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Incorporation of modified soy protein isolate as filier in BR/SBR blends

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Abstract The surface modification of soy protein isolate (SPI) and the use of modified SPI as reinforcing filler replaced carbon black in BR/SBR composites were studied. The effects of coupling agents γ-aminopropyltriethoxysilane (KH-550), γ-methacryloxypropyltrimethoxysilane (KH-570), bis-(γ-triethoxysilylpropyl)-tetrasulfide (Si-69), isopropyl tri-(dioctylpyrophosphate) titanate (NDZ-201) on the physical and mechanical properties of the composites were also investigated. Modified SPI was analyzed by Infrared spectra, scanning electron microscopy, and X-ray diffraction. The results showed that the optimal reaction conditions were determined, that is, the optimal reactions were 4 g SPI, 50% Glycidyl methacrylate (by SPI weight), 3 h of reaction time and 80 °C reaction temperature. Through the physical and mechanical properties of composite, the results showed that when a small number of modified SPI (3–5 phr) as reinforcement agent was used, the mechanical properties were improved. KH-550 had good effect on enhancing the overall properties of the composites.

Introduction

In most of industrial applications, elastomers are used as composite materials. The incorporation of various fillers into rubbery polymers imparts many interesting and useful properties to the particle-filled composite materials. It is well known that the properties mainly depend, among other things, on the dispersion condition of filler particles and their principal relevant properties (e.g., particle size, surface area, aggregate structure, and surface activity) and on rubber–filler interactions [1]. During the last years, the effects of different types of fillers on rubber compounds have been studied, in search of improvements on its physical and mechanical properties. Among these fillers are carbon black, silica, calcium carbonate, etc. Recently, the application of fillers of organic nature has attracted interest due to their low cost, renewable, and environment friendly nature [2].

Experiments in the fabrication of biodegradable materials from renewable plant resources showed that protein from soybean was a potential raw material, because it is largely available, renewable, and biodegradable. Soybean proteins are composed of polypeptides, which consist of 20 types of amino acids covalently linked by peptide bonds. Approximately, 38% of amino acid residues are nonpolar and nonreactive, whereas 58% of amino acid residues are polar and reactive. By taking the advantage of protein water solubility and reactivity, the food functionality, adhesive properties, and plastic performance of soy protein could be improved by modifications including denaturation. Denaturation can modify the secondary, tertiary, or quaternary structures of protein molecules without breaking peptide bonds. Methods of denaturation include exposure to heat, acid or alkali, detergent, or organic solvent [3].

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Research on functional properties of modified proteins has focused on food applications such as solubility, viscosity, gelation, and emulsion stability [4]. Little has been reported on modifications of soy protein to apply in rubber. Thus, it is the aim of this contribution to assess the potential utilization of modified soy protein isolate (SPI) in rubber compounds. Therefore, the objective of the present investigation is to study the influence of soy protein content and particle size on the rheological and mechanical behavior of rubber compounds. A comparative study was also considered with conventional fillers such as carbon black, silica, and calcium carbonate.

Experimental

Materials

Unmodified SPI powder was obtained from Bo Feng Co. (Liaoning, China). Glycidyl methacrylate (GMA) was purchased from Dow Chemical Co., United States. Urea, ammonium persulfate ($(NH_4)_2S_2O_8$), sodium bisulfite ($NaHSO_3$) were purchased from Bodi Chemical Co. (Tianjin,China). All other chemicals and solvents were of analytical grade and used without further purification. Butadiene rubber (BR) and styrene–butadiene rubber (SBR) were supplied by Petrochemical Co., Jilin. The silane coupling agents used in this study were as follows: γ-aminopropyltriethoxysilane KH-550, γ-methacryloxypropyltrimethoxysilane KH-570, and bis-(γ-triethoxysilylpropyl)-tetrasulfide Si-69. The titanate coupling agent in this study was isopropyl tri-(dioctylpyrophosphate) titanate NDZ-201. They were purchased from Shuguang Chemical Co. (Nianjing, China). Zinc oxide (ZnO), stearic acid, sulfur, and other chemicals used were all commercial grades.

