Emulsion Grafting Vinyl Monomers onto Starch for Reinforcement of Styrene-Butadiene Rubber

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Abstract: Three types of modified starches (MST): Starch-*g*-poly(butyl acrylate) (ST-*g*-PBA), starch-*g*-poly (methyl methacrylate) (ST-*g*-PMMA) and starch-*g*-polystyrene (ST-*g*-PS) latexes were successfully synthesized by emulsion polymerization. These synthesized MST latexes were then directly compounded with styrene-butadiene rubber (SBR) latex in order to prepare MST/SBR compounds. The vulcanization characteristics, morphology, swelling ratio, mechanical and dynamic mechanical properties were investigated. Results indicated that the incorporation of starch or MST led to both an increase in the torque values and the cure rate of SBR compounds. MST with a particle size of approximately 200-400 nm uniformly dispersed in the SBR matrix, indicating the significantly improved dispersion. MST/SBR compounds exhibited better mechanical properties compared with starch/SBR (ST/SBR) compounds. Among the MST/SBR compounds, ST-*g*-PMMA/SBR compounds showed optimum tensile strength, which was even higher than that of carbon black/SBR (CB/SBR) compounds with the same loading of fillers. Finally, the reinforcing mechanism of MST in the SBR matrix was discussed.

Keywords: starch, SBR, modification, grafting, physical entanglement.

Introduction

Rubber products are widely applied in many industry fields, such as automobiles, medical devices, mining, and many manufacturing systems.[1] The incorporation of reinforcing fillers into elastomeric polymers can significantly improve their thermal, mechanical, dynamic mechanical and abrasion resistance properties. Over the past few decades, carbon black and silica have been considered as two main reinforcing fillers in the rubber compounding industries. However, it is well known that carbon black is derived from petroleum or natural gas, which is non-renewable resource. Silica is produced from minerals, while it consumes much energy for production. With the rapid development of the industry, the consumption of the non-renewable fossil fuels has been gradually increasing. Therefore, to maintain the sustainability of global economy, the renewable natural materials are required.

Recently, the "green" rubber composites have attracted great attention due to their "green" advantage.[2-10] Especially, the use of various green fillers such as starch,[5,6] rice husk,[7,8] wood flour[9] and microcrystalline cellulose[10] as reinforcing fillers in rubber matrix has been extensively reported. Compared with traditional reinforcing fillers, such as carbon black, silica, calcium carbonate and clay, green fillers possess many advantages, such as low density, low price, non-toxicity, renewability and biodegradability. In addition, earlier studies have reported that partial replacement of carbon black or silica by green fillers could reduce the rolling resistance and improve the wet traction.[11,12] Therefore, green fillers not only offered a "green" advantage, but also improved the fuel efficiency of tire tread materials.

Starch is a natural carbohydrate, which is composed of a mixture of amylose, a linear polysaccharide and amylopectin, a highly branched polysaccharide. The particle size of starch ranges from 5 to 50 μm depending on its original resources. In general, the particle size of starch increases as the following order: rice starch < corn starch < wheat starch < potato starch. It is well known that fillers with particle size from 1 to 10 μm primarily act as diluents and have no reinforcing capability in rubber matrix; fillers with particle size greater than 10 μm generally deteriorate the physical properties rather than reinforcing. Therefore, one of the major bottlenecks for starch used as reinforcing filler in the rubber compounds is its large particle size. Recently, several technologies, such as gelatinization,[5] acid hydrolysis,[13] enzyme hydrolysis[14] and precipitation[15] have been developed to decrease the starch particle size. It has been reported that starch nanocrystals with a thickness of 6-8 nm, a length of 40-60 nm, and width of 15-30 nm were obtained through sulfuric acid hydrolysis.[16] Another one of the major bottlenecks is its hydrophilic surface, which lead to poor inter-

facial adhesion with the hydrophobic rubber matrix, especially for the non-polar rubber, such as SBR. Therefore, various surface modification methods, such as grafting of poly(butyl acrylate),[17] esterification with xanthate,[18] crosslinking with resorcinol-formaldehyde[19] and isocynate[20] have been reported to enhance the interfacial bonding.

Emulsion grafting polymerization has been considered as a promising way to modify the surface properties of fillers in the past decade. It has been reported that various inorganic or organic fillers, such as nanosilver,[21] carbon black,[22] and methylcellulose[23] were successfully modified through emulsion grafting polymerization. In this study, three types of modified starch (MST) latexes (ST-*g*-PBA, ST-*g*-PMMA, and ST-*g*-PS) were synthesized through emulsion grafting polymerization, and then directly mixed with SBR latex to produce MST/SBR compounds. The method of emulsion modification and latex compounding was designed to form an even distribution of starch particles in the SBR matrix and to enhance the interfacial interaction between starch and SBR matrix in the presence of vinyl grafts.

Experimental

Materials. Styrene-butadiene rubber latex 1502 (styrene content 23.5 wt%) was kindly provided from Korea KumHo Petrochemical Company (KKPC). Corn starch (branched amylopectin 75%, linear amylose 25%) was kindly supplied by Samyang Genex Company, South Korea. Vinyl monomers used for grafting, such as methyl methacrylate (MMA), butyl acrylate (BA), and styrene (S) were purchased from Dae Jung Chemical and metal Co., Ltd, South Korea. Initiator potassium persulfate (KPS) was purchased from DukSan Pharmaceutical Co., Ltd. Carbon black Corax N550 was purchased from Evonik Company. Emulsifier dodecyl-

bezenesulfonic acid sodium salt (DBS-Na) was purchased from JunSei chemical Co., Ltd. All the chemicals and rubber additives were used as received without further purification.

Gelatinization of Starch. Approximately 20 g of starch were dispersed into 250 g of deionized water. The starch suspension was vigorously stirred at 80 ℃ in a water bath under nitrogen atmosphere for about 30 min.

