

Chemically modified starch reinforced natural rubber composites

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ABSTRACT

Chemically modified starch paste (MST) with polybutylacrylate (PBA) graft chains is investigated as a reinforcing filler of rubber through mixing and co-coagulating with natural rubber (NR) latex. The PBA graft chains are designed to prevent hydrogen bonding and crystallization of starch and to improve compatibility between starch and rubber. Through the comparison of mechanical properties and phase morphology, MST is proved to be much superior to unmodified starch paste. Unmodified starch paste acts as essentially inert filler causing a decrease of tensile strength, tear strength and elongation at break. In contrast, optimum MST shows obvious reinforcement effect on NR matrix by increasing tensile strength, elongation at break and tear strength besides modulus and hardness. Moreover, fine starch dispersion and strong interfacial interaction are achieved in NR/MST composites. The observed reinforcement effect is interpreted based on the results of X-ray diffraction (XRD), differential scanning calorimetry (DSC) and scanning electron microscope (SEM) analyses of grafted starch in comparison with natural starch and gelatinized starch.

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1. Introduction

The development of starch as a rubber-reinforcing filler has drawn increasing interest in recent years. Due to the use of starch with carbon black and/or silicon in tires, a number of improved properties, such as reduced tire weight, decreased rolling resistance and increased wet grip have been achieved accompanied with maintained abrasion resistance [1–4]. In addition, as a renewable, biodegradable, inexpensive and widely obtainable biopolymer, the application of starch is also attractive due to energy shortage and environmental pollution [5].

However, starch has many disadvantages for its application as a rubber-reinforcing filler, such as its large particle size, strong polar surface, high cohesion energy and high soft temperature [6–10]. Modifications of starch, such as plasticization [3,4], mechanical smashing [11], gelatinization (combined with co-coagulating rubber latex) [6,12] and acid hydrolysis (to prepare starch nanocrystals) [13,14] have been examined. The main objective of these modifications is fining starch dispersion and/or improving interfacial strength between starch and rubber, two of the critical factors for rubber reinforcement [9,10].

As natural rubber (NR) is also renewable resource but much costly compared to starch, the composites of NR and starch will become important in the future. Some researches have been

performed on NR/starch composites based on NR or modified NR [15–18]. Furthermore, the modification of starch matrix materials by NR latex (NRL) and modified NRL has also been examined [19].

Graft copolymerization is an efficient method to modify polymers. Various vinyl monomers have been investigated to graft onto starch, and the starch graft copolymers have been used as flocculating agents, superabsorbents, ion exchanges and matrix or filler of thermoplastics [20–26]. In this paper, modified starch paste (MST) by grafting with butylacrylate (BA) is firstly investigated as a rubber-reinforcing filler. Three types of NR/starch composites are prepared: NR/NST composites from natural starch powder (NST) by direct compounding with NRL coagulum; NR/PST composites from unmodified starch paste (PST) by co-coagulating with NRL; and NR/MST composites from MST by co-coagulating with NRL. Properties and morphology of these composites and corresponding starch powders are examined. The observed reinforcement effect of MST on NR/starch composites is interpreted.

2. Experimental

2.1. Materials

Natural starch purchased from Hebei Changli Co., Ltd was common cornstarch. NRL with 61% solid contents was provided by 11th Rubber Plant of Guangzhou, China. Butylacrylate and ammonium persulfate (APS) were chemical pure reagents. Other reagents and ingredients were commercially available and were used as received.

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2.2. Preparation of modified starch

About 6% starch aqueous suspension was gelatinized at 80 °C for 30 min under nitrogen atmosphere. Graft copolymerization was then conducted with the starch paste, BA and initiator APS at 80 °C for 2 h to give a modified starch paste, the MST. Modified starch powders were obtained by precipitating the paste and then extracting the precipitate with acetone to remove ungrafted PBA. The grafting ratio of PBA was 21.6%, the ratio of ungrafted PBA was 2.4% and the grafting efficiency was 90%, measured as in Ref. [20]. Gelatinized starch was prepared in the same procedure without addition of APS/monomer and acetone extraction. Unmodified starch paste was noted as PST.

2.3. Preparation of NR/starch composite

NR/MST or NR/PST composites were prepared with corresponding paste in following procedure: starch paste was mixed with NRL and stirred vigorously for 20 min, and then 10% calcium chloride solution was used to co-coagulate the mixture. The coagulum was washed by water and then dried in an oven at 70 °C for 24 h to give the blends. Basic formulation of all compounds is shown in Table 1. Compounding was carried out on a two-roll mill at 50–60 °C in a standard procedure. The rubber compound sheets were compressed and vulcanized at 150 °C for t_{90} . The NR/starch vulcanizates are referred to as NR/starch composites in this paper.