Preparation of modified SPI powder

About 1 mol/L urea was used to prepare in distilled water at room temperature. Four grams of SPI powder was then mixed with 40 mL of the urea/distilled water solution at room temperature and stirred at high speeds for about 15 min. The slurry mixture was prepared in an oil bath maintained at 50 °C for about 30 min. Ammonium persulfate (0.44 g; 0.4 mol/L) as an initiator and sodium bisulfite(0.2 g; 0.4 mol/L) as an antioxidants were both dissolved in 5 mL of distilled water and were added, and then it was kept at 80 °C for 10 min. After that GMA (50% of SPI weight) monomer was added and the reaction was maintained at 80 °C for 3 h. Graft copolymers were separated by filtration, washed with ethanol and acetone, and air-dried for 12 h. The excess water was decanted and was dried in a vacuum drying oven at 50 °C for 24 h.

Preparation of compounds

BR and SBR were masticated on a laboratory two-roll mill and fillers were added at different percentages. The blends were prepared as per the formulation given in Table 1. All rubber compounds were compression molded into sheets and different shapes for testing, in a hydraulic press at 150 °C and 10 MPa according to their t_{90}. All specimens were then cut from the vulcanized sheets.

Table 1 Formulations

Material	A	B	C	S1	S2	S3	S4	S5	T1	T2	T3	T4
BR	60	60	60	60	60	60	60	60	60	60	60	60
SBR	40	40	40	40	40	40	40	40	40	40	40	40
CB	50	40	40	47	45	42	40	38	40	40	40	40
Silica	–	10	–	–	–	–	–	–	–	–	–	–
Calcium carbonate	–	–	10	–	–	–	–	–	–	–	–	–
NS	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
4020	1	1	1	1	1	1	1	1	1	1	1	1
ZnO	5	5	5	5	5	5	5	5	5	5	5	5
Stearic Acid	2	2	2	2	2	2	2	2	2	2	2	2
Modified SPI	–	–	–	3	5	8	10	12	10	10	10	10
S	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1
Si-69	–	–	–	–	–	–	–	–	1.5	–	–	–
KH-570	–	–	–	–	–	–	–	–	–	1.5	–	–
KH-550	–	–	–	–	–	–	–	–	–	–	1.5	–
NDZ-201	–	–	–	–	–	–	–	–	–	–	–	1.5

Analysis

Infrared SPI and modified SPI were carried out by infrared spectrophotometer (Buck Scientific Inc. Norwalk, CT USA, Model M500). X-ray diffraction (XRD) patterns of the samples were recorded with a Bruker D8 Advance X-ray diffractometer. The angular range was from 10° to 40° (2θ).

Morphology

Scanning electron microscopy (SEM) was performed to investigate the morphology of SPI powder and fractured surfaces of rubber vulcanizates with a JEOL JSM 6360LV instrument. The surface was sputter coated with gold before examining under the microscope.

Mechanical properties

Tensile properties were measured following GB/T528-1998 using a MTS tensometer at 500 mm/min crosshead speed. Hardness (shore A) was done using XHS (China) hardness tester according to GB/T531-1999. Resilience and abrasion loss tests were also done using Gaotie (Taiwan) resilience and abrasion testers according to GB/T1681-91 and 1689–1998, respectively.

Water absorption measurements

Water absorption was measured according to the standard GB/T1690-2006 method. The specimens were dried at 50 °C until constant weight was achieved, and then immersed in water at room temperature. Rectangular slabs 40 mm long, 10 mm wide, and 2 mm thick were cut from the compression-molded samples and totally immersed in water maintained at room temperature (25 °C) for 24 h. The percentage water absorbed was estimated from the difference in weights of the as-molded samples and the immersed sample.

Results and discussion

Modified soy protein isolate analysis

Infrared spectroscopy

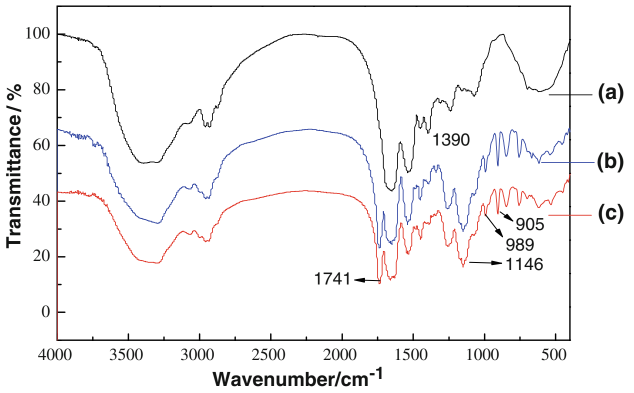

Fig. 1 IR spectra of raw SPI (*a*), SPI-g-GMA (*b*), and extracted graft copolymer (*c*)