Emulsion Grafting Vinyl Monomers Onto Starch. MST was synthesized by conventional emulsion polymerization using DBS-Na as emulsifier as reported previously.[24-26] Approximately 10 g of vinyl monomers (MMA, BA or S). were first mixed in 50 mL of 1 wt% DBS-Na solution with mechanically stirring. After 30 min pre-emulsifying, the vinyl monomer emulsions were slowly added into the starch paste. Graft copolymerization was initiated by the addition of 20 mL of 0.5 wt% KPS solution. The reaction was carried out under nitrogen atmosphere at 80 ℃ for 3 h.

Compounding. MST/SBR compounds were prepared by directly mixing of the MST emulsion and the SBR latex. The mixtures were vigorously stirred at a speed of 1,000 rpm for 30 min to make a well dispersion of MST, and then dried in an oven at 70 ℃ until the weight kept constantly. Compounding was conducted on a two-roll mixing mill. The dried MST/SBR compounds were compounded with the conventional elastomeric additives, such as sulfur, zinc oxide, stearic acid, accelerator *n*-cyclohexyl-2-benzothiazole sulfenamide (CBS), accelerator dibenzothiazole disulfide (D), antioxidant 2,2,4-trimethyl-1,2-dihydroquinoline polymer (TMQ) as shown in Table I. Note that sulfur and accelerators were mixed in the final step to avoid the pre-vulcanization. Finally, the compounds were vulcanized under 10 MPa for t_{90} at 150 ℃ in a hot-pressing machine. The thickness of the specimens was about 2 mm. For the purpose of comparison, we also prepared neat SBR, unmodified starch/SBR

Table I. Compounding Formulation Used in This Study

Compounds (phr)[a]	Neat	ST/SBR	ST-*g*-PBA/SBR	ST-*g*-PMMA/SBR	ST-*g*-PS/SBR	CB/SBR
SBR	100	100	100	100	100	100
Starch	0	20	20	20	20	0
PBA[b]	0	0	10	0	0	0
PMMA[b]	0	0	0	10	0	0
PS[b]	0	0	0	0	10	0
CB	0	0	0	0	0	20
Zinc oxide	3	3	3	3	3	3
Stearic acid	1	1	1	1	1	1
Sulfur	2	2	2	2	2	2
CBS	2	2	2	2	2	2
D	0.5	0.5	0.5	0.5	0.5	0.5
TMQ	1	1	1	1	1	1

[a]Per hundred rubber. [b]Including grafted and ungrafted polymers.

(ST/SBR) and carbon black/SBR (CB/SBR) compounds.

Characterization. The grafting percentage (GP) and grafting efficiency (GE) were measured as reference.[27] First, MST emulsion was poured into an excess amount of methanol solution. The precipitates were filtered, washed with methanol and water, and then dried at 50 °C in an oven. To remove the homopolymers, the precipitates were extracted with chloroform for 24 h in a soxhlet extractor. Vinyl grafts could be separated from the MST copolymers by oxidation of the starch section. The oxidation process was described as below. A certain amount of extracted MST was first added into 100 mL of glacial acetic acid in a three-neck flask. And then, the three-neck flask was heated in a water bath at the temperature of 90 °C. After 1 h, about 2 mL perchloric acid (60 wt%) was dropwise added into three-neck flask with mechanically stirring for about 2 min. The mixtures were directly poured into cold water and filtrated in a filter flask. Finally, the vinyl grafts were obtained after washing and drying. The weight of vinyl grafts was accurately measured. GP and GE were calculated by using the following equation:

$$GP = \frac{W_1}{W_2} \times 100\% \tag{1}$$

$$GE = \frac{W_1}{W_3} \times 100\% \tag{2}$$

Where W_1 is the weight of vinyl grafts in the MST copolymers, W_2 is the weight of starch in the MST copolymers, and W_3 is the initial weight of vinyl monomers. Molecular weight of vinyl grafts was measured on an agilent gel permeation chromatography (GPC, 1200 series, Agilent Technologies) equipped with a refractive index detector calibrated with polystyrene standards. A small amount of vinyl grafts were dissolved in tetrahydrofuran (THF) solvent and then injected into the GPC test cells for testing. The grafting reaction between starch and vinyl monomers was confirmed by using attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR). The FTIR spectra of pure starch, extracted MST and their corresponding homopolymers were recorded on a PerkinElmer FTIR spectrum 100S, equipped with Universal Diamond Crystal ATR accessory, in the reflectance mode over the range of 650-4000 cm^{-1} with a resolution of 4.0 cm^{-1}. Before analysis, the samples were crushed into powder in an extra accessory plate with a conic awl without any other previous preparation.

The MST/SBR compounds were characterized by using moving die rheometer (MDR), field emission scanning electron microscopy (FE-SEM), dynamic mechanical analysis (DMA), mechanical test machines and swelling test. Vulcanization characteristics, including scorch time (t_{S2}), optimum cure time (t_{90}), minimum torque (M_L), and maximum torque (M_H) were determined on a MDR 2020 reometer (Myung Ji Tech Co., Ltd) at 150 °C. Curing rate index (CRI) was employed to evaluate the cure rate of rubber compounds, which was

calculated by the following equation:

$$CRI = \frac{100}{t_{90} - t_{S2}} \tag{3}$$

The tensile fracture surface of compounds was coated with a thin layer of gold and then observed on a JSM-7500 FE-SEM (JEOL). Dynamic mechanical properties of the vulcanizates were investigated by a DMA 8000 (Perkin Elmer Instruments) from -80 to 0 °C with a frequency of 1 Hz and a rising temperature rate of 3 °C/min under nitrogen atmosphere. Tensile tests were performed on a Tinius Oisen H5KT-0401 testing machine at a speed of 500 mm/min according to ASTM D412. Tear strength was also measured on a Tinius Oisen H5KT-0401 testing machine at a speed of 50 mm/min according to ASTM D642. Hardness values were measured according to ASTM D2240 using a shore Durometer type A machine. Five different specimens were measured to give the average value. Swelling tests were carried out in toluene for 1, 3, 6, 12, and 24 h according to ASTM D471-79. Swelling ratio was calculated using the following equation:

$$\text{Swelling ratio\%} = \frac{w_2 - w_1/\rho_s}{w_1/\rho_r} \times 100\% \tag{4}$$

