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Modification of starch for high performance elastomer

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Abstract

Because conventional filler carbon black (CB), used for elastomer reinforcement, is wholly dependent on the non-renewable petroleum resource, a novel starch modification for filler-reinforced elastomer is developed using two types of modifiers, i.e. resorcinol–formaldehyde (RF) and a silane surfactant (S). Originally used as a curing agent for rubber vulcanization, the RF is here designed to interact with starch and rubber, and thus improve the interface. The S is expected to improve the dispersion of starch particles and enhance the compatibility. The RF achieved much higher reinforcement than the S. When the starch was co-modified by both, the mechanical property improvement of styrene–butadiene rubber (SBR) was superior to that reinforced by CB. Modification mechanism was explained as that (a) the RF forms oligomer, and (b) the oligomer then undergoes condensation/crosslinking, which combines starch particles and SBR macromolecules firmly. This mechanism was subsequently proved by a suspension experiment, which refers to the experiment that measures the compatibility of modified starches with SBR in solutions of dissolved compounded SBR. Transmission electron microscopy shows that most of the modified starch particles are dispersed on nano-scale; scanning electron microscopy indicates fine morphology achieved by the modification.

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Keywords: Modification; Starch; Styrene–butadiene rubber

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1. Introduction

High performance elastomer means a type of elastomers, which are characteristic of high tensile strength, high tear strength and low abrasion. Carbon black (CB) remains the predominant filler for high performance elastomer; it reinforces elastomer significantly, but pollutes environment and depends on the non-renewable source of petroleum and natural gas. The other fillers have thus been extensively studied, such as starch [1–3], silica [4–7], clay [8–13], etc. Silica is efficient for reinforcing silicon rubber, but not for the other elastomers. Clay is an environmentally friendly filler; our series of research shows that, if modified and compounded properly, clay can reinforce rubber as efficiently as CB [8–13]. Starch is of great potential due to its limitless source and friendly environmental processing, but unfortunately, previous research indicates an unsatisfied reinforcement by starch [14–19]. The pioneering research of rubber/starch compound started in the late 1960s [14]. Buchanan prepared styrene–butadiene rubber (SBR) composites by a co-precipitation procedure, but the mechanical property improvement was not ideal: the tensile strength only improved from 2.6 to 6.3 MPa with 10 phr of zinc starch. Very recent research shows the improvement depends on the starch particle size in situ formed during coagulation as well as the degree of starch crystallization [3]. Based on our knowledge and experience on the clay modification for high performance elastomer [8–13], a hypothesis is made in this research that starch will be an ideal filler if modified properly; a benchmark well known in rubber field is that a filler would be efficient if it achieves similar reinforcement to CB.

In general, there are three approaches to prepare rubber/starch compounds. The first is to modify a polymer matrix and then mix starch with the modified matrix [1,20,21]; this method is relatively expensive, but it can obtain good comprehensive properties; it is often used for degradation purpose [20,21]. The second approach is to use compatibilizers, which leads to finer morphology and may produce higher mechanical properties [2,22,23]; without

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involving any modification of matrix or starch, this method is simple, but depends on the availability and efficiency of the compatibilizers. The last method is to modify starch [14–19,24] and mix the modified starch with matrix; it is particularly useful for reinforcing polymers, as the starch modification can be tailor-made according to various matrixes and purposes.

As hydrophilic starch is not compatible with hydrophobic SBR, latex compounding is a simple process to prepare SBR/starch composite [3]. The combination of the latex compounding process and the starch modification is necessary to achieve ideal reinforcement in our opinion.

In order to achieve a maximum reinforcement, we investigated in this work the effect of the starch modification on the mechanical properties, compatibility, morphology and curing property of SBR. This modification technique developed here will be applicable in preparation of high performance elastomer; it will also advance the body of knowledge of how to reinforce polymer using the environmentally friendly starch.

2. Experimental section

2.1. Materials

Styrene–butadiene rubber latex (SBR 1502) was provided by Jilin Petrochemical Corp. of China, with a solid content 20.3%. Corn starch (100% amylopectin) was purchased from Changchun Dacheng Special Corn-Modified Starch Development Corp. of China. Resorcinol–formaldehyde (RF) was prepared in our laboratory. The silane surfactant, *N*-β(aminoethyl)-γ-aminopropyl trimethoxy silane (denoted as S), was offered by Nanjing Crompton Shuguang Organosilicon Specialties Corp., China (Fig. 1).

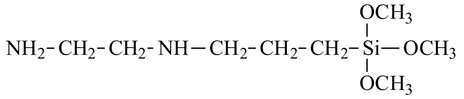
2.2. Preparation

2.2.1. Preparation of starch paste

0.5 L of water was boiled in 1 L beaker and 2 wt% starch was added and vigorously mechanically stirred at 95 °C for 30 min until the suspension became transparent. A starch paste was obtained when the above suspension cooled down.