The Infrared (IR) spectra of the raw SPI and SPI-g-GMA (10 g per 20 g of SPI) are shown in Fig. 1. The IR spectra of SPI-g-GMA (Fig. 1b) indicated the appearance of new peaks in the region of 1741, 1146, 989, and 905 cm^{-1} confirming the presence of ester carbonyl group (C=O) [5], C–O–C, C=C, and the epoxy groups [5]. These four peaks are absent in the raw SPI (Fig. 1a). The IR spectra by measuring the intensity of the 989 cm^{-1} band attributed to the C=C vibrations of ethylene. The peak observed at 1390 cm^{-1} is due to the –COOH group of SPI. The drastic reduction in the –COOH group in the SPI-g-GMA composite spectra may be ascribed to the consumption of –COOH groups during the grafting reactions.

The IR spectra of extracted graft copolymer (Fig. 1c) therefore gives supporting evidence that the GMA had been successfully grafted onto SPI.

X-ray diffraction analysis

Figure 2 shows the X-ray patterns of the pure SPI powder and modified SPI. It can be seen that SPI gives two strong characteristic peaks at 2θ values of around 9° and 19° whereas modified SPI results in only one strong peak at 2θ value of 19°. This, in turn, indicates that the crystalline

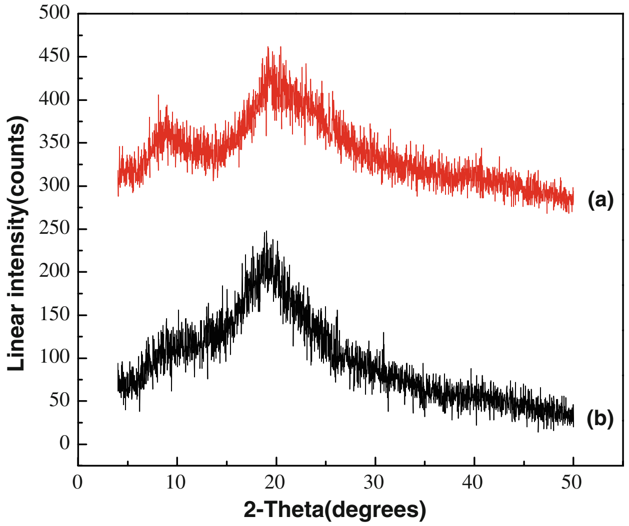

Fig. 2 X-ray diffraction pattern of SPI (*a*) and modified SPI (*b*)

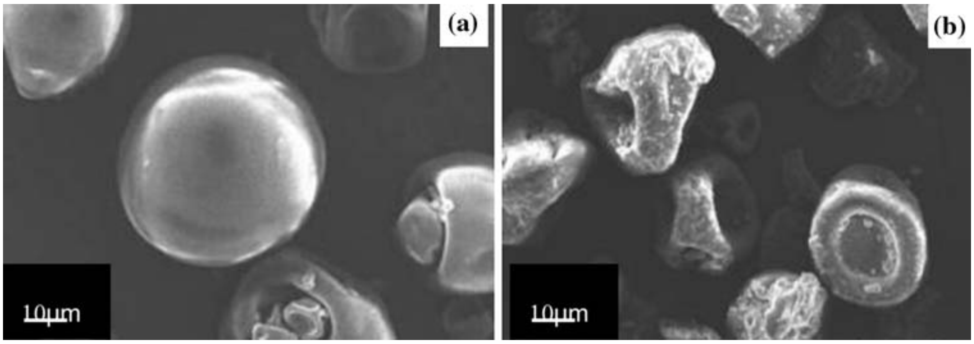

Fig. 3 SEM micrographs of comparison of SPI (**a**) and modified SPI (**b**)

structure of SPI has collapsed after modification. Figure 2b shows that the XRD characteristic peak is gentle, and its intensity is decreased after the SPI compatibilized by GMA, indicating that the presence of GMA reduces the crystallinity of modified SPI.

