

Water-swellaable rubber blend from epoxidized natural rubber and superabsorbent polymer composite

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Abstract

Epoxidized natural rubber (ENR) and a superabsorbent polymer composite (SAPC) along with other minor components were mechanically blended in an internal mixer (Brabender Plasticorder) at 40°C and 60 r/min rotor speed with 80% fill factor. The SAPC was synthesized by grafting polyacrylamide onto hydroxyethyl cellulose backbones and adding bentonite clay. The first water-swelling behavior was investigated with alternative epoxidation levels of the ENR. Water-swellaable rubber (WSR) performed well in terms of water absorbency, and weight loss was achieved with 50 mole% epoxidation level, so this ENR was chosen for the rubber matrix from which WSR was prepared with various contents of SAPC (0, 5, 10, 15, and 20 phr). The results indicated that SAPC loading positively affected water absorbency, which was resulted by increasing weight loss and loss of mechanical properties, such as tensile strength and elongation at break. However, the modulus increased with SAPC content. WSR formulated from ENR-50, SAPC, and other ingredients resulting in good water-swelling behaviors and modulus, while the tensile strength and elongation at break had opposition. SAPC was an important factor to control the overall WSR properties.

Keywords

Water-swellaable rubber, epoxidized natural rubber, superabsorbent polymer composite, graft copolymerization

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Introduction

Natural rubber is a hydrophobic material with almost no swelling in water, and its surface is not wettable with water unless functional chemical modifications are done. A new functional material named water-swallowable rubber (WSR) is composed mainly of elastomer with added hydrophilic polymer.¹ The WSRs possess not only the general rubber properties, such as high elasticity, resilience, and high toughness, but can also absorb large quantities of water. Their volumetric expansion can be up to 1.5-fold in water (or in other fluids). They have been applied in underground engineering as caulking, sealing, and leakage-stopping materials.² WSRs are generally manufactured by one of the two methods, namely by grafting hydrophilic monomers on rubber backbone or by mechanical blending of a rubber matrix with a superabsorbent polymer to form a composite. The latter is the most promising way due to ease of production, desirable product properties, and low cost.

Therefore, multicomponent polymer blends received attention from both academic technologists and manufacturers producing WSR, and excellent water absorption and mechanical properties have been achieved. Various rubbers have been used as the elastomeric material on producing WSR by mechanical blending with various types of superabsorbent polymers/composites (SAPs/SAPCs), such as natural rubber,^{3–6} epoxidized natural rubber (ENR), maleated natural rubber,⁷ chloroprene rubber,^{8,9} epichlorohydrin rubber,^{10–12} and synthetic chlorinated polyethylene rubber.¹³ Further components have been incorporated to modify the final properties of WSR composites. The typical SAP in WSR composites used to be synthetic polyacrylate, the cost of which depends strongly on petroleum products. Despite no definitely known threat to human health, the waste disposal of these composites is problematic due to a wide range of environmental pollutants.^{14,15} Biodegradable SAPCs derived from natural polymers have been used in several research studies to produce WSR, for example, cassava starch grafted with polyacrylamide (PAM) and combined with bentonite clay.⁷ Sodium salt of polyethylene glycol was blended with chlorinated polyethylene to form a water-swallowable elastomer (WSE) that gave higher swelling capacities and faster swelling rates than WSE prepared by grafting polyethylene glycol onto chlorinated polyethylene.¹⁶ However, there are no prior reports about WSR prepared with the SAPC from hydroxyethyl cellulose grafted PAM (HEC-g-PAM)/bentonite dispersed in a rubber matrix. Thus, the current study focused on using this SAPC dispersed as the water-absorbing polymer in ENR, with an expectation of good water swelling behavior and mechanical properties.

In this work, the WSRs were prepared by mechanical blending of ENR with an SAPC using an internal mixer (Brabender Plasticorder). The SAPC was synthesized by graft copolymerization of PAM onto HEC backbones, with also bentonite clay in the composite. First, producing the WSR was tested using ENR-25 and ENR-50 as alternatives for the matrix, with fixed contents of SAPC and other ingredients, and the first water absorbency and weight loss were assessed. High water absorbency and low weight loss were targeted, so ENR-50 was selected to make WSR with various contents of SAPC. The influences of SAPC content on swelling behavior, such as first water absorbency, weight loss, and second water absorbency, on mechanical properties, and on morphology of the blends were further investigated.

Experimental methods

Materials

ENR (ENR-25 and ENR-50, with 25% and 50% mole epoxide contents) was manufactured by Muang Mai Guthrie Public Co., Ltd (Surathani, Thailand); HEC (analytical reagent (AR) grade)

was purchased from Merck KGaA Corporate (Frankfurter Strasse, Germany); bentonite clay was manufactured by Sigma-Aldrich (St Louis, Missouri, USA); acrylamide (AM) of 99% purity used for synthesis was supplied by Merck K GaA Corporate (Frankfurter Strasse, Germany); potassium persulfate (KPS) with 99% purity manufactured by Ajax FineChem was used as initiator; *N, N'*-methylenebisacrylamide (MBA) and sodium hydroxide (NaOH, AR grade) purchased from Fluka (Buch SG, Switzerland) were used as a cross-linker and in alkaline hydrolysis treatment, respectively; zinc oxide (ZnO), white seal activator, lab grade, was purchased from Metoxide Thailand Co., Ltd (Pathumthani, Thailand); stearic acid activator, lab grade, was purchased from Imperial Industry Chemical Co., Ltd (Pathumthani, Thailand); *N*-tert-butyl-2-benzothiazyl sulfenamide (TBBS) accelerator, chemical grade, was purchased from Flexsys America L.P. (Reliance Technochem Co., Ltd, Bangkok, Thailand); and sulfur, vulcanizing agent for NR, lab grade, was obtained from Ajax Chemical Co., Ltd (Auckland, New Zealand).