2.2.2. Modification of starch paste

To modify starch effectively, a RF solution was made by the following procedure. Reactants at a ratio of 1 resorcinol to 3 formaldehyde molecules were dissolved in water, into which a diluted NaOH solution was dropped slowly until PH reached 9. The above RF solution was added into the paste, followed by vigorously stirring at 95 °C for 30 min.



$$\mathrm{NH_2\text{-}CH_2\text{-}CH_2\text{-}NH-CH_2\text{-}CH_2\text{-}CH_2\text{-}}\overset{\mathrm{OCH_3}}{\underset{\mathrm{OCH_3}}{\mathrm{Si}}}\mathrm{-OCH_3}$$

Fig. 1. Structure of the silane surfactant S.

2.2.3. Preparation of SBR/starch compound

The modified starch paste was added into the SBR latex and stirred vigorously for 30 min at room temperature. 1.0–1.5 wt% $CaCl_2$ solution was used to coagulate the mixture. The coagula was thoroughly washed with water and then dried in an oven at 80 °C for 18 h until containing less than 2% moisture.

2.2.4. Processing and vulcanization of styrene–butadiene rubber (SBR)/starch compound

The dried SBR/starch compound was mixed with the surfactant S, conventional additives (zinc oxide and stearic acid) and the curing agent sulfur by a two-roll mill, followed by vulcanization at 150 °C. The two-roll mill process is a common procedure in rubber field and so omitted here.

2.3. Characterization

Curing characteristics were measured at 150 °C with an oscillating disc rheometer, P3555B2, manufactured by Beijing University of Chemical Technology. X-ray diffraction (XRD) analysis was carried out on a Rigaku D/Max-III C under a Cu target, with 40 kV, 200 mA and 6.00° at 2θ/min. Mechanical tests were carried out at a constant temperature and humidity depicted by GB method [25], which is similar to ISO. Five specimens per sample were tested for each data. The value reported was the median of those observed. If any value deviated more than 20% from this median, five additional specimens would be tested and the median of all ten values was reported.

The morphology of the tensile-fractured samples was coated with gold and then observed with scanning electron microcopy (SEM), S-250-III SEM from Cambridge Corp. and XL-30 ESEM-TMP from FEI Corp.

Transmission electron microscopy (TEM) experiments were performed using a JEM2010 from JEOL Corp., at 200 kV, in order to acquire direct visualization of the particular starch morphology of the composites. Ultrathin sections of bulk samples were produced at −100 °C using a Leica Ultracut UCT with EMFCS cryo-attachment. The sections were floated off the diamond knife and transferred to the grids.

3. Results and discussion

3.1. Modification of starch

In previous efforts, starch is not ideal for high performance applications [14–19]; this is in our opinion due to improper modification of starch, which cannot make starch dispersed finely in rubber and the interface between the starch particle and the matrix is not good enough. Based on the hypothesis made in Section 1, we investigated the effect of starch modification on the mechanical properties using two types of modifiers as below.

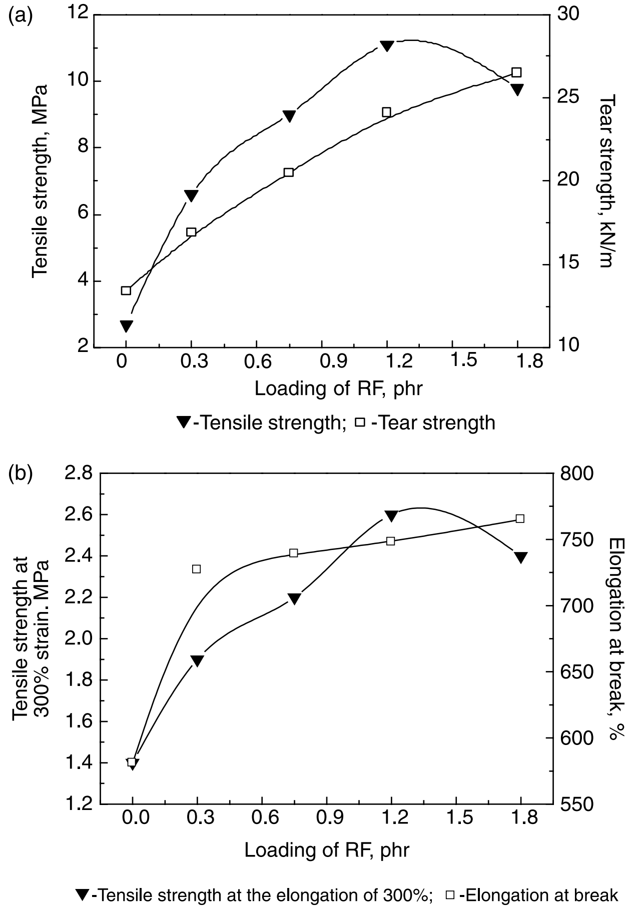


Fig. 2. Mechanical properties of SBR/RF-starch (100/10) with different loading of RF.