SEM analysis

Scanning electron micrographs of the materials show surface morphology of the SPI and modified SPI samples revealing some differences in the shape of them as well as the changes resulting from modification (Fig. 3a, b). Modified SPI particles (Fig. 3b) seem to be somewhat smaller and rougher compared to those of pure SPI (Fig. 3a). Considering the different surface areas, an important factor of fillers in polymers, the presence of smaller particles gives an advantage to modified SPI over pure SPI. Large particles may be of importance considering a possible decrease or even absence of the reinforcing effect in the polymeric or elastomeric matrix, especially for unmodified filler surface where adhesion on the face boundaries is low.

Rubber/modified SPI composite analysis

Mechanical properties

Figure 4a–f shows the mechanical properties of BR/SBR/modified SPI rubber blend vulcanizates. It can be found that elongation at break and abrasion loss of vulcanizates increase and tensile strength, modulus at the elongation of 300%, hardness decrease, but resilience hardly changes when modified SPI content increases. Table 2 shows that the tensile strength and elongation at break of S4 are higher than C, but them lower than A and B, and modulus is lower than others. These can be attributed to filler presence in vulcanizates, particle size of filler and its compatibility with elastomeric matrix (Table 2). It can be seen that better interaction between modified SPI and rubbers is obtained when a small number of modified SPI employed; however, the tensile strength is higher than pure CB added and that it decreases gradually when filler content increased (Fig. 4a). Studies on reinforcement generally agree that the surface interaction (physical or chemical) between fillers and rubber molecules or network segments promotes better final properties [2]. Figure 4b shows that it is better than pure CB added when modified SPI added to 3 phr and modulus at 300% strain of compounds tend to decrease with filler increased. Figure 4c shows higher elongation at break due to a reaction between the filler and the polymer thanks to the appearance on the surface of novel functional group, e.g., vinyl group. This agrees with the change of hardness (Fig. 4d). When modified SPI are added to 12 phr, elongation at break slightly decreases and that is due to the formation of higher filler aggregates between the flexible chain segments, which act as obstacles to their sliding.

Figure 4e shows the abrasion loss of the samples with increasing proportions of modified SPI. In the case of the samples, the abrasion loss increases with increasing proportion of modified SPI and the increase of volume loss is much larger at higher proportions of modified SPI. This behavior can be correlated with the mechanical properties and morphology of the system. Previous studies [6] also show that wear properties are dependent on the mechanical strength and morphology of the system. When the rubber content is higher and forms a continuous phase, dynamic crosslinking imparts high strength to the rubber phase. This increases the wear resistance.

As follows from the data (Table 3), optimum mechanical properties are obtained for vulcanizates containing modified SPI filled with KH-550 (T3) silane coupling agent compared with others and unfilled blends, especially tensile strength and volume loss. This result seems to be due mainly to the higher affinity of amine groups compared with the groups of else coupling agents toward the functional groups of BR/SBR rubber blends, vulcanized with sulfur. The increase in mechanical properties of KH-550 treated modified SPI also indicates the presence of good interfacial interactions and adhesion between the polymer matrix and filler particles, moreover, KH-550 is effective to improve the dispersion of modified SPI.

