

## Water swellable rubber composites: An update review from preparation to properties

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**ABSTRACT:** In recent years, water swellable rubber composites have been the subject of many scientific and research investigations as well as many industrial programs. Here, we present an updated overview of the developments in the area of water swellable rubber composites with different kinds of fillers, compatibilizers, and cross-linked agents, in terms of their manufacturing methods, synthesis, chemical, physical, and mechanical properties. Several critical issues and suggestions for future work are detailed, underscoring the roles of material scientists and manufacturing engineers in the bright future of this new material through value addition to enhance its usage and fields of application. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42786.

**KEYWORDS:** electrospinning; rubber; structure–property relations; swelling

Received 26 April 2015; accepted 23 July 2015

DOI: 10.1002/app.42786

### INTRODUCTION

Polymer blend systems are new kinds of material that have come into wide use in recent years. The relative ease of mixing, low cost of processing (compared to synthesizing), and novel properties are the major advantages of developing combined polymer materials.<sup>1</sup> One of the most industrially multicomponent blends is water swellable rubber (WSR). WSR is a kind of functional polymer composed of elastomer with water-absorbent resins. It retains the properties of general rubbers such as high elasticity, resilience, and high toughness. Moreover, with the absorption of water its volume can expand to more than 1.5 times the original.<sup>2</sup>

### Main Raw Materials

The most common hydrophobic rubbers used as a matrix in WSRs are natural rubber, chloroprene rubber, chlorohydrin rubber, and silicon rubber specially room temperature vulcanization silicone rubber (RTV Silicone) which is a type of silicone rubber made from a two-component system (base plus curing agent; A+B).<sup>3–9</sup> They are usually mixed with various water-absorbent materials known as superabsorbent polymers (SAPs). SAP is a kind of hydrophilic polymer (cross-linked hydrogel) having water-absorbing capacity from 100 up to 2000 g/g, in which the absorbed water is scarcely removable even under pressure, because the water molecules are held tightly in the network by hydrogen bonding. Using SAP into rubber will help the water go through its three-dimensional network structures and retain into the rubber structure which can force it to swell. Some of the com-

mon SAPs that are used by researchers are cross-linked forms of polyacrylate (acrylic acid and acrylamide), polyvinyl alcohol, poly(ethylene oxide), starch-acrylate copolymer, carboxymethyl cellulose, and many other polymers.<sup>9–12</sup> The degree of swelling and swelling rate of SAPs basically depends on the type of rubber, the conditions of the water are using for test such as pH, salinity, temperature, pressure, and time of immersing in a solution and also the design of the samples.<sup>13</sup>

The dependency of molecular weights and grafting frequencies on swelling behavior of graft copolymers was investigated by Fanta *et al.*<sup>14</sup> He showed that by decreasing the number of grafted chains of polyacrylonitrile (PAN) and increasing their average molecular weight, swelling of starch granules would be enhanced significantly. In a similar work, he reported that incorporation of selected co-monomers such as vinylsulfonic acid, acrylic acid (AA), methyl acrylate (MA), methyl methacrylate (MMA), and styrene has a great influence on water absorbency of the PAN-starch.<sup>15</sup>

The first commercial SAP was produced in 1970 through alkaline hydrolysis of starch-*g*-polyacrylonitrile.<sup>2</sup> Because of their excellent characteristics, SAPs have stimulated considerable interest in various fields. They were industrialized in the US and Japan in the early 1980s as hygienic products and to reduce cost. They are now used in a broad range of applications in health, such as controlled drug delivery, and in agricultural and horticultural applications such water conservation in soil and soil conditioning.<sup>16–19</sup> Figure 1(a) illustrates a typical SAP in

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dry and water-swollen states. Absorption capacity (ability of WSR to absorb/incorporate water), absorption rate (the rate of transferring mass/volume at the interface between the water and composite), and the swollen gel strength are the three main functional features of SAPs. In the swollen state, however, the mechanical properties of SAPs are relatively weak. By manipulating the structure of hydrogels, such as by increasing the cross-linking density, surface treatment of the SAP and incorporation of suitable polymers, the mechanical, thermal, and physical properties of SAPs can be improved.<sup>12,20,21</sup>