Where w_1 is the original weight of specimens and w_2 is the weight of specimens after swelling, ρ_r is the density of rubber (ρ_{SBR}=0.933 g/cm^3), and ρ_s is the density of solvent ($\rho_{toluene}$=0.867 g/cm^3).

Results and Discussion

Synthesis and Characterization of MST. The grafting mechanism is proposed as shown in Figure 1. It is well known that KPS is a thermal dissociation initiator and
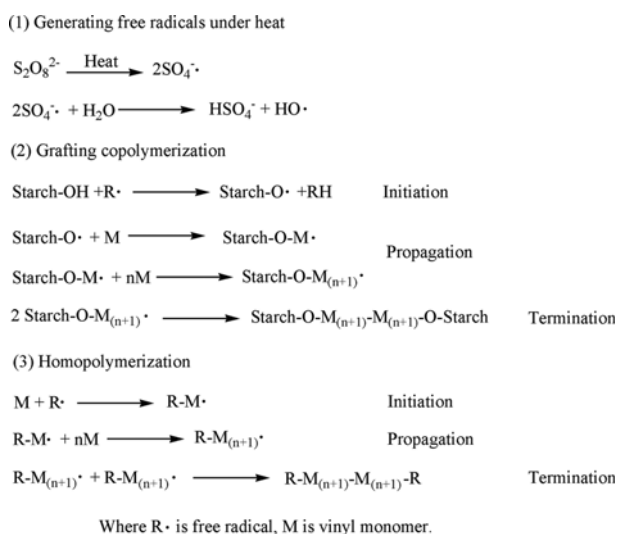

Figure 1. The proposed reaction mechanisms of graft copolymerization and homopolymerization.

widely used in the emulsion polymerization. When an aqueous solution of KPS was given heat, two sulfate radicals were generated via the dissociation of persulfate. Besides, a small amount of hydroxyl radicals could be also generated due to the reaction between sulfate radicals and water. In the presence of vinyl monomers and starch, the sulfate or hydroxyl radicals would react with both vinyl monomers and starch to generate vinyl monomer radicals and starch micro-radicals, resulting in the simultaneous occurrence of both graft copolymerization and homopolymerization. If starch particles were much closer to the sulfate radicals than vinyl monomers, it is believed that starch micro-radicals were generated firstly. In the presence of vinyl monomers, such as MMA, BA and S, these generated starch micro-radicals would add onto the double bond of vinyl monomers, producing the starch-graft-vinyl monomer radicals. After propagation and termination, MST copolymers, such as ST-*g*-PBA, ST-*g*-PMMA and ST-*g*-PS could be obtained. It is noteworthy that the polarity of vinyl monomer notably influenced the reactivity between starch micro-radical and vinyl monomer even in the presence of emulsifier. Vinyl monomer with higher polarity was easier to approach the surface of starch micro-radicals, resulting in higher GP and GE. However, if vinyl monomers were much closer to the generated radicals than starch particles, it is believed that the vinyl monomer radicals would be produced firstly. Homopolymerization occurred when the vinyl monomer radicals propagated and terminated with vinyl monomer radicals rather than starch radicals.

The grafting parameters of MST, such as GP and GE were presented in Table II. Among them, ST-*g*-PBA showed the highest values in both GP and GE, while ST-*g*-PS exhibited the lowest values. These observations could be explained by considering the combined effect of the monomer polarity and the tendency of homopolymerization. First, styrene had much lower polarity than butyl acrylate and methyl methacrylate. Thus, it is difficult for styrene to approach the surface of starch-macro radicals as above we discussed, resulting in the lowest GP and GE values. Second, compared with methyl methacrylate and styrene, butyl acrylate had much longer branched chains, which largely separated butyl acrylate monomer radicals and consequently restrained the tendency of homopolymerization, resulting in the highest GP and GE values. The molecular weight M_w of PBA, PMMA and PS grafts was 2.31×10^5, 0.46×10^5, and 0.53×10^5 g/mol, respectively.