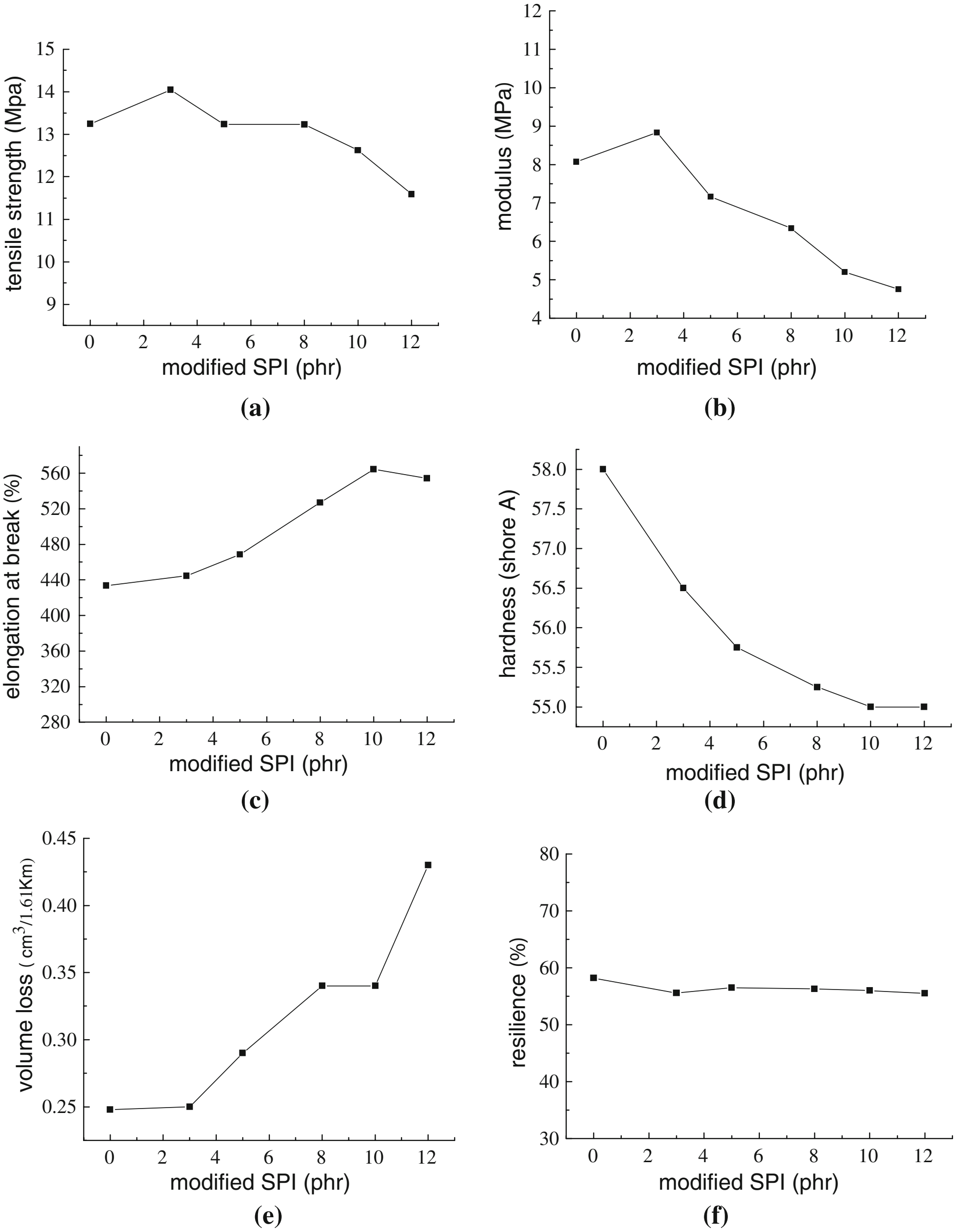

Fig. 4 Mechanical properties of the materials showing the effect of different modified SPI content, tensile strength (**a**), modulus (**b**), elongation at break (**c**), hardness (**d**), volume loss (**e**), and resilience (**f**)

Table 2 Mechanical properties of BR/SBR blends filled with different filler

	A	B	C	S4
Tensile strength (MPa)	13.24	13.76	11.04	12.62
Elongation at break (%)	433.54	513.24	464.73	564.37
Modulus at 300% strain (MPa)	8.07	6.67	6.14	5.2
Hardness (shore A)	58	52.75	52.5	55
Volume loss (cm^3)	0.248	0.30	0.35	0.34
Resilience (%)	58.2	53.7	57	56
Density (g/cm^3)	1.119	1.121	1.127	1.102

SEM analysis

The fracture surfaces of the specimens were also examined by SEM. The scanning electron micrographs of statically vulcanized 50 phr CB, 10/40 Silica/CB, 10/40 calcium carbonate/CB, and 10/40 modified SPI/CB, are shown in Fig. 5a–d. Figure 5a and b shows that the dispersion and compatibility of CB and silica in rubber are better than calcium carbonate and modified SPI, because the particle sizes CB and silica are smaller than them. The vulcanized blend (Fig. 5c) shows a large number of voids and

Table 3 Mechanical properties of modified SPI/BR/SBR blends filled with different coupling agents

	S4	T1	T2	T3	T4
Tensile strength (MPa)	12.62	12.38	11.23	13.47	11.3
Elongation at break (%)	564.37	560.79	844.89	561.8	656.59
Modulus at 300% strain (MPa)	5.2	5.01	3.93	5.9	3.48
Hardness (shore A)	55.25	55.75	55	54.5	52.5
Volume loss (cm^3)	0.34	0.39	0.40	0.22	0.44
Resilience (%)	56	56.9	55	56.3	52.6
Density (g/cm^3)	1.102	1.102	1.105	1.106	1.104