2.4. Mechanical tests

Tensile property measurements were performed in a standard testing procedure according to ISO 37 using a U-CAN 2060 Electronic Tensile Machine. Tear strength was measured on the same machine according to ISO 34-1. Three to five specimens were measured for each particular sample and the average values were reported with standard deviation showing the error range. The hardness of the samples was measured by a Shore A Durometer.

2.5. X-ray diffraction (XRD) studies

The XRD studies of starch powders were carried out using a Rigaku D/MAX-III X-ray diffractometer with Cu target. The voltage and the current were 40 kV and 40 mA respectively. Starch samples were scanned with 2θ between 5 °C and 50 °C.

2.6. Differential scanning calorimetry (DSC) analysis

Thermal analysis of starch powders was performed with a Universal V1.7F TA Instruments MDSC-2190 differential scanning calorimeter. The samples were heated from 25 °C to 200 °C and kept at 200 °C for 2 min to eliminate the thermal history, then the samples were cooled to –50 °C and followed with the heating scan from –50 °C to 200 °C using a heating rate of 20 °C/min.

Table 1
Compounding formulation (phr)

Compounds	NR	NR/starch	NR/modified-starch
NR	100	100	100
Starch	0	7.5, 15, 22.5, 30	7.5, 15, 22.5, 30
PBA (grafted and ungrafted)	0	0	24% of starch
Sulphur	2	2	2
Stearic acid	1	1	1
Zinc oxide	5	5	5
Accelerator CZ	1	1	1
Accelerator DM	0.5	0.5	0.5
Antioxidant RD	1	1	1

2.7. Scanning electron microscope (SEM) experiments

Surface morphology of starch powders and freeze-fractured composites was studied on a Philip XL30 SEM. The specimens had been coated with thin film of gold before observation.

3. Results and discussion

3.1. Reinforcement effect of MST on natural rubber

The mechanical properties of NR/MST composites with different MST contents, in which the amount of PBA was 24% of starch, are examined as shown in Fig. 1a–e. The points corresponding to 0 phr starch reflect the mechanical properties of pure NR from NRL coagulum. Similar curves of NR/PST composites are also shown in the diagrams for comparison. In addition, NR/NST composite containing 15 phr starch powders is also shown in the diagrams as separated points. As expected, direct filling of natural starch powders causes deteriorated mechanical properties of NR with decreased tensile strength, tear strength and elongation at break. The addition of PST from 0 phr to 30 phr causes a monotone decrease of tensile strength and elongation at break. The results mean that the PST acts essentially as an inert filler, which differs from the report of Wu and Ji et al. [6] in which an increase of strength by adding 10% amylopectin cornstarch paste from its 2% suspension was reported.

The mechanical properties of NR/starch composites are obviously improved by using MST replacing PST with same amount of starch. Except Shore A hardness is almost unchanged, the tensile strength, 300% modulus, elongation at break and tear strength of NR/MST composites are all obviously higher than those of corresponding NR/PST composites. This improvement may be interpreted as follows. As an important design of the MST, many PBA graft chains with partial hydrophilic carbonyl group and hydrophobic alkyl groups would distribute inside the expanded starch particles. Owing to much larger size and more irregular structure compared to hydroxyl groups, the PBA graft chains would effectively prevent the gathering as well as regular packing of starch and enhance compatibility between hydrophilic starch to which PBA is grafted and the hydrophobic NRL. This would promise a great decrease of cohesion energy and crystallization of the grafted starch. Therefore, better dispersion of starch in NR matrix as well as better interfacial interaction between grafted starch and NR could be expected, which would allow an improvement of mechanical properties of the composites [6–9].

Furthermore, NR/MST composites with optimum amount of MST, e.g. corresponding to 15 phr starch, achieve best comprehensive mechanical properties compared with pure NR. The maximum elongation at break is presumably ascribed to the entanglement of PBA chains with NR molecular chains and free motion of PBA segments during stretching due to its low T_g about –60 °C. The much higher tensile strength may be caused mainly by increased strain-induced crystallization of NR, which might be enhanced by increased physical entanglements of NR [27–29].