Table II. Grafting Parameters of MST and Molecular Weight of Vinyl Grafts

MST	ST-*g*-PBA	ST-*g*-PMMA	ST-*g*-PS
GP (%)	38.5	30.8	20.1
GE (%)	62.4	52.8	43.6
M_w of grafts$\times 10^5$/g/mol	2.31	0.46	0.53
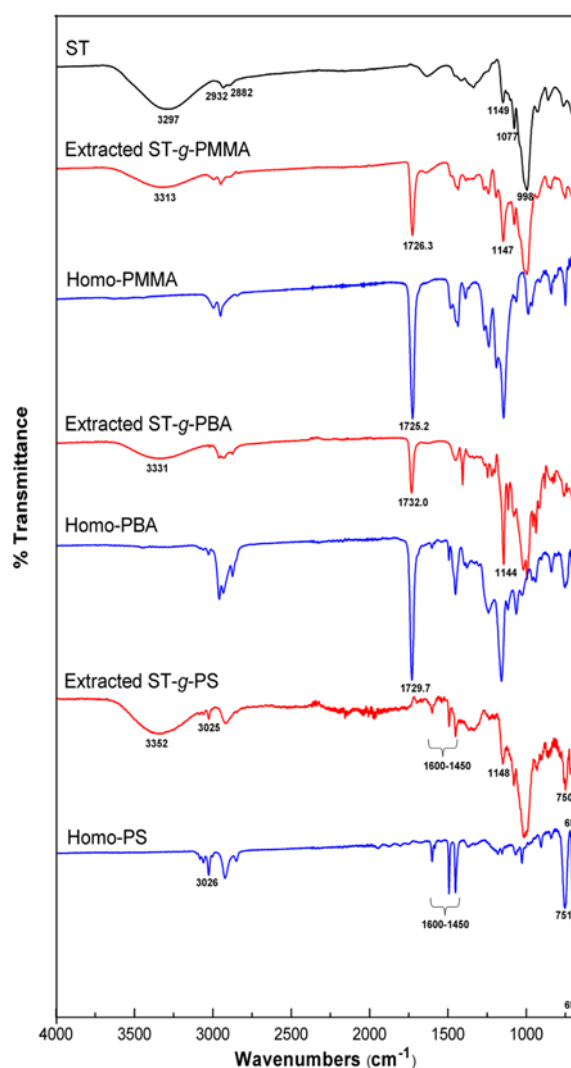
Figure 2. ATR spectra of pure starch, MST and their corresponding homopolymers.

The ATR-FTIR spectra of pure starch, extracted MST and their corresponding homopolymers are shown in Figure 2. In the spectrum of starch, the characteristic absorption peaks at 2882, 2932, and 3313 cm^{-1} were assigned to C-H and O-H stretching, respectively. In general, the C-O and C-O-C absorption peaks appeared in the range of 1000-1300 cm^{-1}.[28] In the case of corn starch, the C-O absorption peaks could be found at 998 and 1077 cm^{-1} and C-O-C absorption peak could be found at 1149 cm^{-1}. In the spectra of ST-*g*-PMMA, ST-*g*-PBA, and ST-*g*-PS, the C-O-C absorption peaks was shifted to 1147, 1144, and 1148 cm^{-1}, respectively, suggesting new C-O-C structure was formed via grafting reaction between starch and vinyl monomers. Moreover, it can be seen that the carbonyl group C=O absorption peaks of homo-PMMA and homo-PBA appeared at 1725.2 and 1729.7 cm^{-1}, respectively. After grafting reaction, the C=O absorption peaks was also shifted to 1726.3 and 1732.0 cm^{-1},

Table III. Vulcanization Characteristics of MST/SBR Compounds

Compounds	Neat	ST/SBR	ST-*g*-PBA/SBR	ST-*g*-PMMA/SBR	ST-*g*-PS/SBR	CB/SBR
M_L (lb-in)	0.9	2.0	1.4	1.8	1.9	1.0
M_H (lb-in)	9.3	16.4	11.0	12.5	13.4	12.5
M_H-M_L (lb-in)	8.4	14.4	9.6	10.3	11.5	11.5
t_{S2} (min)	0.92	1.33	1.33	1.33	1.35	0.93
t_{90} (min)	7.72	3.42	3.13	3.23	3.27	10.60
CRI (min^{-1})	14.7	47.8	55.6	52.6	52.1	10.34

respectively. It is note-worthy that ST-*g*-PBA exhibited higher-frequency in the carbonyl group absorption peak than ST-*g*-PMMA due to the stronger inductive effect of butyl group on the carbonyl group compared with methyl group. ST-*g*-PS showed the characteristic peaks of polystyrene grafts: 697-750, 1450-1600 and 3027 cm^{-1} for C-H stretching of aromatic ring, 1600-2000 cm^{-1} for C=C group in aromatic ring.[29] Thus, the appearance of new peaks and the changes in the position of C-O-C and C=O absorption peaks confirmed that vinyl monomers were chemically grafted onto the starch backbones.

Vulcanization Characteristics of MST/SBR Compounds. The vulcanization characteristics of MST/SBR compounds are summarized in Table III. It can be seen that the incorporation of starch in the SBR matrix led to a significant increase in the torque values due to the formation of filler-matrix interaction, indicating the reinforcing effect of starch. It is believed that the incorporation of starch also gave rise to a strong filler-filler interaction due to hydrogen bonding formed via hydroxyl groups in the starch surfaces, which also led to an increase in the torque values. Compared with ST/SBR vulcanizates, MST/SBR vulcanizates exhibited relative lower torque values. This may be attributed to the reduced filler-filler interaction as well as the improved dispersion. Since the vinyl grafts were grafted onto the starch surface instead of hydroxyl groups, the hydrogen bonding between starch-starch particles became weak, resulting in well dispersion of MST particles. This result suggested that the method of emulsion modification and latex compounding had a positive effect on the starch dispersion, which could be also observed on the FE-SEM micrographs. ST-*g*-PS/SBR and ST-*g*-PMMA/SBR compounds exhibited higher torque values than ST-*g*-PBA/SBR compounds. It well known that the glass temperature of Homo-PMMA, Homo-PS and Homo-PBA was 105, 100, and -56 ℃, respectively. It seems that the torque value of MST/SBR compounds was dependent on the stiffness of vinyl grafts.