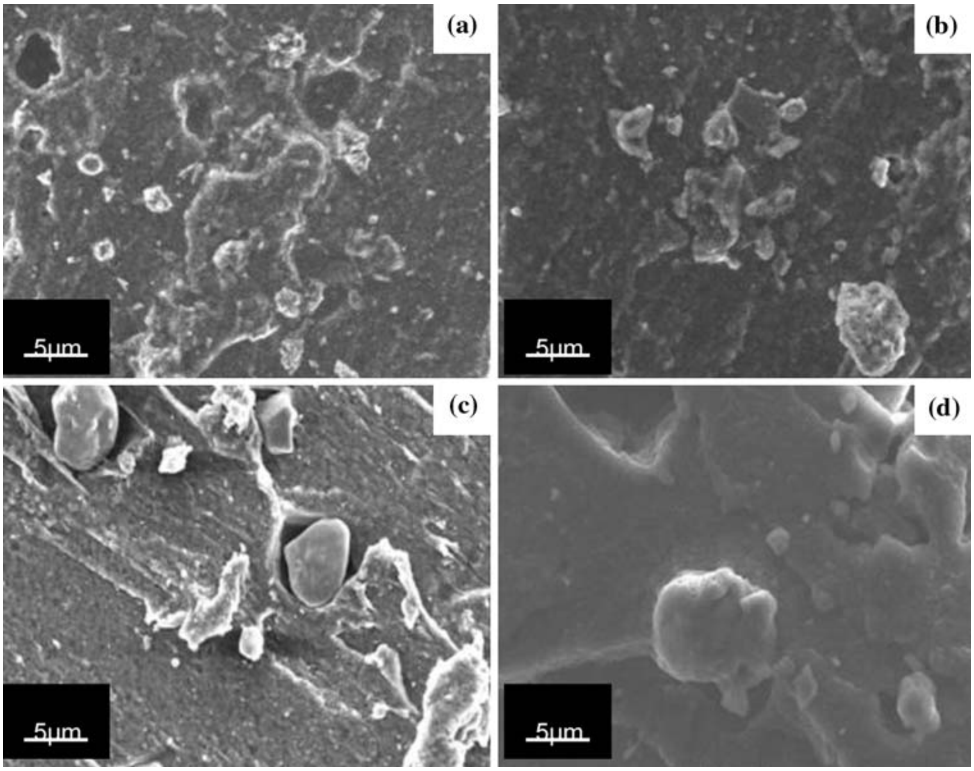

Fig. 5 SEM micrographs of comparison of fracture surfaces of vulcanized blends: 50 phr CB (**a**), 10/40 silica/CB (**b**), 10/40 calcium carbonate/CB (**c**), and 10/40 modified SPI/CB (**d**)

discontinuity on the fracture surface of the samples. This is an indication of uncompatibility or heterogeneous phase structure of the blend. Figure 5d shows the SEM microphotograph of BR/SBR blend sample in the presence of modified SPI. It can be see that modified SPI enhances the interfacial interaction between particles and elastomeric matrix.

Water absorption measurements

The percentage water absorbed by the materials after immersion in water at room temperature for 24 h is shown in Fig. 6a. A dramatic increase in the intrinsic water absorption tendency of BR/SBR blends by incorporating the modified SPI fillers is clearly evident in the figures. When modified SPI added to 10 phr, water absorption is saturant. Properties such as elastic modulus, impermeability, and resistance to weathering agents including aggressive waters, are directly related to durability [7]. Figure 6b shows results of the sorption of water by immersion, which is related to the open porosity of the specimens tested and the group of filler such as modified SPI. Because of remaining polar groups, water absorption of S4 is highest.

Figure 6c shows the moisture content of the different coupling agents added. This increase in water absorption of the composites is further enhanced by applying Si-69(T1), KH-570(T2), and NDZ-201(T4) coupling agents to the fillers, except KH-550(T3). It may be that the KH-550 coupling agent can react spontaneously with the surfaces of the modified SPI and rubber matrix to form crosslink, and undergo a condensation reaction leading to polysiloxane and polymer–matrix bond formation. The covalently bonded structure in the interface between the polymer and the fillers is resistant to water, leading to the observed water resistance behavior of the coupled composite. It is important that the alkyl group of the coupling agent be selected to be compatible with the soy protein matrix. Because soy protein is composed of poly(amino acids), γ-aminopropyltriethoxysilane (KH-550) was found to produce optimum results at very low levels [8].