3.1.1. *Modification by resorcinol–formaldehyde (RF)*

Since, hydrophobic SBR is not compatible with hydrophilic starch, modification was designed to make starch hydrophobic. Fig. 2(a) shows the tensile strength and the elongation at break with the content of RF. With increasing the RF content, the tensile strength increased from 2.7 MPa for unmodified SBR to a maximum 11.1 MPa with 1.20 phr RF, and then decreased. The tear strength increased with the addition of starch, jumping from 14 to 24 kN/m with 1.2 phr RF, and then increased slowly. This means that 1.20 phr RF is appropriate for modification of the SBR/starch (100/10) compound. Fig. 2(b) indicates the trend of elongation at break and tensile strength at 300% elongation with RF concentration. Tensile strength at 300% elongation demonstrates the same trend a the tensile strength shown in Fig. 2(a). Elongation at break enhanced with increasing RF, since the RF oligomer plasticizes the SBR/starch compound. In conclusion, 1.2 phr of RF is most appropriate for the modification of SBR/starch (100/10).

3.1.2. *Co-modification by RF and a silane surfactant*

One of the common methods for filler modification is to use surfactants. Considering the above effective modification by RF, we investigated the influence of the surfactant on the mechanical property of SBR/RF-starch compound, instead of SBR. Given the fact of the starch containing a large amount of hydroxyl groups, the chosen surfactant must contain hydroxyl group or other groups that can interact with the starch. Hence, in addition to using RF, we chose a surfactant, *N*-β(aminoethyl)-γ-aminopropyl trimethoxy silane (denoted as S), which contains two amine groups for each molecule. The S was expected to improve the mechanical properties of the SBR/starch. The SBR/RF-starch compounds modified further by the S are here denoted as SBR/M-starch compounds. In Table 1, there was indeed a little improvement, but it is not high as expected. Since, the tensile strength reaches maximum at 3 phr surfactant, and the elongation at break is also good, this quantity of surfactant is considered appropriate for SBR/starch (100/10).

Table 2 shows the influence of modification methods on the mechanical properties. The tensile strength of SBR increased from 2.3 to 3.4 MPa with the addition of 10 wt phr of unmodified starch, which means starch cannot reinforce rubber unless modified properly. When SBR was compounded with RF-starch, the tensile strength increased from 2.3 to 11.1 MPa, 383% improvement. For SBR compounded with S-starch (starch modified only by the surfactant), the tensile strength increased to 7.7 MPa, 235% improvement. Comparison of the above improvements shows that the RF enhances the mechanical properties better than the surfactant. However, the disadvantage of the RF is the higher permanent set, which is caused by the RF oligomer. When SBR was compounded with M-starch (starch co-modified by the RF and the surfactant S), the tensile strength increased to 12.4 MPa, 439% improvement, with a moderate permanent set value. This means that excellent comprehensive mechanical properties can be achieved when both modifiers are employed.

Table 1
The mechanical properties of the SBR/M-starch (100/10) compounds with various content of the surfactant

Sample	SBR/M-starch[a]				
Surfactant content (wt phr)	0	1	2	3	4
Hardness (shore A)	57	57	57	57	57
Stress at 300% strain (MPa)	2.6	3.4	3.6	3.1	3.7
Tensile strength (MPa)	11.1	11.3	11.7	12.4	10.3
Elongation at break (%)	748	689	688	724	683
Permanent set (%)	20	16	20	16	20
Tear strength (kN/m)	24	24	25	25	24

[a] Each sample in this table contains 1.2 wt phr RF.

Table 2
Mechanical properties of SBR/starch (100/10) compounds with various modifications

Sample	SBR/starch	SBR/RF-starch[a]	SBR/S-starch[b]	SBR/M-starch[c]
Hardness (shore A)	50	57	52	57
Stress at 300% strain (MPa)	1.4	2.6	2.1	3.1
Tensile strength (MPa)	3.4	11.1	7.7	12.4
Elongation at break (%)	581	748	753	724
Permanent set (%)	8	20	12	16
Tear strength (kN/m)	16	24	28	25

[a] Starch/RF: 10/1.2 wt phr.
[b] Starch/S: 10/3 wt phr.
[c] Starch/RF/S: 10/1.2/3 wt phr.

The chemical modification employed as above is efficient, because the mechanical property enhancement surpasses all previous efforts and is similar to that achieved by CB. The corresponding modification mechanism was identified as below.