The incorporation of filler also influenced on the cure rate of rubber compounds. However, the cure rate of filled rubber compounds was dependent on the types of fillers. For example, silica retarded the cure rate of rubber compounds due to the absorption of rubber accelerators on the silica surface; while clay and organic-modified clay accelerated the cure rate of rubber compounds due to its plate-like shape and amine groups.[30-32] As shown in Table III, the incorporation of the starch or MST accelerated the cure rate of SBR compounds. For example, the CRI values of ST/SBR, ST-*g*-PBA/SBR, ST-*g*-PMMA/SBR, and ST-*g*-PS/SBR compounds were 47.8, 55.6, 52.6, and 52.1 min^{-1}, respectively, which were much higher than neat SBR and CB/SBR compounds. Similar results were also observed from rice husk/ENR,[7,8] sisal/oil palm hybrid fibre/NR,[33] wood flour/ENR,[9] cellulose/NR,[34] and chitosan/rubber[35] compounds. It seems that the introduction of organic fillers promoted the vulcanization process of rubber compounds. The reasons for this observation have been extensively discussed. Bulter and Freakley[34] reported that the humidity and water content of rubber compounds strongly affected the cure rate. Jacob *et al.*[33] suggested that the increased cure rate was attributed to the higher time the rubber compounds remain on the mill during mixing. H. Ismail *et al.*[35] indicated that the interaction between organic filler groups (-OH) and rubber additives would be the reason for the cure enhancement. However, until now, there is no appropriate explanation for this result. From the results of vulcanization studies, we can conclude that starch or MST not only acted as reinforcing filler, but also behaved as effective vulcanizing agent for SBR compounds.

Morphology of MST/SBR Compounds. FE-SEM micrographs of the tensile fracture surface of MST/SBR compounds are shown in Figure 3. As the case of ST/SBR compounds, the particle size of starch ranged from 1 to 15 μm as shown in Figure 3(b), which was almost same as its original particle size. Liu *et al.*[17] explained that due to the strong re-crystallization and hydrogen bonding, an even distribution of starch particles in rubber matrix was difficult to be achieved. It is believed that the range of starch particle size (1-15 μm) greatly exceeded the distance of the SBR macromolecular chains and it could introduce an area of localized stress, resulting in an easy rupture on the SBR chains when stretching. In addition, lots of voids were clearly observed on or near the boundaries of starch particles, suggesting the poor compatibility between the starch and SBR matrix. However, as the case of MST/SBR com-
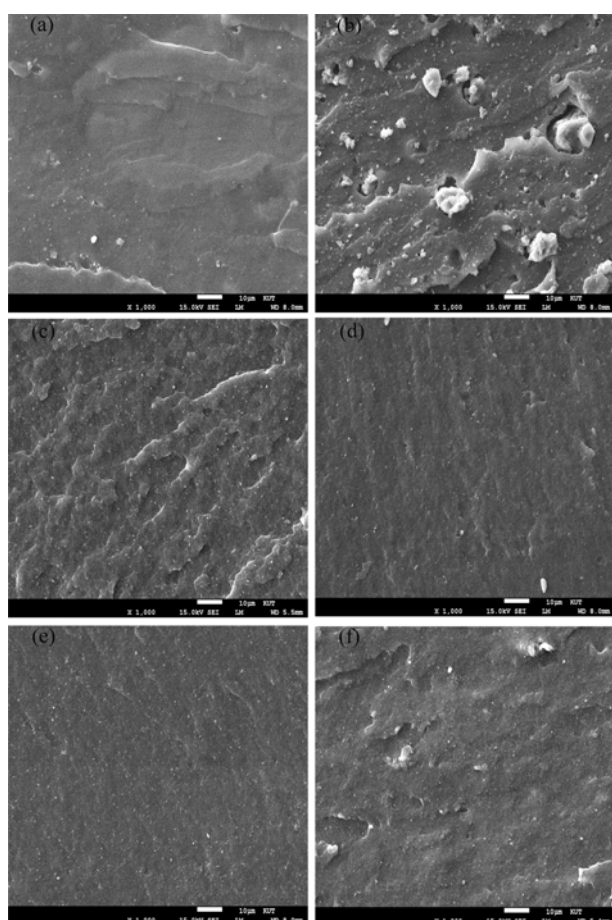
Figure 3. FE-SEM images of tensile fractured surface of (a) neat SBR, (b) ST/SBR, (c) ST-*g*-PBA/SBR, (d) ST-*g*-PMMA/SBR, (e) ST-*g*-PS/SBR, and (f) CB/SBR; Scale bar: 10 μm.

pounds, very clean fracture surfaces were observed as shown in Figure 3(c), (d), and (e). The particle size of MST was significantly deceased to less than 1 μm. A high multiple electron micrographs were observed in Figure 4. It can be seen that the particle size of MST was approximately 200-400 nm. From the comparison of the FE-SEM micrographs, we conclude that the method of emulsion modification and latex compounding truly had a positive effect on the dispersion of starch particles, which not only largely decreased the starch particles, but also led to a uniform dispersion of MST
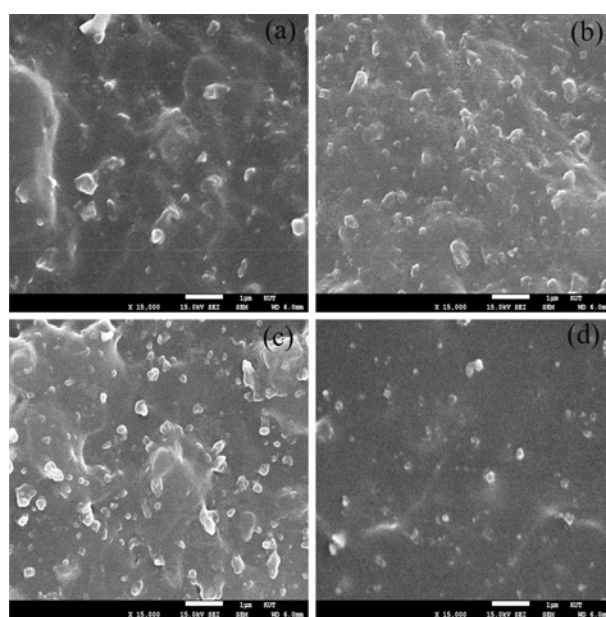

Figure 4. FE-SEM images of tensile fractured surface of (a) ST-*g*-PBA/SBR, (b) ST-*g*-PMMA/SBR, (c) ST-*g*-PS/SBR, and (d) CB/SBR; Scale bar: 1 μm.

particles in the SBR matrix. Figure 4(d) showed the fracture surface of the CB/SBR compounds. It can be seen that the CB N550 particle size was smaller than MST.