However, excess addition of MST more than 22.5 phr starch causes an overall decrease tendency of almost all examined mechanical properties. The rapid decrease of tensile strength and elongation at break is generally ascribed to increased defects resulting from gathered fillers in the composites. Similar improvements have also been achieved by the addition of modified starch paste prepared by grafting with styrene, methyl methacrylate (MMA) and their mixture with BA (to be reported in subsequent papers).

3.2. Structure and properties of starch powders

Considering the main disadvantages of starch for rubber reinforcement is high cohesion, high polarity and high soft temperature,

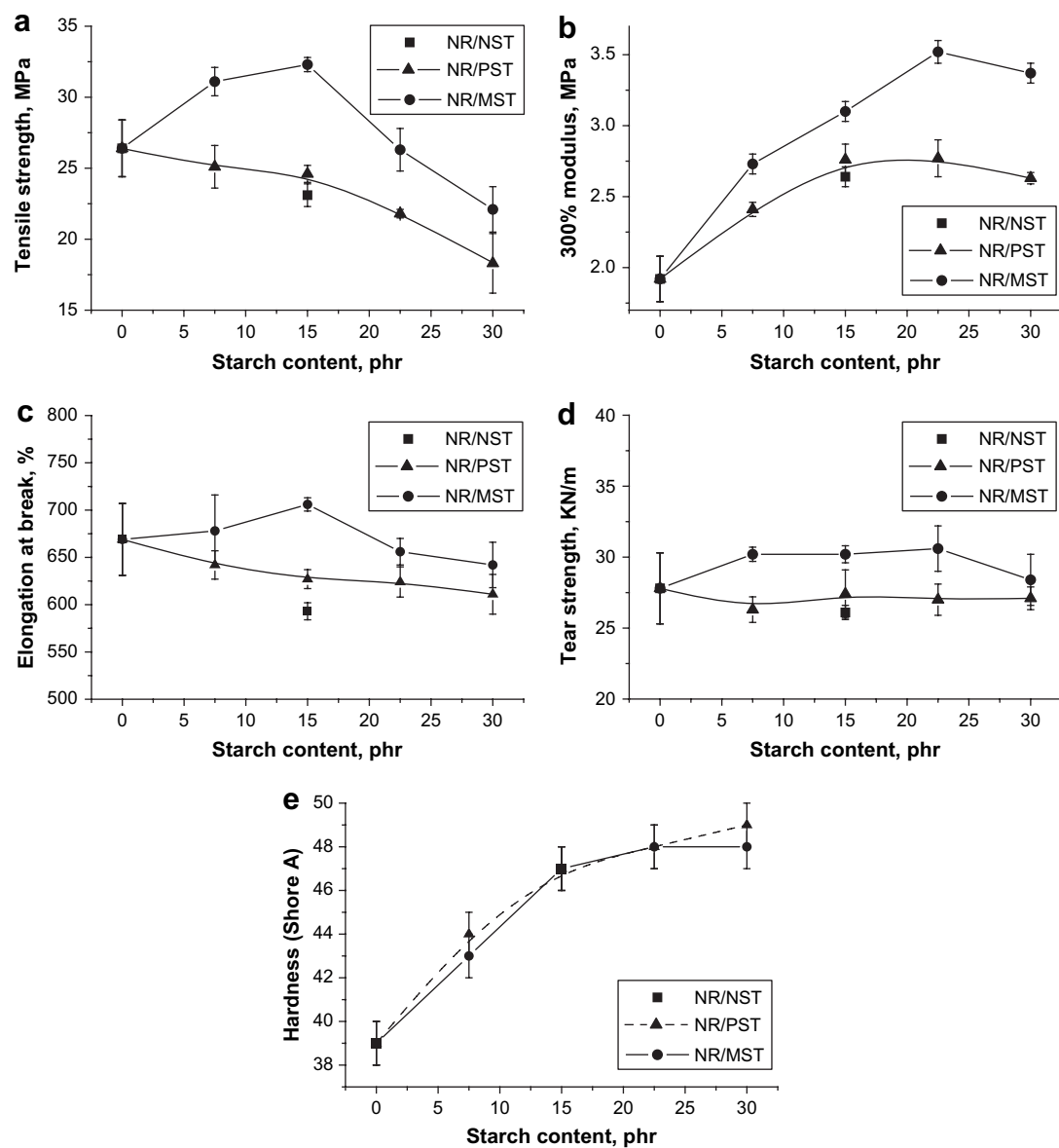


Fig. 1. Variation of mechanical properties of NR/starch composites via starch content. The values are given by average and the error ranges are given by standard deviation as evaluated by results from 3–5 parallel samples. (a) Tensile strength, (b) 300% modulus, (c) elongation at break, (d) tear strength and (e) hardness (Shore A). Lines are to guide the eye.

the XRD pattern and thermal behavior of the modified starch are investigated in comparison with natural starch and gelatinized starch.