Preparation of SAPC

The SAPC was prepared first by dispersing 40%wt% bentonite clay in distilled water and then by mixing with 1.2 g HEC until gel formation; 0.3 mol/100 g HEC of KPS and 12 g AM with MBA 0.1 mmol/100 g HEC solution were reacted in a four-necked reactor under nitrogen atmosphere at a rotor speed of 100 r/min, 70°C, and 120 min. The crude SAPC in gel form was purified by multistep Soxhlet extraction to finally obtain SAPC, which was further treated with 2 M NaOH solution while stirring at 100 r/min and 60°C for an hour. The procedure was as described by Adair et al.¹⁷ The SAPC with 538 g/g water absorbency was used to prepare WSR by means of mechanical blending with the ENR matrix.

Preparation of WSR

The experiments were performed at ambient temperature using an internal mixer (Brabender Plasticorder) with chamber temperature controlled to 40°C. Two grades of ENR, namely with 25 mole% epoxide groups (ENR-25) and with 50 mole% of epoxide groups (ENR-50), were tested as the rubber matrix by dispersing 10 phr SAPC with ZnO 6 phr, stearic acid 0.5 phr, TBBS 1 phr, and sulfur 2 phr. The obtained WSRs were investigated for water-swelling behavior, specifically water absorbency and weight loss. High water absorbency and low weight loss are desirable, so these were the criteria to select the better ENR matrix. With this matrix, the influence of SAPC content on water-swelling behavior and mechanical properties was tested. The total mixing time was 14 min with the procedure described in Nakason et al.,⁷ and the blend proportions are given in Table 1.

Swelling measurements

Swelling measurements including water absorbency and weight loss were performed in triplicate, and average values are reported. About 300 mg samples of the dried sheets were cut, weighed accurately, and soaked in distilled water at ambient temperature (around 28–30°C). At regular intervals, the swollen sample was taken out from the distilled water, superficial moisture was carefully removed using blotting paper, and the weight of the sample was measured immediately and the sample was placed back in the same bath. After the swelling test completed, the samples

Table 1. Formulations of WSR with varying SAPC loadings.

Ingredients	Quantity (phr)
ENR-50	100
SAPC	0, 5, 10, 15, 20
ZnO	6
Stearic acid	0.5
TBBS	1
Sulfur	2

WSR: water-swollable rubber; SAPC: superabsorbent polymer composite; ENR: epoxidized natural rubber; TBBS: *N*-tert-butyl-2-benzothiazyl sulfenamide; ZnO: zinc oxide.

were dried at 50°C until constant weight. The first and second water-swelling ratio by mass (S_w) and the first percentage of weight loss (L_w) were calculated using equations (1) and (2)^{9,12}:

$$S_w = \frac{w_2 - w_1}{w_1} \times 100 \quad (1)$$

$$L_w = \frac{w_1 - w_3}{w_1} \times 100 \quad (2)$$

where w_1 and w_2 are the weights of the sample before and after the water absorption, respectively, and w_3 is the dried weight of a sample after water absorption.

Tensile properties

Tensile properties in terms of tensile strength, elongation at break, and modulus were tested at room temperature, according to ASTM D412 using a universal tensile testing machine (Hounsfield Tensometer, model H 10KS, Hounsfield Test Equipment Co., Surrey, UK). The dumbbell-shaped specimens were first die cut from the vulcanized rubber sheets with ASTM die type C. Furthermore, the hardness was tested using a durometer, Shore A (Frank GmbH, Hamburg, Germany), according to ASTM D2240.

Determination of the cross-link density

For cross-link density estimation, the equilibrium swelling was first determined by immersion of WSR sample in toluene for 7 days in the dark. The swollen WSR was then removed and weighed immediately. The weights of absorbed toluene and remaining rubber were determined by evaporating the toluene off in a hot air oven at 70°C. The cross-link density of WSR was calculated using the Flory–Rehner equation (3)^{18,19}:

$$\frac{-\left[\ln(1 - v_p) + v_p + \chi v_p^2\right]}{nv_0 \left[v_p^{1/2} - \frac{v_p}{2}\right]} \quad (3)$$

$$v_p = \frac{1}{1 + Q}$$

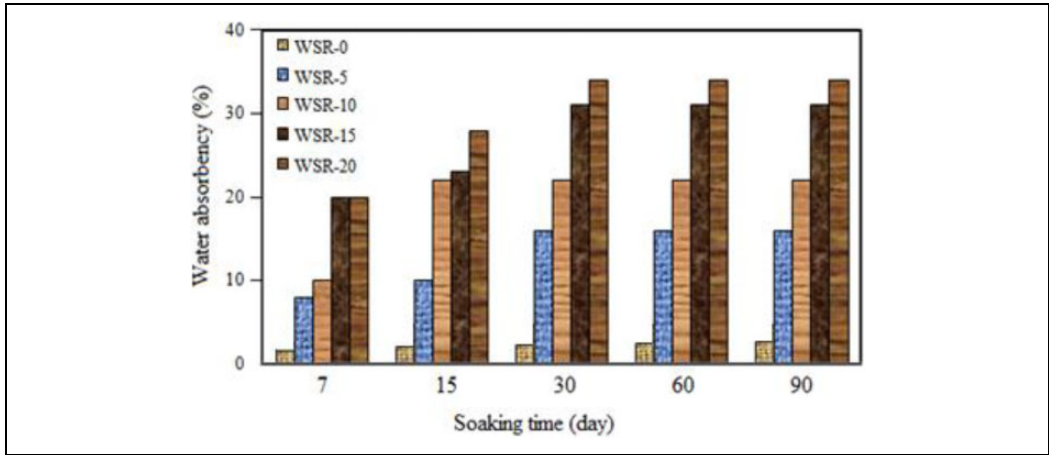


Figure 1. Time profiles of first water absorbency for WSRs with various SAPC loadings. WSR: water-swollable rubber; SAPC: superabsorbent polymer composite.