Mechanical and Dynamic Mechanical Properties of MST/SBR Vulcanizates. Table IV summaries the mechanical properties of all samples prepared; and their corresponding stress-strain curves are shown in Figure 5. It can be seen that the incorporation of starch slightly increased the overall mechanical properties of SBR vulcanizates. For example, the tensile and tear strength were increased to 3.3 MPa and 21.3 kN/m, respectively. These results agreed with the report of Wu *et al.*[6] However, this improvement was not enough for the application of SBR vulcanizates. In the case of MST/SBR vulcanizates, it can be seen that the incorporation of MST significantly enhanced the mechanical properties of SBR vulcanizates. For example, the tensile strength of ST-*g*-PBA/SBR, ST-*g*-PMMA/SBR, and ST-*g*-PS/SBR vulcanizates was increased to 6.5, 9.7, and 5.7 MPa, respectively. The tear strength of ST-*g*-PBA/SBR, ST-*g*-PMMA/SBR, and ST-*g*-

Table IV. Mechanical Properties of MST/SBR Vulcanizates

Compounds	Neat	ST/SBR	ST-*g*-PBA/SBR	ST-*g*-PMMA/SBR	ST-*g*-PS/SBR	CB/SBR
100% Modulus (MPa)	0.7	1.1	1.0	1.4	1.5	1.0
300% Modulus (MPa)	1.2	2.1	1.8	2.7	3.2	2.3
Tensile Strength (MPa)	2.9	3.3	6.5	9.7	5.7	9.5
Elongation (%)	636	564	1101	940	544	916
Tear Strength (kN/m)	10.2	21.3	30.8	43.7	24.9	40.0
Hardness (Shore A)	57.3	65.3	63	67	69.5	64.6
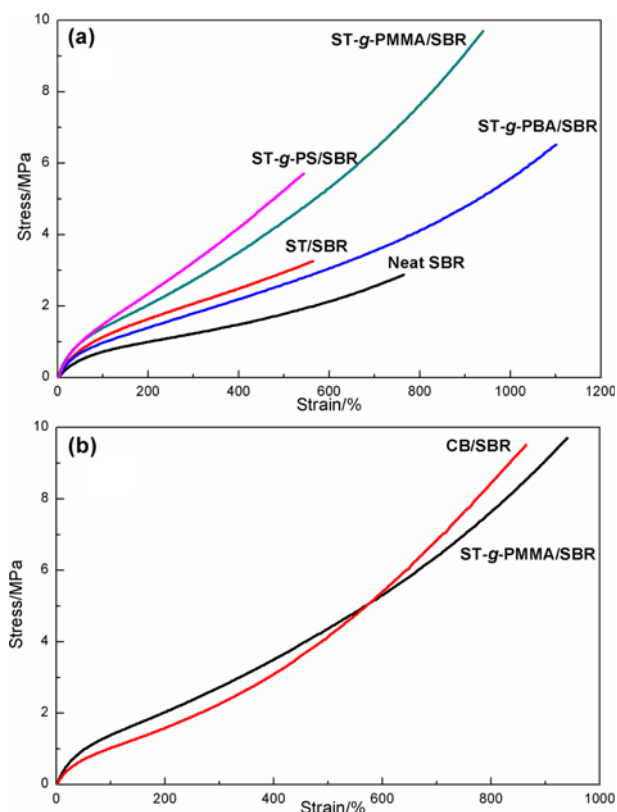
Figure 5. Stress-strain curves of (a) ST/SBR and MST/SBR; (b) ST-*g*-PMMA/SBR and CB/SBR vulcanizates.

PS/SBR vulcanizates was also increased to 30.8, 43.7, and 24.9 KN/m, respectively. Interestingly, the elongation of ST-*g*-PBA/SBR and ST-*g*-PMMA/SBR were found to be increased to 1101% and 940%, respectively. In a common case, the incorporation of reinforcing fillers improved the tensile strength and modulus while decreased the elongation. However, in this research, a different behavior that the incorporation of ST-*g*-PBA and ST-*g*-PMMA caused the simultaneous increase of tensile strength and elongation was observed. It has to be said that the complex vinyl grafts-starch-SBR vulcanizates were formed and the PBA and PMMA grafts could contribute to both tensile strength and elongation. Among the MST/SBR vulcanizates, ST-*g*-PBA/SBR vulcanizates showed the highest effect on the elongation, which was 1.7 times of neat SBR vulcanizates; whereas the 300% modulus was lower than ST/SBR vulcanizates. This observation seems to be contradicted with the report by Liu *et al.*[17] in which the 300% modulus of ST-*g*-PBA/NR vulcanizates was higher than that of ST/NR vulcanizates. It has to say that the different reinforcing mechanisms between NR and SBR resulted in the different observations. For NR, the fine state of dispersion fillers and the ability of strain-induced crystallization are two crucial factors in improving the mechanical properties of NR compounds. For SBR, due to its lack of self-reinforcing ability, the fine state of dispersion fillers