The XRD patterns of natural starch, gelatinized starch and modified starch are shown in Fig. 2. Natural starch is a semi-crystalline material, which shows five diffraction peaks of A-type starch at 15.2°, 17.2°, 18.0°, 19.9°, and 23.1°, respectively (curve a in Fig. 2). However, the gelatinized starch (curve b in Fig. 2) shows a V-type starch pattern with diffraction peaks at 7.2°, 12.8° and 19.8°. As A-type crystallites are formed by parallel-packed double helices, while V-type crystallites relate to single helical complexes [30–32], so this variation of crystal pattern suggests that the original crystals have been destroyed by gelatinization and new crystals are formed when the paste was precipitated, reflecting the high cohesion and strong hydrogen bonding of the gelatinized starch. An amorphous hill accompanied by very weak crystalline peaks is apparent in the diagram of modified starch (curve c in Fig. 2), indicating a high ratio of amorphous structure and low crystallization, and proving that the graft PBA chains effectively prevented the regular packing of the modified starch, as proposed in Section 3.1.

The DSC curves in Fig. 3 suggest some information on soft temperature of starch in addition to crystallization. The strong and broad endothermic hill of natural starch (curve a in Fig. 3) from 88 °C to over 200 °C with peak temperature at 156 °C can be

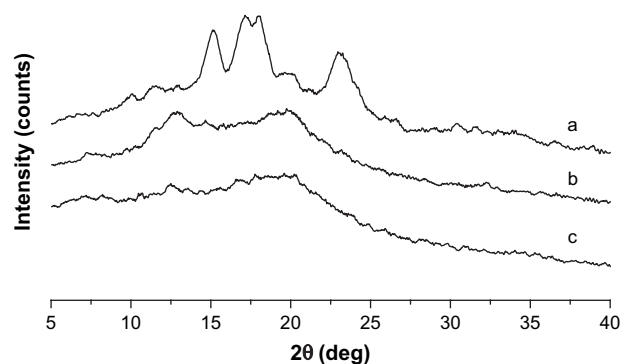


Fig. 2. XRD patterns of starch powders. (a) Natural starch, (b) gelatinized starch and (c) modified starch with PBA grafts.

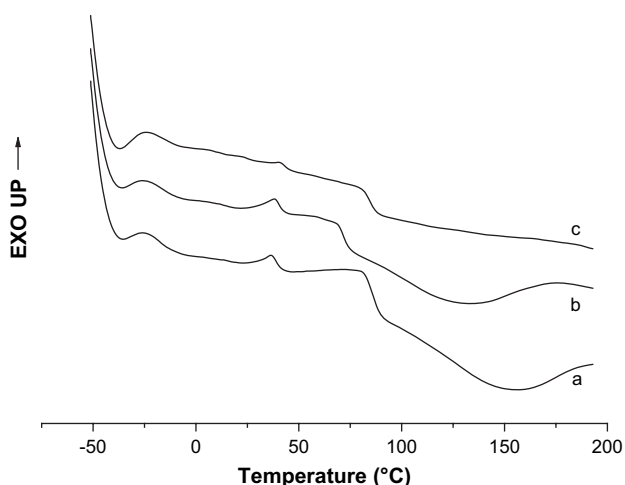


Fig. 3. DSC curves of starch powders. (a) Natural starch, (b) gelatinized starch and (c) modified starch with PBA grafts.

ascribed to the melt of starch, reflecting its high cohesion, high re-crystallization and high soft temperature [33,34]. The relative narrow hill of gelatinized starch (curve b in Fig. 3) from 75 °C to 175 °C with lower peak temperature at 133 °C indicates that the crystallization and soft temperature are decreased but still high. For the modified starch, a typical glass transition step at 84 °C instead of endothermic hill is apparent on the curve c in Fig. 3, further proving its amorphous structure and greatly decreased crystallization. From this, lowered cohesion energy and soft temperature of modified starch could also be inferred. Peaks around -25 °C is proved to be caused by the thermal process of a long cooling followed with a fast heating; while the exothermic peaks around 40 °C might relate to the hydrogen bonding and/or crystallization of starch, due to the fact that it is much affected by moisture [35].