where n is cross-link density, v_p is volume fraction of rubber in the swollen polymer, χ is Huggins rubber–solvent interaction constant (0.41 for ENR), D_p is density of rubber (1.09 g/cm^3), V_0 is molar volume of toluene ($1.069 \times 10^{-4} \text{ m}^3/\text{mol}$ at 25°C), and D_0 is density of toluene (0.8623 g/cm^3 at 25°C).

Cure characterization

A rotorless rheometer (Rheo Tech MD+, Tech Pro, Inc., Cuyahoya Falls, Ohio, USA) was used to determine the curing characteristics of the rubber composites at 160°C with 1° arc amplitude over 60 min testing. The optimum cure time (t_{c90}) and scorch time (t_{s1}), the minimum and maximum torques (M_L and M_H , respectively), and δ torque ($M_H - M_L$) were determined from the curing curves. Cure rate index (CRI) was measured based on ASTM D5289 and calculated as shown in equation (4)^{20,21}:

$$\text{CRI} = \frac{100}{t_{c90} - t_{s1}} \quad (4)$$

where t_{s1} is the time a unit increase in torque takes from the M_L , and t_{c90} is the time at which 90% cure is achieved.

Morphological properties

Morphological properties of the WSRs were characterized using a scanning electron microscope (SEM) equipped with energy-dispersive X-ray (EDX) spectroscopy (Quanta, FEI, the Netherlands).

Results and discussion

Swelling properties of WSR

Figure 1 shows the water-swelling capacity of WSR with tested SAPC contents at various soaking times. It is generally seen that the water swelling of WSR increased with soaking time of up to 30

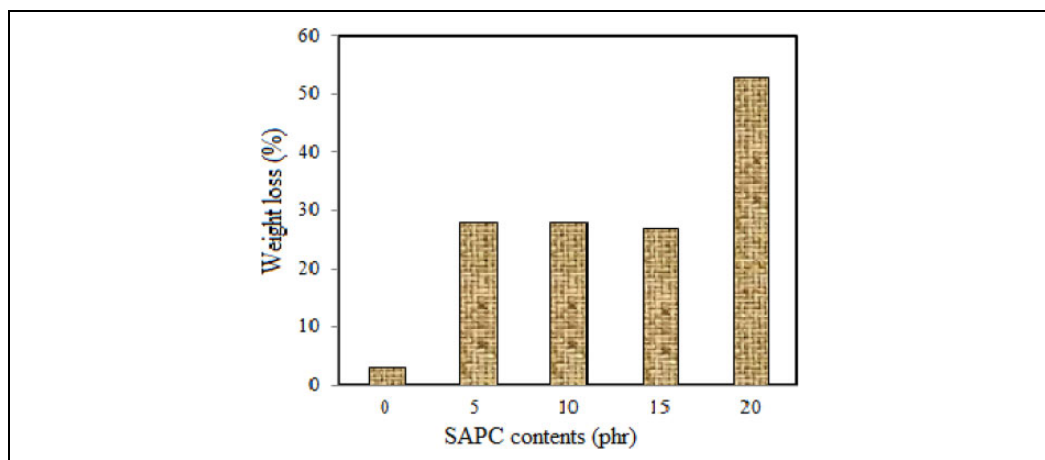


Figure 2. The weight loss (%) during first water immersion of WSR prepared from ENR-50 with various loadings of SAPC.

WSR: water-swallowable rubber; SAPC: superabsorbent polymer composite; ENR: epoxidized natural rubber.

days and then tended to level off. It is also seen that the water absorbency of WSR increased with the content of water-absorbent polymer composite (SAPC) in the composites. This was attributed both to the decrease of cross-linked density and to the increase of active sites for water absorption. Similar dependence of water absorbency on SAP/SAPC content has been reported earlier.^{2,8,22} Thus, the SAPC content plays an important role in the water absorbency of the WSR, as expected.

Figure 2 shows the weight loss of WSR with various SAPC loadings at 30 days of soaking. The weight loss tended to increase with SAPC loading, being highest for the case with maximal 20 phr SAPC in WSR. The results match well with the water absorbencies of the WSR samples.

Tensile properties

The moduli at 100% and 300% strains for the WSR filled with various SAPC contents were shown in Figure 3. Both moduli slightly increased with SAPC content, indicating stiffness increase with the addition of SAPC. Generally, for a composite, the modulus at low strains depends on various factors, such as interatomic bonding strength or the nature of bonds and the binding energy. Usually, materials with greater bonding strength exhibit higher stiffness.

Figure 4 shows the effects of SAPC addition on tensile strength and elongation at break of the WSR. SAPC decreased both tensile strength and elongation at break, which could be explained as follows. SAPC reduced cross-linked density (Figure 5) and the SAPC phases in WSR matrix acted as stress concentration points that caused easier/earlier failure with SAPC added.