and strong interfacial interaction are two crucial factors in improving the mechanical properties of SBR compounds.[37] The increase in the 300% modulus of ST-*g*-PBA/NR vulcanizates was mainly attributed to the improved ability of strain-induced crystallization of NR in the presence of ST-*g*-PBA.[17] However, for SBR system, the presence of PBA grafts had no contribution on the ability of strain-induced crystallization, since SBR is lack of self-reinforcing ability. On the contrary, it is believed that the flexible PBA grafts could favor the movement of SBR macromolecular chains, resulting in a decrease in the 300% modulus value of ST-*g*-PBA/SBR. ST-*g*-PS/SBR vulcanizates displayed the highest effect on 100% and 300% modulus and hardness, which were 2.1, 2.7 and 1.2 times of neat SBR vulcanizates. It is well known that PS grafts had benzene groups and hence there would be a strong delocalized π-π adhesion between PS grafts and SBR macromolecular chains.[38-40] This strong π-π adhesion resulted in the highest values in the 100% and 300% modulus for ST-*g*-PS/SBR vulcanizates. ST-*g*-PMMA/SBR vulcanizates exhibited the highest effect on the increase of tensile and tear strength, which were 3.3 and 4.3 times of neat SBR vulcanizates. In addition, it is found that the mechanical performances of ST-*g*-PMMA/SBR compounds were even superior to those of CB/SBR compounds with the same loading (20 phr) of fillers, as shown in Figure 5(b).

The significantly reinforcing effect of MST on the SBR vulcanizates can be also confirmed by dynamic mechanical analysis (DMA). Figure 6(a) and (b) shows the logarithm of the storage modulus (log E') and the loss factor (tan δ) as a function of temperature, respectively. MST/SBR vulcanizates exhibited higher log E' values compared with neat SBR, suggesting the reinforcing effect of MST, which confirmed that MST strongly restricted the movement of SBR macromolecular chains. ST-*g*-PBA/SBR vulcanizates displayed relative lower E' in both glassy and rubbery regions compared with ST-*g*-PMMA/SBR and ST-*g*-PS/SBR vulcanizates. In addition, the glass temperature T_g could be obtained from the temperature of tan δ peak value, as shown in Figure 6(b). We noticed that the T_g values were slightly increased with the incorporation of ST-*g*-PMMA and ST-*g*-PS, while slightly decreased with the incorporation of ST-*g*-PBA.

The value of tan δ_{max} could be considered as an efficient parameter to evaluate the interfacial interaction between two phases. The interaction parameter B between polymer matrix and filler phase was calculated by using the following equation:[41,42]

$$B = \frac{1}{V_f}\left(1 - \frac{\tan\delta_{filled}}{\tan\delta_{unfilled}}\right) \tag{5}$$

Where tan δ_{filled} and tan $\delta_{unfilled}$ are the loss factor of filled and unfilled polymer matrix, respectively; V_f is the volume fraction of filler. Greater value of B means greater interfacial strength. We noticed that the interaction parameter B is inversely dependent on the value of tan δ_{filled}. Therefore,
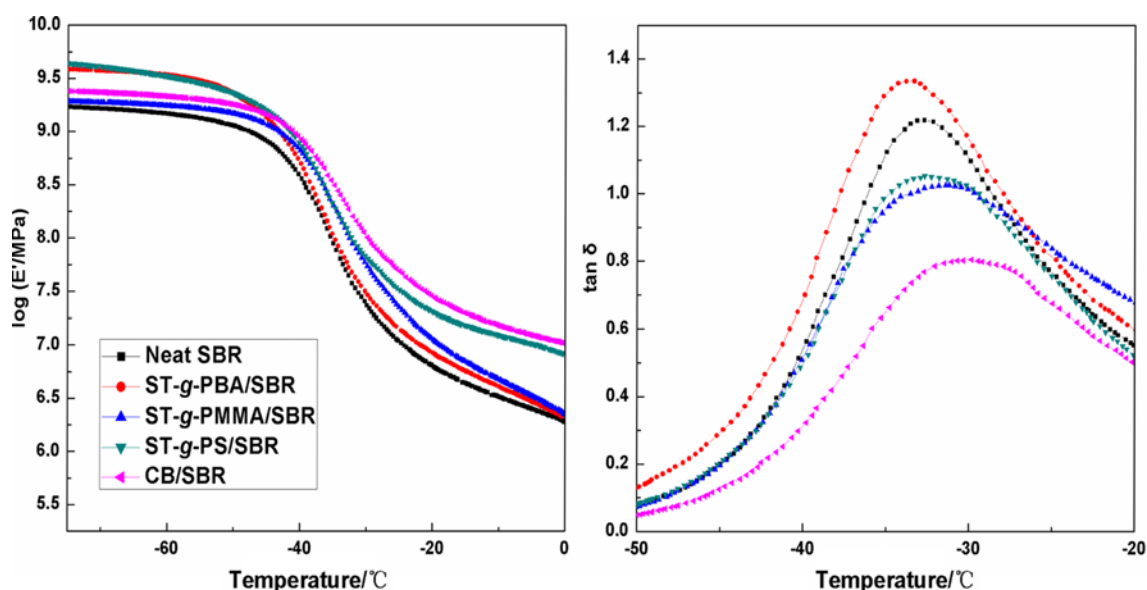
Figure 6. Dynamic mechanical curves of MST/SBR vulcanizates (a) logarithm of the storage modulus (log *E*') and (b) the loss factor (tan δ) as a function of temperature.

lower value of tan δ_{filled} means stronger interfacial strength for the filled rubber compounds. As shown in the Figure 6(b), ST-*g*-PMMA/SBR and ST-*g*-PS/SBR vulcanizates exhibited much lower tan δ_{max} values, indicating the stronger interfacial bonding between two phases. ST-*g*-PBA/SBR vulcanizates showed an opposite result that the tan δ_{max} value was even higher than that of neat SBR. Based on these observations, we conclude that ST-*g*-PMMA and ST-*g*-PS acted as effective reinforcing fillers in the SBR matrix; while ST-*g*-PBA acted as plasticizer in the SBR matrix. This result corresponded with the mechanical test result. Owing to the long and flexible branched butyl groups, the PBA chains could easily interposed itself between the SBR macromolecular chains and then broke down the interactions between SBR macromolecular chains. Consequently, the mobility of SBR macromolecular chains was notably enhanced.