3.3. Morphology of starch in powders and in composites

As mentioned above, fine dispersion of starch and enhanced interfacial interaction between starch and NR phase are two main goals of the application of modified starch paste with internal PBA grafts. The morphology micrographs of NR/starch composites characterized by SEM from their freeze-fractured surface are shown in Fig. 4. For comparison, the powder morphology of starches is also investigated as shown in Fig. 5. It should be noticed that those float particles in the composites (about 0.5 μm) have been proven to be zinc oxide.

Both the size and shape of the starch particles in NR/NST composites (Fig. 4A) are almost the same as those of the original starch in Fig. 5A. This result reflects that usual compounding shear force combined with high cure temperature (150 °C) is not enough to break or soften the starch particles due to their high cohesion and high soft temperature. Both the smooth surface of starch and the smooth holes on the fractured surface left by starch particles give an indication of weak interfacial interaction between starch and NR.

Though gelatinized at 80 °C for 2.5 h, most of the PST particles in Fig. 5B are slightly deformed, in agreement with its strong re-crystallization and hydrogen bonding as proved by XRD and DSC. After processes of mixing, co-coagulating, compounding and curing, the morphology of starch is rather different, as shown in Fig. 4B. Except those united granules larger than 20 μm, the starch granules are approximately 2–10 μm in size, much smaller than original particles which are roughly 5–20 μm. This difference in size may be due to softening and diffusing of gelatinized starch. However, the compatibility between the hydrophilic starch and hydrophobic NRL is not strong enough to effectively prevent the starch from gathering, re-crystallization and hydrogen bonding. Thus, the well re-organized parts (always smaller than the original size) with high cohesion will not be significantly influenced by compounding and curing and hence remained in the composite; and those destructed parts would be broken, softened and re-gathered to form irregular

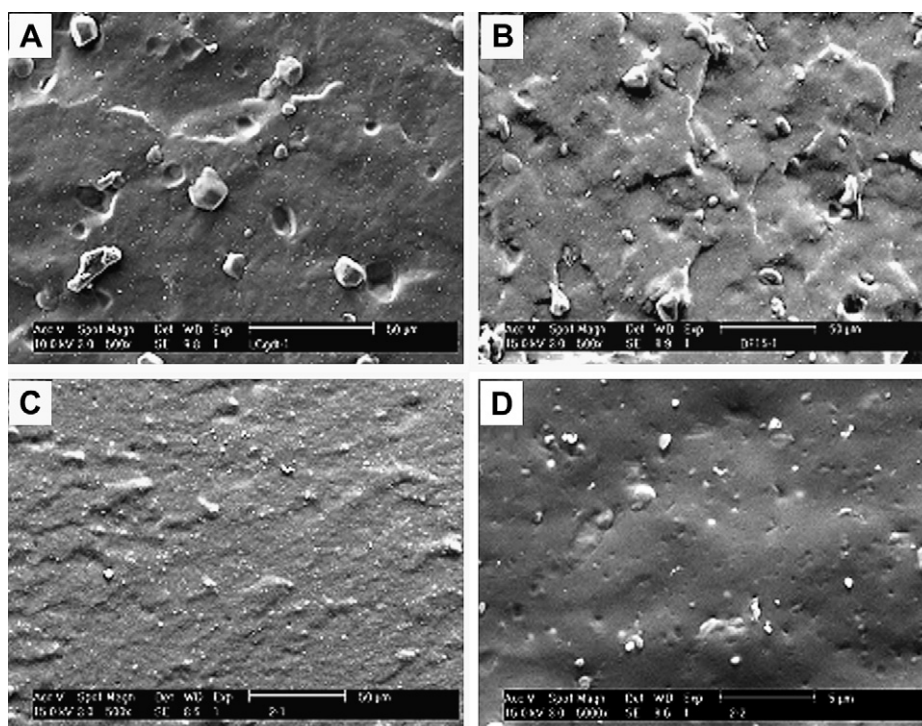


Fig. 4. SEM micrographs of freeze-fractured surfaces of NR/starch composites. (A) NR/NST from natural starch, (B) NR/PST from unmodified starch paste and (C, D) NR/MST from modified starch paste with PBA grafts. Starch content, 15 phr/100 phr.

