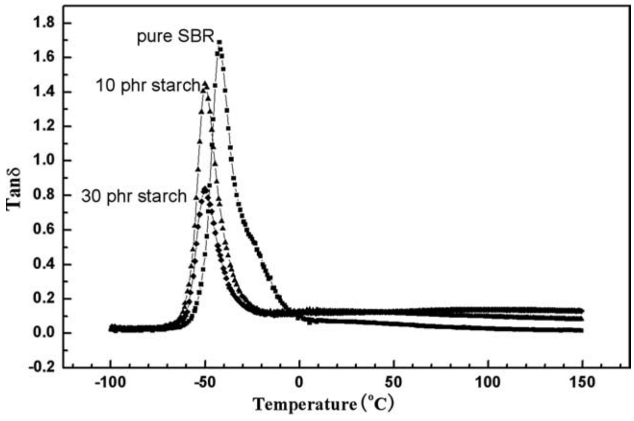

Fig. 4. Relationships between tan δ and temperature of pure SBR and starch/SBR composites modified by RF and KH792 tested by DMTA: a—pure SBR; b—10 phr starch; c—30 phr starch.

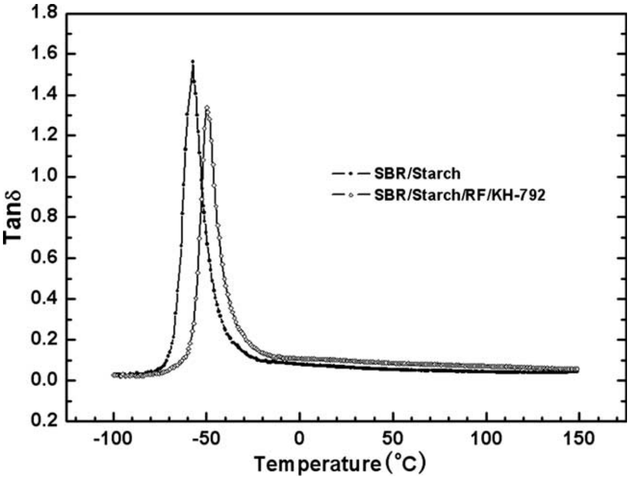

Fig. 5. tan δ of starch/SBR composites containing 10 phr starch as the function of temperature: a—without modification; b—modified by RF and KH792.

One possible explanation is that the size of starch granules is too small to exhibit obvious glass transition. In starch/EPMA blends, the size of starch granules ranged from 5 to 20 μm, whereas the starch granules in starch/SBR composites were less than 0.1 μm. A detailed study is necessary to evaluate this explanation.

Another important phenomenon worthy to be discussed is that the glass transition in starch/SBR composites, corresponding to SBR, shifts to the lower temperature, compared to that of pure SBR. Since starch is the reinforcing filler in this system, the decrease in SBR glass transition should not originate from the plasticization of starch. A similar observation was reported for bis(triethoxysilylpropyl) tetrasulfide (TESPT)-treated silica-filled SBR system (Arrighi, McEwen, Qian, & Serrano Prieto, 2003). This behavior may have the same origin as the shift of the glass transition temperature of a polymer film. The glass transition temperature of a polymer film depends on its thickness and can either decrease or increase depending on the nature of the interaction between the film and its substrate (Berriot, Montes, Lequeux, Long, & Sotta, 2002). To testify the influence of interfacial interaction, we carried out DMTA measurements of both modified starch/SBR composite containing 10 phr starch and the unmodified one, and the results are presented in Fig. 5. Relative to the starch/SBR composite without modification, the glass transition of starch/SBR composite modified by RF and KH-792 together shifts to the higher temperature because of the better interfacial adhesion. This is consistent with the results of ESEM observation and mechanical properties, as discussed above.

4. Conclusions

RF and KH792 in situ modification can efficiently improve the interfacial strength between starch and SBR in starch/SBR compounds prepared by LCM. After modification, the mechanical properties of starch/SBR composite were greatly improved. This method to improve interfacial strength should also be suitable for other starch/rubber composites, such as starch/NR and starch/NBR prepared by LCM. The glass transition of SBR in starch/SBR composites shifted to lower temperature, and the glass transition of starch did not appear.

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