3.2. Modification mechanism

As indicated in Section 2, 1 mol resorcinol was mixed with 3 mol formaldehyde in water. Based on the general knowledge of organic chemistry, a reaction shown in Fig. 3 occurred for 1 mol resorcinol and 3 mol formaldehyde. The hydrophobic benzene group in the middle of the oligomer molecule is compatible with the rubber matrix SBR; the hydroxyl groups interact strongly with starch particle by hydrogen bonding. Thus, the oligomer can combine with the starch and makes it hydrophobic. During the solution mixing (Section 2.2.3) before coagulation, therefore, the oligomer combined starch particle with the matrix. Since the SBR/RF-starch was dried in an oven, a crosslinked structure was produced by the intercondensation of the multi-functional oligomers, through which the starch particle and the matrix macromolecules were interlocked. This interlocked structure improves interfacial adhesion, and prevents the starch particles agglomerating, thus leading to fine morphology. Actually, the morphology of the SBR/RF-starch is proved to be very fine in Figs. 9 and 11, and the interface is confirmed to be strong via the experiment below.

Since, SBR is readily dissolvable in toluene, the modification effect can be monitored by observing the suspension of starch particles in SBR/starch solution. 0.05 g of SBR/starch and SBR/RF-starch were, respectively, placed in a glass tubes containing 3 mL of toluene. To improve contrast, trivial amount of carbon black (CB) was mixed into both compounds before dissolved. The tube was heated in an oil bath at 100 °C with frequently shaking until all solute disappeared. Photos were taken through the procedure of dissolving and storing. As shown in Fig. 4, the SBR/starch was completely dissolved after 7 min of mixing, but precipitation was found during storage. Because SBR is fully dissolvable in toluene, the precipitation must be the unmodified starch; this is caused by the poor interaction between starch and SBR. In Fig. 5, SBR/RF-starch took double time to dissolve; this is due to that the RF-starch and SBR are combined by the condensed/crosslinked oligomers. However, no precipitation was observed after 24-h storage; this means a high level of combination of starch and SBR by the condensed/crosslinked obligomer, and so the starch can suspend longer.

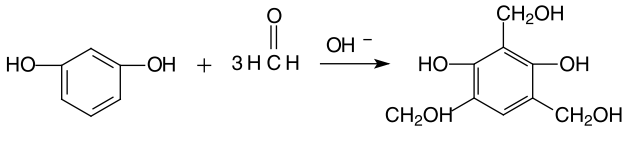


Fig. 3. Reaction schematic for reinforcement mechanism.

CB is an outstanding filler in rubber industry; its reinforcement mechanism is often generalized as the nano-size of particle and good interfacial interaction with the rubber matrix. As RF-starch reinforces SBR efficiently, is the interfacial adhesion of CB with SBR comparable with RF-starch? The following experiment was designed and conducted to answer this question. 0.001 g of CB was mixed with 30 g of SBR via a two-roll mill, and than the mixture was dissolved with a similar way to SBR/RF-starch. In Fig. 6, SBR/CB was fully dissolved in toluene after 30 min of mixing. Although not observed after 24 h storage, precipitation was found after 10-day storage. However, RF-starch suspension in Fig. 5 is still stable even after the 10-day storage; this indicates the combination of RF-starch with SBR is superior to CB. The combination of RF-starch with SBR is provided by the condensed/crosslinked oligomer, which locks the starch particle and rubber macromolecule together. Hence, it remains fairly stable as long as dissolved, because the procedure of dissolving and storing cannot unlock the crosslinked structure. In contrast, the combination of CB with SBR is provided by hydrogen bonding, which can be readily weakened in dilute solution.

3.3. Morphology

Previous efforts only achieved rubber/starch composites [3]; that is, the micron-sized starch particles dispersed in the rubber matrixes and the mechanical property improvement was not ideal. As hydrophobic rubber is not compatible with unmodified starch, fine starch particles cannot be in situ formed during the coagulation process. When the compatibilizer resorcinol–formaldehyde (RF) and the surfactant S were employed in this research, however, the mechanical property improvement is obvious, as shown in Table 2. In many cases, significantly enhanced mechanical properties correspond to improved compatibility and finer morphology [8–13,26–29]. Thus, we expected a fine morphology to be obtained in this study. A series of SBR/M-starch were microtomed and observed with TEM. But it is hard to obtain a good image after trying staining

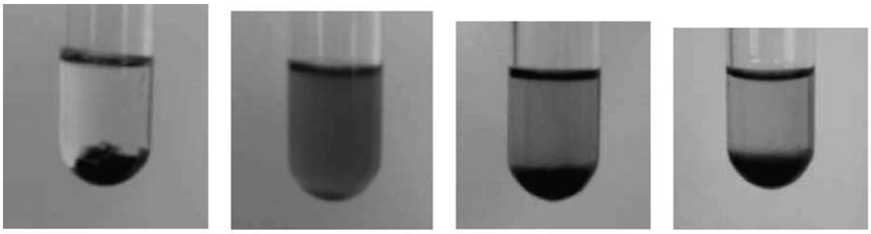

Rub/starch before dissolving
After 7m of heating
After 4h of storage
After 24h of storage

Fig. 4. Suspension of un-modified starch/SBR in toluene with time.