Cross-link density

Effects of SAPC addition on the cross-link density in WSR are based on estimates from the Flory–Rehner equation. Figure 5 shows the effects of SAPC content on the cross-link density of WSR. It is very interesting that the cross-link density of WSR decreased with the addition of SAPC. As can be seen in Figure 5, the cross-link density decreased sharply when 5 phr SAPC was added, while

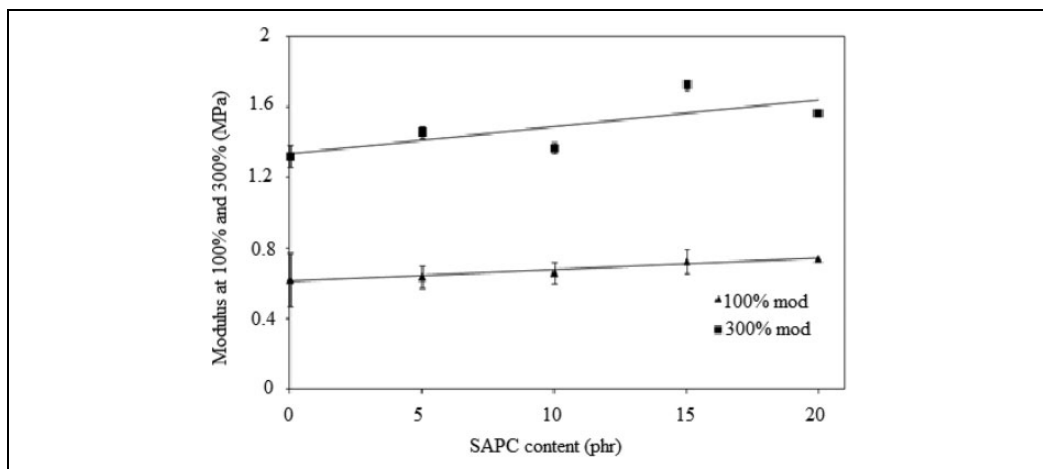


Figure 3. The moduli at 100% and 300% strains for the WSR with various SAPC contents. WSR: water-swallowable rubber; SAPC: superabsorbent polymer composite.

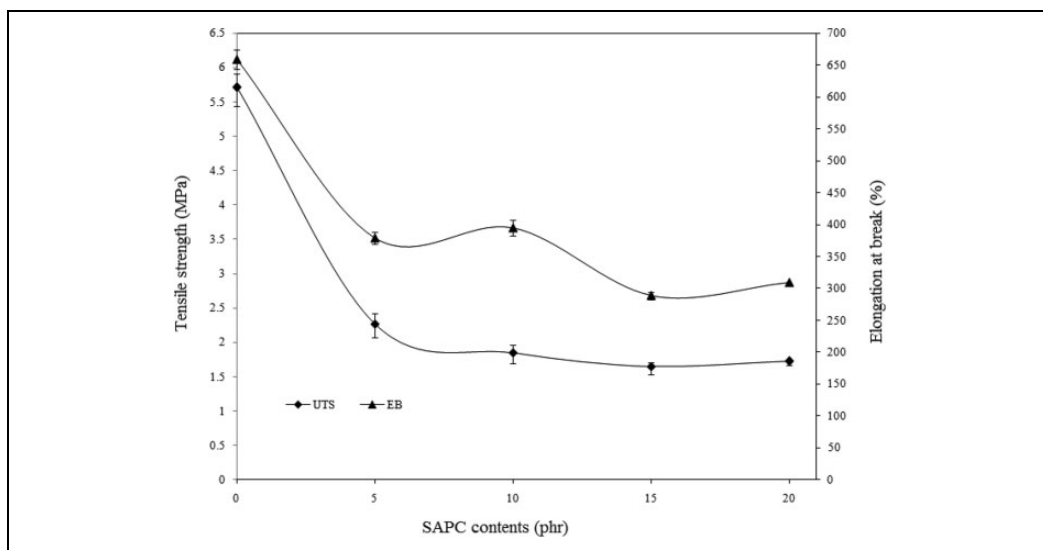


Figure 4. Tensile strength and elongation at break for the WSR with various SAPC contents. WSR: water-swallowable rubber; SAPC: superabsorbent polymer composite.

further addition had no significant effect. In other words, SAPC hindered cross-linking, but this effect saturated quickly.

The mechanism by which SAPC hindered cross-linking may relate to the sulfur vulcanization system. It is well known that in sulfur curing, there are at least five steps involved, and in the first step, the accelerator reacted with ZnO forming Zn^{2+} -accelerator complex, while in the second step, sulfur reacted with the Zn^{2+} -accelerator complex forming an intermediate sulfur- Zn^{2+} -accelerator or

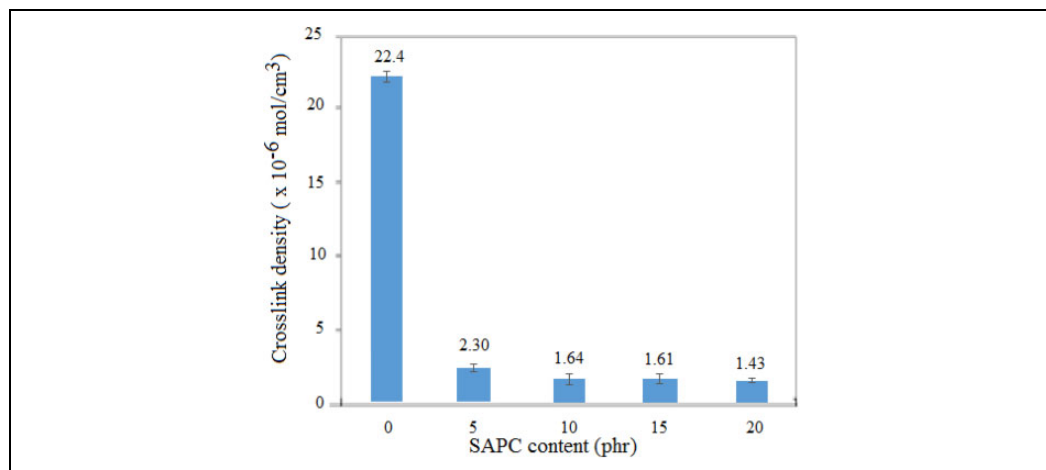


Figure 5. Cross-link density of WSR with various SAPC contents.
WSR: water-swollable rubber; SAPC: superabsorbent polymer composite.