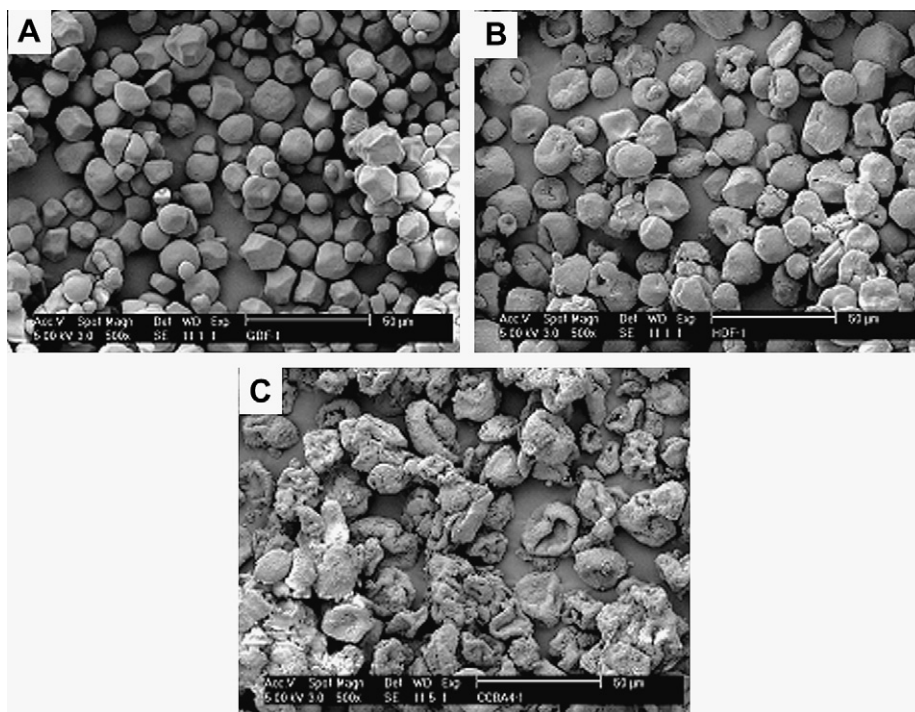


Fig. 5. SEM micrographs of starch powders. (A) Natural starch, (B) gelatinized starch and (C) modified starch with PBA grafts.

smaller granules. The irregular small granules have more contact area and hence slightly improve the interfacial interaction between the granules and NR matrix as reflected by the out-brought NR around the holes left by starch particles.

The modified starch powder (Fig. 5C) still has a complete frame though heavily deformed. The completion of the particle frame suggests its plasticity presumably due to the entanglement of amorphous amylopectine. The heavy deformation indicates the plasticity of the internal structure of starch particles, which should be ascribed to the internal graft of flexible PBA. This result is consistent with the XRD and DSC analyses. Therefore, the starch granules in NR/MST composites would be much more easily broken, softened and diffused into NR phase during compounding and curing, as the influence of NRL might further decrease the cohesion and soft temperature of MST due to better compatibility between grafted starch and NR. This diffusion of soft tiny grafted starch finally allows for the fine dispersion of starch, as shown by the SEM micrographs of the NR/MST composite containing 15 phr starch (Fig. 4C and D). Almost no starch granules are larger than 5 μm . Most are smaller than 1 μm , either buried in the NR matrix or projected out with NR remains on the surface. This result strongly suggests a significantly enhanced interfacial interaction between starch granules and NR phase. Dual effects of the fine starch dispersion and the enhanced interfacial interaction lead to the observed reinforcement effect of MST on mechanical properties of NR/starch composites.

4. Conclusions

Addition of two types of starch paste (unmodified starch paste and modified starch paste by grafting with BA) into natural rubber latex shows very different effects on the mechanical properties and phase morphology of NR/starch composites. Similar to natural starch powders by direct mixing with pure NR, unmodified starch paste acts essentially as an inert filler and deteriorates the tensile strength, elongation at break and tear strength of NR matrix. However, the modified starch paste shows an obvious reinforcement on

both NR/starch composites and NR matrix. Almost all examined mechanical properties have been obviously improved in optimum starch content. Fine starch dispersion with most starch granules smaller than 1 μm and strong interfacial interaction between starch and NR has been achieved. All the improvement caused by the modified starch could be interpreted by the influence of PBA graft chains on the structure and thermal properties of starch. The PBA chains lead to greatly decreased crystallization and soft temperature of starch, as well as better compatibility between starch and NR. Therefore, the modified starch can be much more easily broken, soften and better diffused into NR phase, hence leads to the observed reinforcement.

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