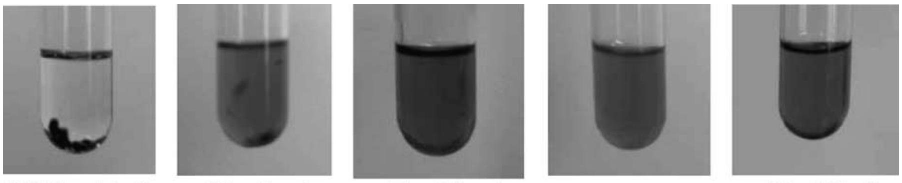

Rub/starch before dissolving
After 7m of heating
After 14m of heating
After 4h of storage
After 24h of storage

Fig. 5. Suspension of RF-starch/SBR in toluene with time.

agents—osmium tetroxide (OsO_4) and ruthenium tetroxide (RuO_4). Fig. 7(a) is a low magnification TEM image of SBR/M-starch compound containing 20 wt phr starch; particles with dimension around 100 nm were found dispersed evenly in the rubber matrix. Fig. 7(b) is a high magnification TEM image, which shows the diameters of most particles are less than 100 nm. This means nano-sized starch particles can be in situ formed during compounding and processing if starch is modified properly. In this work, starch was modified first to improve hydrophobicity, and then it may disperse finely and evenly in matrix after coagulation. This fine structure was fixed by drying in oven, as the oligomer interlocked it. This is why TEM shows a certain amount of nano-particles.

All samples were scanned by XRD to investigate the crystallization of the starch particles. In Fig. 8, unmodified starch shows three characteristic diffraction patterns, meaning the structure of semi-crystalline. After the starch was modified and compounded with SBR, all of the patterns disappeared, indicating the amorphous nanoparticles. If the particles are crystalline, some bright dots should have been observed on selected-area diffraction TEM image, as we did before (in Figs. 9 and 10 of Ref. [30]). We cannot find any feature for the SBR/M-starch samples on selected-area diffraction TEM image; this means these particles are amorphous.

Fig. 9 is SEM microphotographs of the fracture morphologies of the SBR/starch compounds by various modifications. When SBR was mixed with unmodified starch, some particles and voids were found on Fig. 9(a); the particles might consist of starch and SBR. When the starch was modified by the RF, smaller particles were shown on Fig. 9(b); this means the modification improves the compatibility between starch and SBR, and forms finer particles. When the starch was co-modified by the RF and the surfactant, less amount of particles were found on Fig. 9(c); this is caused by the improved interface between starch and SBR, making the particles less visible.

Compared with SEM, ESEM reflects the fractured surface more accurately, since it runs with a normal column pressure, instead of high vacuum, which might damage the sample surface. Fig. 10(a) is a low magnification ESEM microphotograph of the SBR/starch. It shows a large amount of particles, which might be aggregates of the starch and SBR, with obvious deformation and a little amount of voids. These characteristics are confirmed by a higher magnification image in Fig. 10(b). In

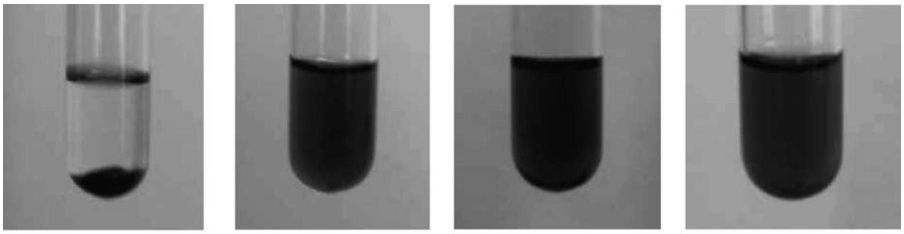

Rub/starch before dissolving
After 7m of heating
After 4h of storage
After 24h of storage

Fig. 6. Suspension of RF-starch/carbon black in toluene with time.

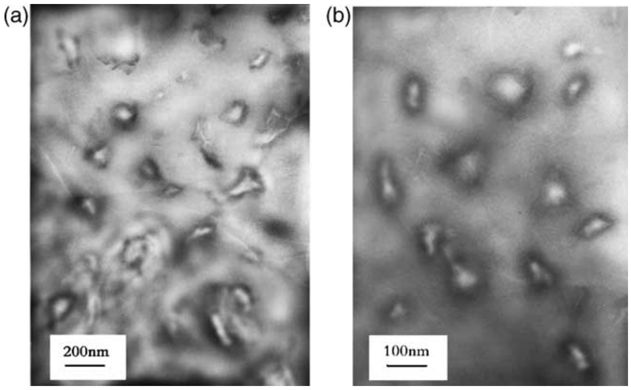


Fig. 7. TEM images of the SBR/M-starch compounds.