polysulfidic accelerator.²³ This is important because the complex containing Zn^{2+} could have ligands, especially in the presence of amine or carboxylate ions. In fact, the SAPC, used as a dispersed hydrophilic polymer phase in the blend, was based on copolymers HEC and PAM. The final structure of the grafted copolymer was probably enclosed by multifunctional groups, such as carboxylic acid, carboxylate, and amide forms, as shown in Figure 6.

The complexation of Zn^{2+} complex and SAPC forms comparatively large-sized complexes. In the third to fifth steps of vulcanization, the intermediate sulfur- Zn^{2+} -accelerator or polysulfidic accelerator that formed rubber-sulfur-accelerator groups then further formed rubber-sulfur-rubber groups, and in the final stage, these formed a network of rubber chains. This process probably had steric effects from increase in size of the complexes, when the Zn^{2+} as a ligand bonded with specific functional groups of SAPC. This obstructed diffusion of the complex into rubber and hindered network formation, thus decreasing the cross-link density. Similar behavior has been found when natural rubber was blended with ENR and montmorillonite modified with quaternary ammonium,²⁴ and the cross-link density of rubber compound based on natural rubber reinforced with octadecylamine-modified bentonite also decreased relative to natural rubber reinforced with organoclay.¹⁸

FTIR determination

The characterization of the blends' compatibility was using Fourier transform infrared (FTIR) determination. In Figure 7, the FTIR spectra of ENR-50 (Figure 7(a)) indicated that the predominant absorption peak at 3037 cm^{-1} (weak) was assigned to stretching vibration of $\text{Csp}^2\text{-H}$, the strong to medium peaks at 2962 , 2924 , and 2859 cm^{-1} were attributed to $\text{Csp}^3\text{-H}$ stretching vibration, and the weak peak at 1664 cm^{-1} ($\text{C}=\text{C}$ stretching), 1449 cm^{-1} ($-\text{CH}_2-$ deformation), and 1378 cm^{-1} (methyl C-H deformation). In addition, the epoxide in molecule was confirmed by the medium intensity of peak at 878 cm^{-1} , while the peak with weak intensity at 837 cm^{-1} was due to $\text{C}=\text{C-H}$ bending vibration of natural rubber.²⁵ The FTIR spectra (Figure 7(b)) represented

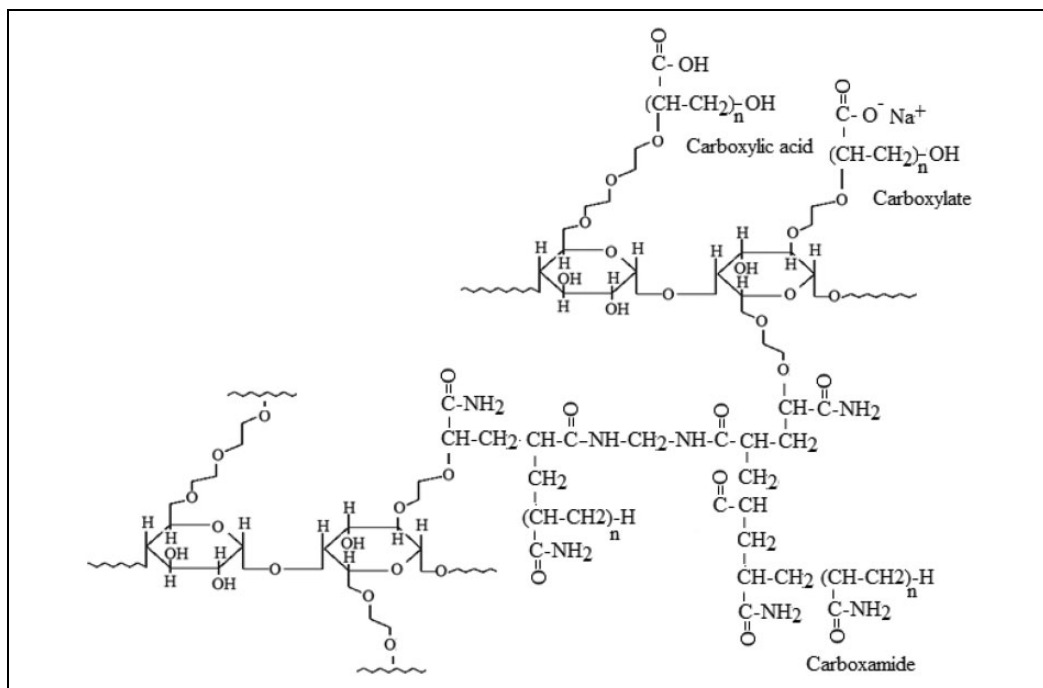


Figure 6. Proposed structure of SAPC that includes multifunctional groups (modified from Adair et al.).¹⁷ SAPC: superabsorbent polymer composite.

before water absorption of WSR and (Figure 7(c)) represented absorption band of WSR after water absorption of 30 days. Moreover, the FTIR peak around $1700\text{--}1550\text{ cm}^{-1}$ clearly indicated that SAPC contained carbonyl groups containing, probably assortments of amide, carboxylic acid, and carboxylate salt. After having water immersion, there was slightly increased intensity of FTIR peak at 1064 cm^{-1} , which was assigned to C–O stretching vibration of ether. This exactly means epoxide ring has been broken and has altered into C–O–C. This phenomenon was supported well with the altering peak of epoxide at 875 cm^{-1} .