Swelling Properties of MST/SBR Vulcanizates. Swelling ratio is a very important factor for rubber vulcanizates, since it is related to the crosslinking density of rubber vulcanizates, but also to the physical or chemical interfacial interactions between the rubber matrix and filler. Thus, it is essential to investigate the swelling ratio of rubber vulcanizates. Figure 7 showed the swelling ratio of MST/SBR vulcanizates in toluene solvent. It can be seen that the swelling ratio increased very fast at the early 6 h and then changed little from 6 to 24 h, indicating the adsorption saturated. The swelling ratio of neat SBR was 352.9%. When starch was incorporated, the swelling ratio decreased to 253.9%. This may be attributed to the hydrophilic characteristic of starch. ST-*g*-PS/SBR and ST-*g*-PMMA/SBR vulcanizates exhibited much lower swelling ratio compared with ST/SBR vul-
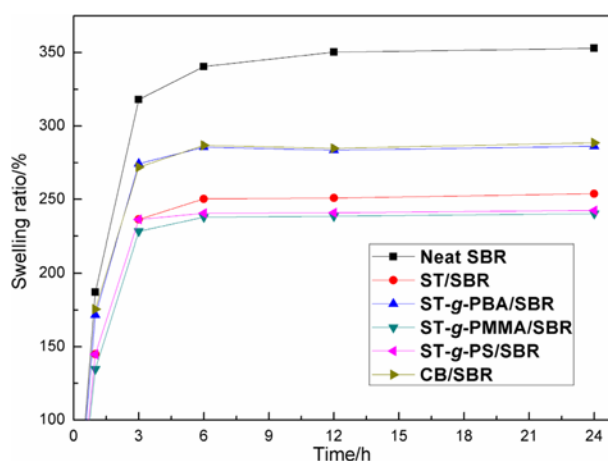

Figure 7. Swelling ratio of MST/SBR vulcanizates.

canizates, indicating the higher cross-linking density values. Interestingly, ST-*g*-PBA/SBR vulcanizates showed higher swelling ratio compared with ST/SBR vulcanizates, which confirmed the plasticizer role of ST-*g*-PBA in the SBR matrix, again.

Reinforcing Mechanism of MST in the SBR Matrix. The significantly reinforcing effect of MST in the SBR matrix can be attributed to the largely improved MST dispersion and the occurrence of physical entanglement between vinyl grafts and SBR macromolecular chains. A proposed reinforcing mechanism of MST in the SBR matrix is illustrated in Figure 8. As the case of ST/SBR compounds, when a tensile force was applied to the rubber matrix, owing to the large particle size of starch and the poor the interfacial bonding between the hydrophilic starch particles and the
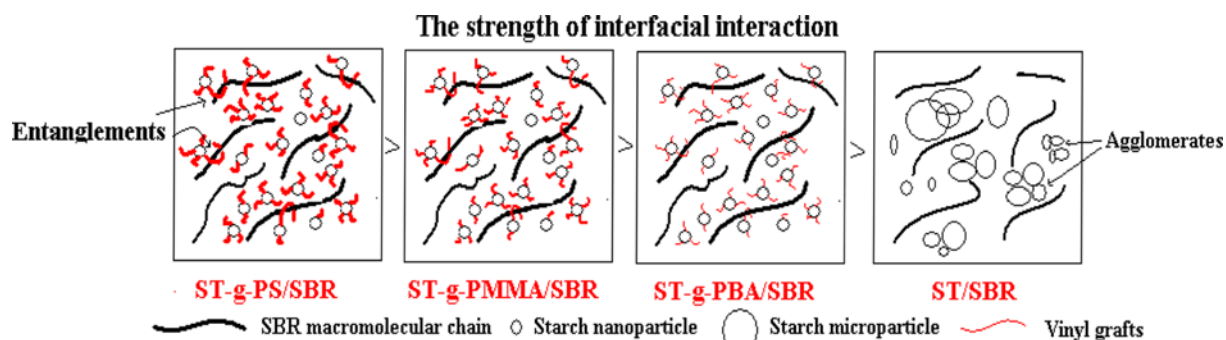
Figure 8. Reinforcing mechanism of MST in the SBR matrix.

hydrophobic SBR matrix, the fracture easily occurred on or near the boundaries of the starch micro-particles. The method of emulsion modification and latex compounding not only remarkably decreased the particle size of starch, but also improved the dispersion. In addition, the vinyl grafts behaved as many "hands" on the surface of MST particles. These "hands" physically entangled or captured onto the SBR macromolecular chains, resulting in many physical crosslinking points in the MST/SBR systems. When a tensile force was applied to the rubber matrix, these points could add much friction and dissipate strain energy. Therefore, the fracture of MST/SBR became more difficult, the impressive mechanical performances were achieved. Besides, we found that the stiffness of the vinyl grafts significantly influenced on the strength of interfacial interaction as well as the performances of MST/SBR compounds. One could make sure that PBA grafts favored the local movement of SBR macromolecular chains rather than restricting due to the flexible butyl chains based on the observed results of vulcanization characteristics, swelling, mechanical and dynamic mechanical tests.

Conclusions

The method of emulsion modification and latex compounding was reported to enhance the performances of starch/SBR compounds. The incorporation of MST, such as ST-*g*-PMMA in the SBR matrix significantly improved both the tensile and tear strength up to 9.7 MPa and 43.7 KN/m, respectively, which were 3.3 and 4.3 times of neat SBR vulcanizates. The remarkably improved mechanical properties could be attributed to the improved dispersion and the occurrence of physical entanglements between vinyl grafts and SBR macromolecular chains. In addition, a suitable selection of grafting vinyl monomers was also important to obtain the high performance of MST/SBR compounds.

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