this system, the starch was unmodified and so the mechanical property improvement was quite limited, as evidenced in Table 2. While fracture occurred, it was the SBR that carried the main load, because of the poor interface between SBR and the starch. Therefore, the fracture surface shows many particles with just a little amount of voids. The images of SBR/RF-starch are shown in Fig. 11. Compared with Fig. 10, the quantity of particles decreased, deformation was less obvious, and more voids were available. In this system, the modified starch by the RF is compatible with SBR; it is dispersed better than the unmodified starch; the mechanical property improvement is higher, as shown in Table 2. While fracture occurred, it was the SBR/RF-starch that carried the main load due to the good interface between SBR and the starch. Therefore, less amount particles are visible on the fracture surface. ESEM photographs of the SBR/M-starch are shown in Fig. 12. Compared with Fig. 11, the particle quantity decreased a little, deformation was less obvious, and more voids were available. This indicates a better interface between M-starch and SBR due to the proper modification, corresponding to the mechanical property analysis. In Table 2, the mechanical property improvement of the SBR/M-starch is the highest, which corresponds to the above morphology analysis .

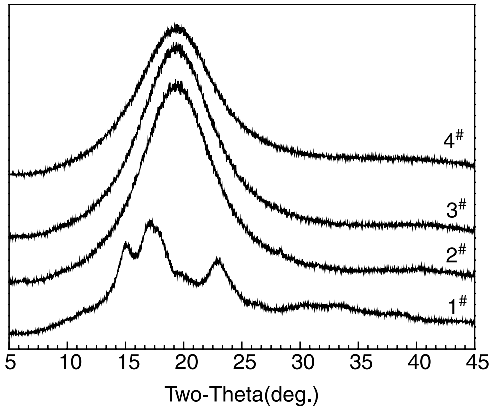
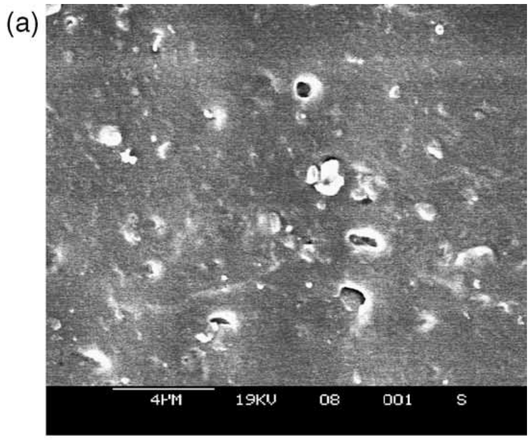
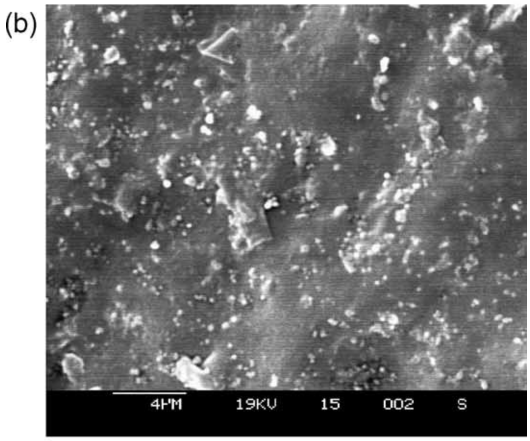


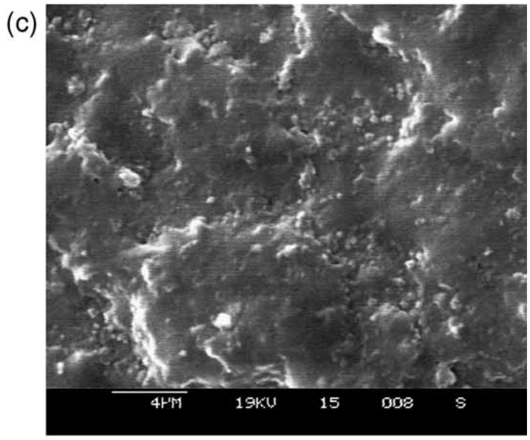
Fig. 8. X-ray diffraction patterns of starch, SBR and SBR/M-starch compounds. ($1^{\#}$, unmodified starch; $2^{\#}$, un-reinforced SBR; $3^{\#}$, SBR/M-starch compound (weight ratio 100/5); $4^{\#}$, SBR/M-starch compound (weight ratio 100/30)).



SBR/starch



SBR/RF-starch



SBR/M-starch

Fig. 9. SEM microphotographs of various SBR/starch (100/10) compounds.