Cure characteristics

Figure 8 showed the time profile of torque of WSR with and without SAPC using oscillating disk rheometer (ODR). It demonstrated that the SAPC content was affected by the increasing torque due to the increased stiffness by the formation of cross-links. The incremental torque values clearly evidenced that the processing of rubber compounds characterized by higher contents of SAPC filler became harder and the cross-link structures between ENR-50 and SAPC hindered its blending. The cure characteristics, such as t_{s1} , t_{c90} , CRI, M_L , M_H , and torque difference ($M_H - M_L$), are summarized in Table 2.

In the scorch region, it was found that all WSRs filled with SAPC exhibited higher minimum torque than the WSR without SAPC. This is due to the interatomic bonding of rubber and SAPC phases that increased viscosity of uncured WSR. In the curing region, the CRI was retarded by the added SAPC. This is attributed to the acid characteristics of SAPC as it contains various hydroxyl

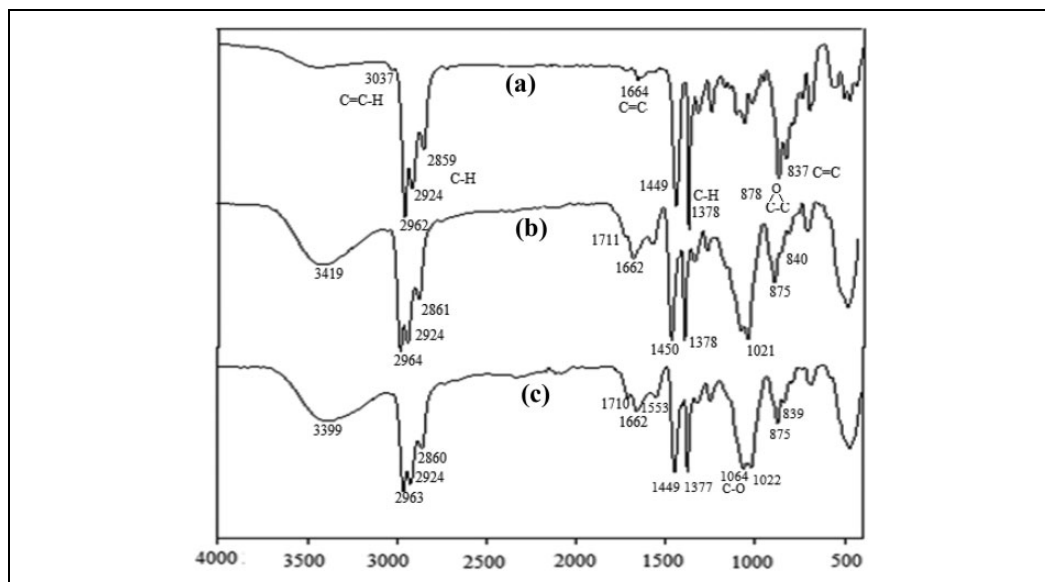


Figure 7. Indicates FTIR spectra of (a) ENR-50, (b) WSR before water absorption, and (c) WSR after water absorption, WSR prepared by blending ENR-50 and SAPC loading 15 phr, ZnO 6 phr, stearic acid 0.5 phr, TBBS 1 phr, and sulfur 2 phr.

WSR: water-swallowable rubber; SAPC: superabsorbent polymer composite; ENR: epoxidized natural rubber; TBBS: N-tert-butyl-2-benzothiazyl sulfonamide; FTIR: Fourier transform infrared.

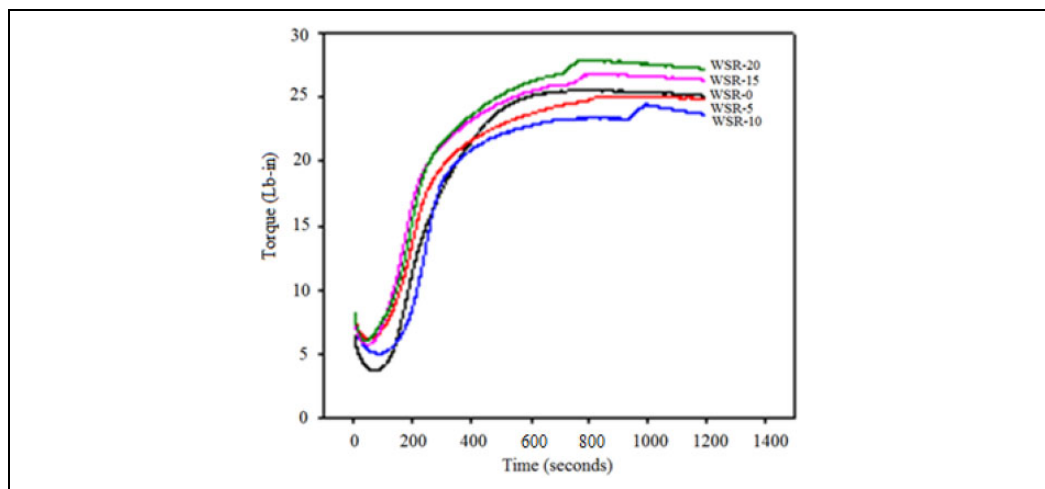


Figure 8. Cure curves for WSR with various contents of SAPC.