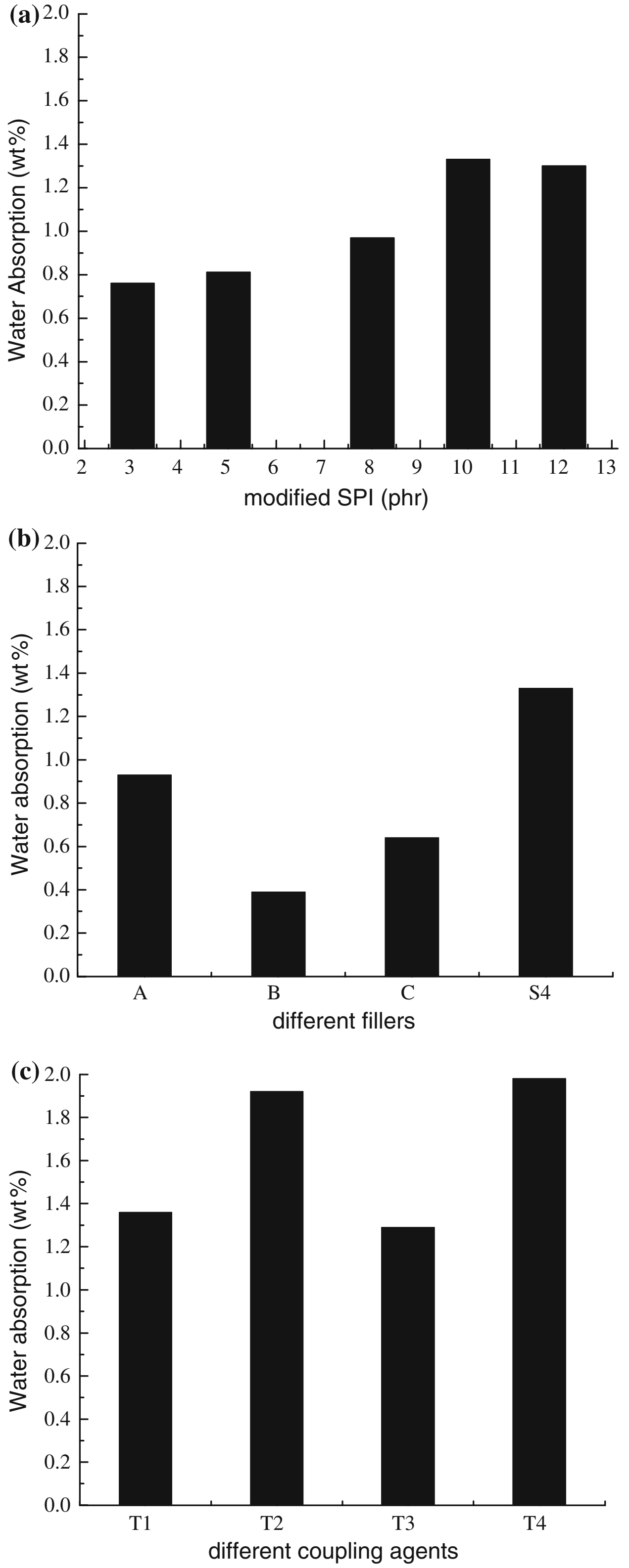

Fig. 6 Water absorption of the materials showing the effects of different modified SPI content (**a**), different fillers (**b**), and different coupling agents (**c**)

Conclusion

Based on the results of this study, we conclude the following:

1. Free radical grafting of GMA onto SPI was effective in urea solution using ammonium persulfate as initiator. IR spectral analysis provided evidence of the grafting of GMA onto the SPI. From the data of XRD can be seen that the partial crystallinity of the SPI is reduced by the modification of GMA.
2. It can be seen that they are good compatibility from the SEM photographs of fractured surface of BR/SBR/modified SPI blend.
3. When 3–5 phr modified SPI and silane coupling agent KH-550 are added, the mechanical properties can be increased.
4. The water absorption of vulcanizates increased when modified SPI is filled, which is due to the remaining groups of modified SPI such as amido group and hydroxyl group, but silane coupling agent KH-550 can improve the water absorption.

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