3.4. Curing characteristics

Most rubber products are useless unless properly cured. Since, the rubber modulus increases dramatically during curing, and so it can be used as a monitor to investigate the progress of curing. Fig. 13 shows the characteristic curves for curing SBR/M-starch compounds. For unmodified SBR, there were three zones available, as described below, according to

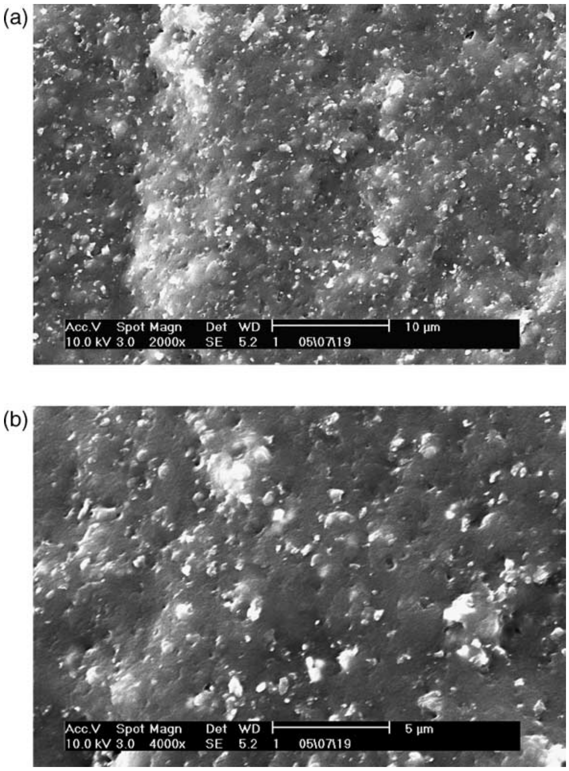


Fig. 10. ESEM morphologies of SBR/starch (100/10) compounds.

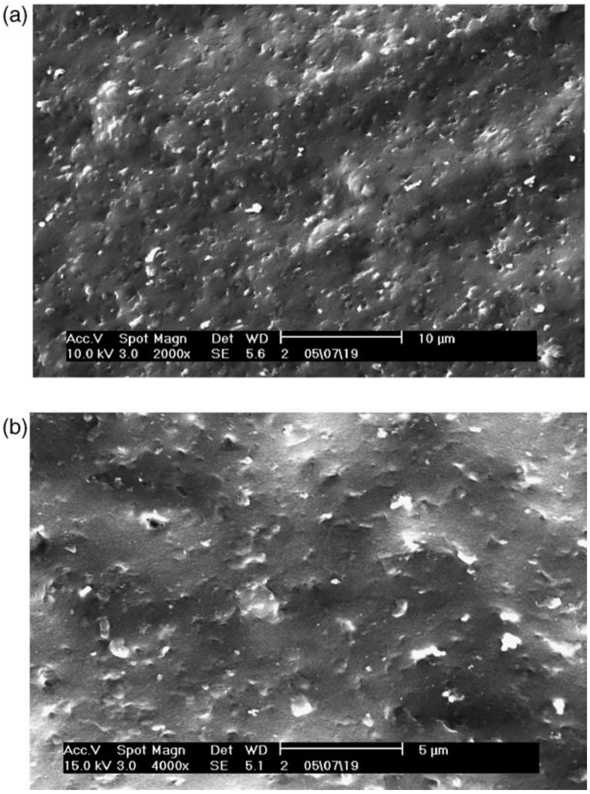


Fig. 11. ESEM morphologies of SBR/RF-starch (100/10) compounds.

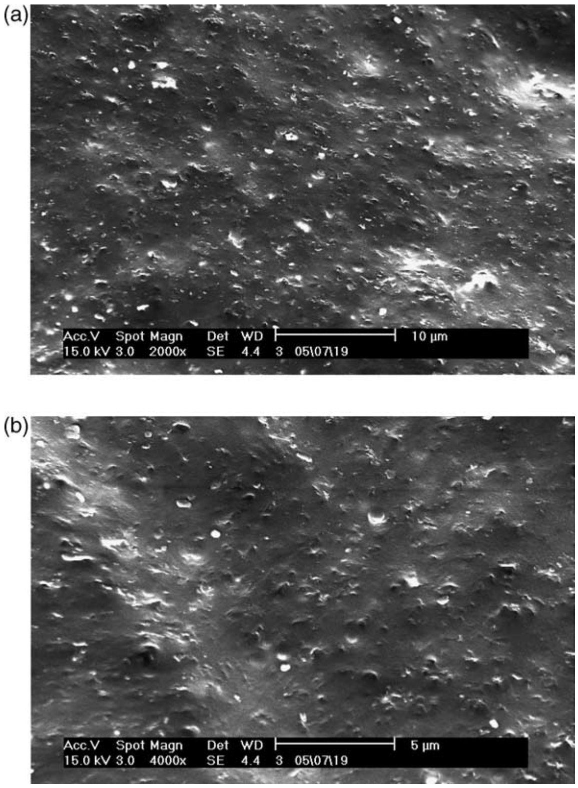


Fig. 12. ESEM morphologies of SBR/M-starch (100/10) compounds.