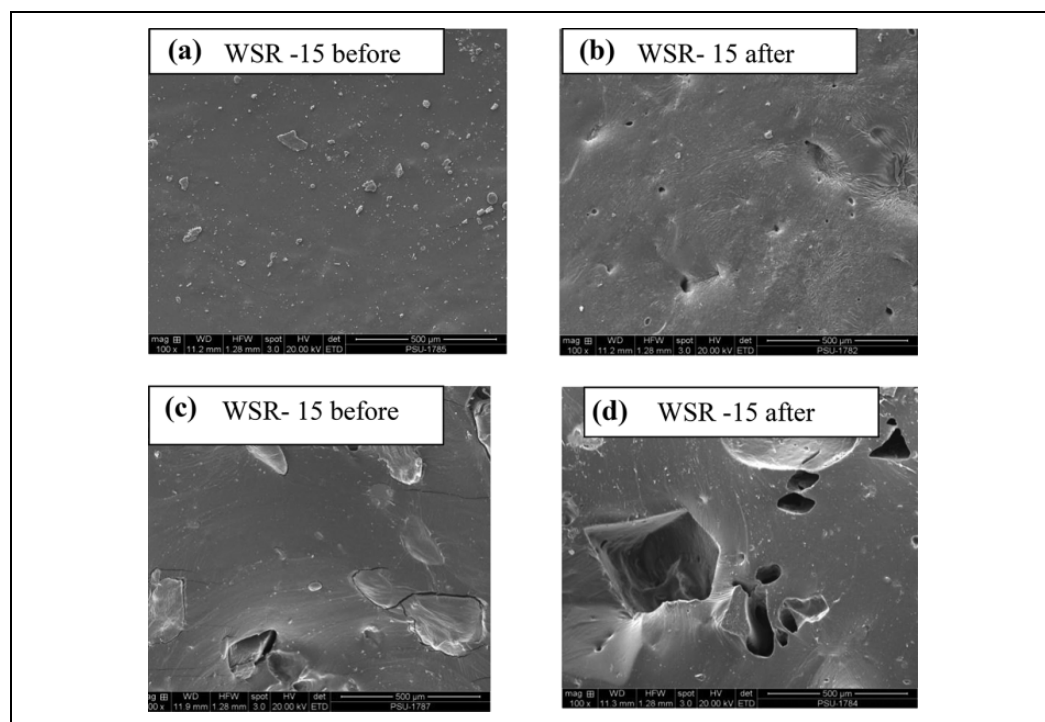
WSR: water-swallowable rubber; SAPC: superabsorbent polymer composite.

groups ($-OH$) from indigenous HEC and amides when treated with alkaline base transformed into acid functional groups in the molecules. Thus, the rate of vulcanization was retarded.²² After curing region, the ODR curves of WSR with 15 and 20 phr SAPC showed higher moduli than

Table 2. Cure characteristics (t_{s1} , t_{c90} , CRI, M_L , M_H , and $M_H - M_L$) of WSR with and without SAPC.

Case	t_{s1}	t_{c90}	CRI	M_L	M_H	$M_H - M_L$
WSR-0	2.03	7.46	18.41	3.64	25.39	21.75
WSR-5	1.47	8.54	14.14	6.21	25.12	18.91
WSR-10	1.55	8.41	14.57	5.01	23.81	18.80
WSR-15	1.29	8.37	14.12	5.73	26.91	21.18
WSR-20	1.22	9.04	12.78	5.98	27.92	21.94

WSR: water-swellable rubber; SAPC: superabsorbent polymer composite; CRI: cure rate index.

**Figure 9.** SEM micrographs of WSR with 15 phr SAPC: (a and b) surface and (c and d) cross section before and after immersion in water (fracture images; magnification $\times 20,000$; scale bar $500 \mu\text{m}$).

WSR: water-swellable rubber; SAPC: superabsorbent polymer composite; SEM: scanning electron microscope.

unfilled WSR. On the other hand, the torques of WSR-5 and WSR-10 showed lower value of modulus than that without SAPC. With increased addition of SAPC, it was found that the t_{s1} , t_{c90} , M_L , and M_H were independent from further addition of SAPC. It is interesting to note that the cure characteristics obtained from ODR did not correlate with the cross-link density from the swelling test. The reason was that the swelling test probably confined solely in the cross-link occurred in rubber phase, which was different for ODR that generally mentioned to overall systems of cross-linking.

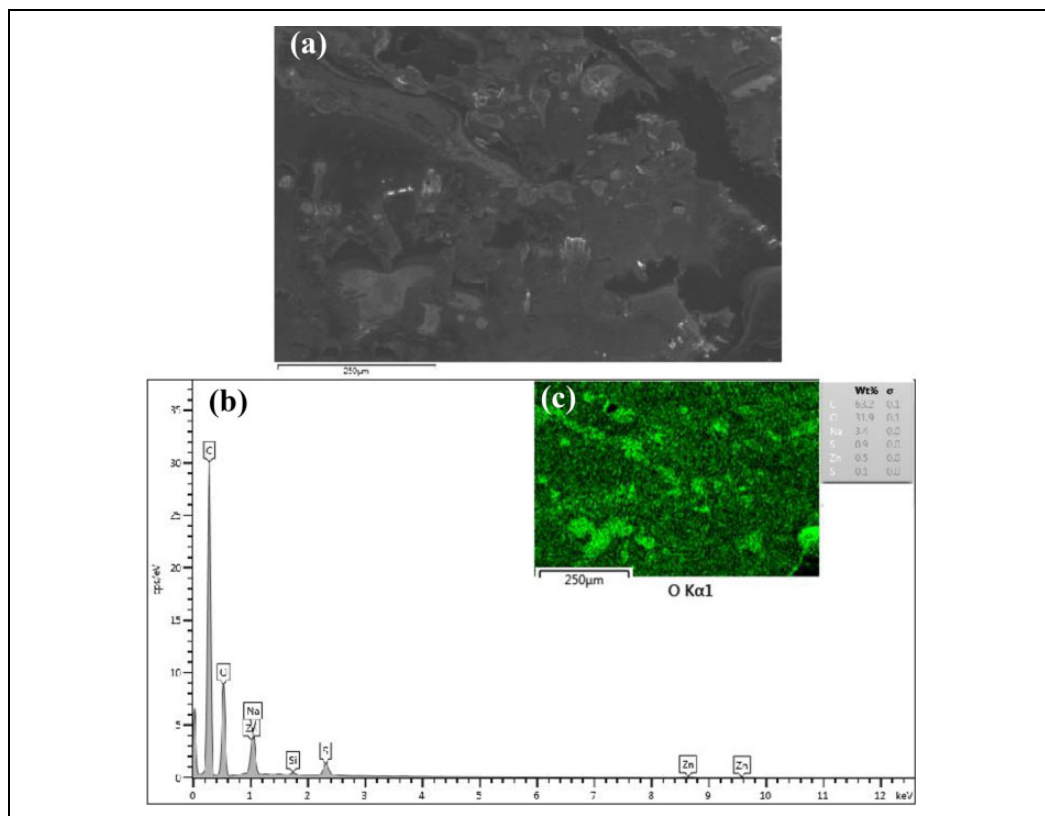


Figure 10. SEM micrographs of WSR with 15 phr SAPC: (a) surface (fracture images; magnification $\times 250$; scale bar 250 μm) and (b and c) SEM/EDX of WSR with X-ray mapping of O. WSR: water-swallowable rubber; SAPC: superabsorbent polymer composite; SEM: scanning electron microscope; EDX: energy-dispersive X-ray.

Morphological property

Figure 9 depicts SEM micrographs of the WSR containing 15 phr SAPC. It was clearly seen that the WSR images, after having an immersion in water, both surface Figure 9(b) and cross section Figure 9(d) are existing the vestiges due to the removal of SAPC. Poor dispersion before and the detachment of SAPC after immersion in water are seen in this sample. The loss of SAPC by immersion in water suggests that the bonding of SAPC to the matrix was very poor. The poor dispersion of SAPC along with the weak bonding also reduced tensile strength and elongation at break.

Figure 10 shows the SEM micrographs of WSR with 15% SAPC (Figure 10(a)) presented that the fracture surfaces of WSR showed fine dispersion with irregular shapes and sizes of particles in the rubber. The EDX analysis was also executed to establish the dispersion of SAPC in WSR (Figure 10(b) and (c)) and the X-ray mapping of O the bright green bars over the darker green background showed the distribution of O in the rubber matrix.

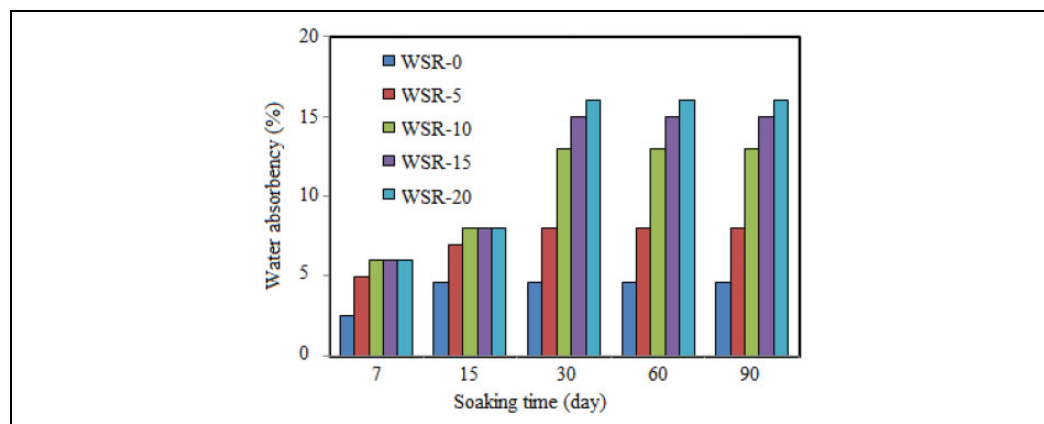


Figure 11. Second water absorbency of WSR with various SAPC loadings and soaking times. WSR: water-swollable rubber; SAPC: superabsorbent polymer composite.

Figure 11 shows the second water absorbency of WSR with various contents of SAPC for different soaking times. The WSR with 20 phr SAPC content had 16% second water absorbency while the first was 34% (2.13-fold difference). The loss of absorbency was due to the loss of SAPC from WSR during first immersion, as seen in SEM micrographs and in weight loss.

Conclusions

1. WSR was successfully prepared by mechanical blending of ENR with 50% oxirane ring (ENR-50) as the rubber matrix and SAPC as the dispersed water-absorbing filler, associated also with an activator, accelerator, and cross-linking agent.
2. The SAPC was first synthesized by grafting copolymerization of PAM onto HEC backbones with association of bentonite clay composites. The compounding was carried out in an internal mixer (Brabender Plasticorder) at 40°C, 60 r/min rotor speed, and 80% fill factor.
3. The first and second water absorbencies of WSR increased with SAPC content, but the second water absorbency was much lower than the first due to the loss of SAPC from WSR during first immersion. The weight loss increased with SAPC content.
4. The mechanical properties, tensile strength, and elongation at break decreased with increasing the SAPC contents, while modulus had an opposition. The morphology of the blends after water immersion clearly evidenced the loss of dispersing SAPC from WSR, which negatively affected the second water absorbency, tensile strength, and elongation at break.


Declaration of conflicting interests

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