the changes of modulus with curing time. Zone 1 was from the 2nd to the 11th min, in which the modulus remained the lowest, meaning no curing occurred in zone 1. From the 11th to the 19th min was zone 2; the modulus increased significantly, showing the occurrence of curing. From the 19th to the 60th min, the modulus remained constant; this meant the compound was fully cured. After SBR was mixed with the M-starch, however, the curing characteristics changed obviously. As evidenced by curves 2, 3, 4 and 5 in Fig. 13, zone 1 disappeared and the boundary of zones 2 and 3 blurred. The difference of the curing behavior between the unmodified SBR and the others is caused by the additives, such as starch,

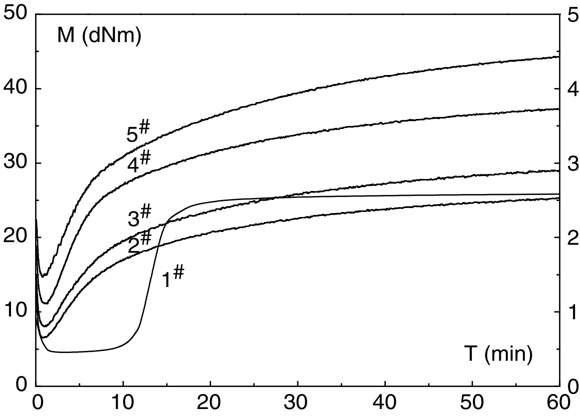


Fig. 13. Curing curves of SBR and SBR/M-starch compounds. ($1^{\#}$, unreinforced SBR; $2^{\#}$, SBR/M-starch compound (weight ratio 100/5); $3^{\#}$, SBR/M-starch compound (weight ratio100/10); $4^{\#}$, SBR/M-starch compound (weight ratio 100/20); $5^{\#}$, SBR/M-starch compound (weight ratio 100/30)).

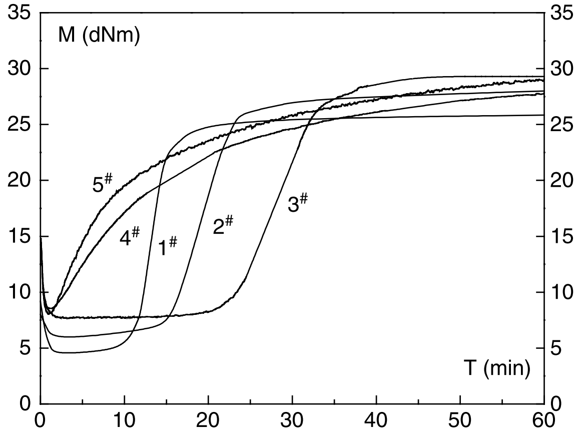


Fig. 14. Curing curves of SBR and SBR/starch compounds with various modifications ($1^{\#}$, un-reinforced SBR; $2^{\#}$, SBR/starch compound; $3^{\#}$, SBR/RF-starch compound; $4^{\#}$, SBR/S-starch compound; $5^{\#}$, SBR/M-starch compound. The weight ratio is fixed at 100/10 from $2^{\#}$ to $5^{\#}$).

the RF and the surfactant; of which, the surfactant should play a main role since it contains amine group.

To confirm the above analysis, we designed an investigation into the curing behavior of SBR and SBR/starch compounds with various modifications. In Fig. 14, the zone 2 was delayed with the addition of either starch or starch/RF, since both of them contain a number of hydroxyl groups, which is well known for the delay of curing. When the surfactant was added, zone 1 was shortened significantly and the boundary of these three zones became blurred; this was caused by the amine groups of the surfactant, which is believed for promoting curing.

4. Conclusions

As starch is an environmentally friendly natural polymer with an abundant source, more interests are attracted to use starch for polymer degradation and reinforcement, as evidenced by publications in recent years. This research achieved the following progress:

1. The starch was co-modified by resorcinol–formaldehyde and the surfactant (*N*-β(aminoethyl)-γ-aminopropyl trimethoxy silane), and most of the modified starch (M-starch) particles were dispersed in the SBR matrix on nano-scale.
2. The SBR/M-starch compounds show significantly improved mechanical properties, which are higher than those reinforced by carbon black. With merely 10 wt phr of starch, the tensile strength increased to 12.4 from 2.3 MPa, 439% improvement, and the tear strength enhanced from 9 to 25 kN/m, 178% improvement. This means the M-starch developed in this study will be an ideal candidate for novel filler in future rubber industry.
3. The starch suspension experiment indicates that the chemical modification by the RF provides strong interactions between the filler and the rubber matrix, which is attributed to the condensed/crosslinked oligomer.

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