One of the SAPs with most commercial applications is polyacrylate partially neutralized with sodium hydroxide (NaOH). Sodium atoms in the center of the molecule are bonded to carbon chains of acrylate. When the polymer comes into contact with water, the concentration of water outside the polymer is higher than that inside it, which draws the water molecules into the network by osmotic pressure formed by the sodium neutralization of the polymer backbone. Because of the cross-linkages between molecules, the polymer chains cannot straighten and, as a result, the particles expand into the network, as shown in Figure 1(b).<sup>22</sup> This expansion continues until the concentration of water is equal within and outside the polymer.

#### How Does WSR Work?

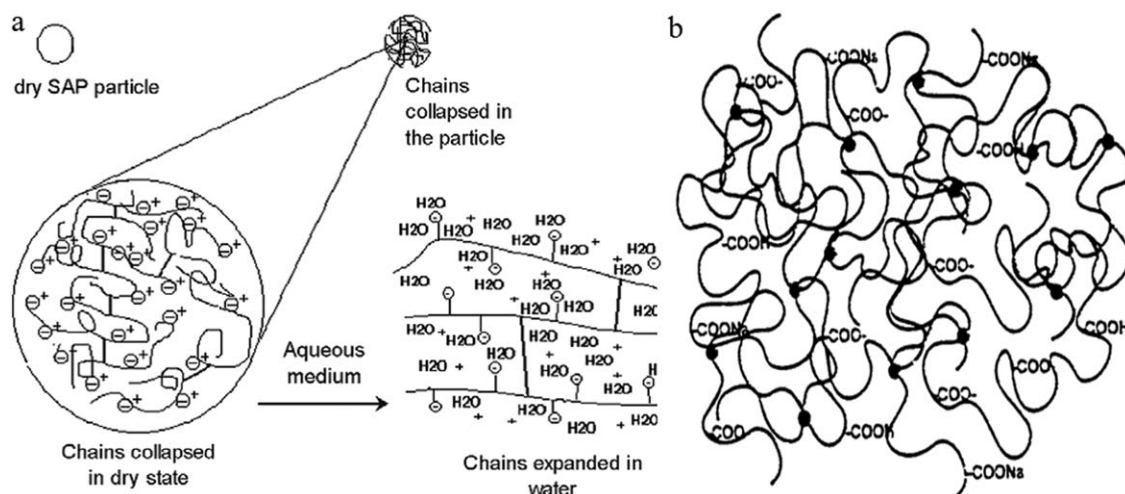
WSR can swell in three dimensions and the swelling rate and capacity are proportional to the contact surface area. Generally, the two main forces for the polymer swelling mechanism are the driving force of the solvent into the polymer network and the resistance of the polymer network to expansion. In a thermodynamically balanced state, these two forces should be equal.<sup>23</sup> For WSR, SAP particles have an interaction with water molecules via hydrogen bonding, which is one of the main driving forces for chains absorbing the water molecules. The water is drawn into the rubber network to be absorbed by SAPs, however, because of the crosslinks of the elastomer chains, dispersion of the water is limited and the absorption ability of SAP also been confined, thus a resistance to expansion develops. This energy disparity manifests itself in an effort to achieve an energy balance by creating a diffusion gradient between the elas-

tomer and the fluid around it, resulting in equilibrium.<sup>13,24</sup> Figure 2 shows the schematic drawing of water swelling mechanism in WSRs. SAP particles inside the cross-linked chains of rubbers accelerate the water penetrating into the rubber chains and become bigger and bigger with time increasing.

When SAP is introduced into a rubber matrix, the degree and rate of swelling of the rubber increase. However, prolonged contact with water causes SAPs migrate from the rubber into the water, so the swellability is ultimately lost, the strength is decreased and the water is polluted. This migration is caused by high interfacial tension between phases of immiscible polymer blends that leads to coarse and unstable morphology of WSR, narrow interfaces, and poor physical and chemical interactions between the phase boundaries. The amount of SAP added into the rubber can notably affect the strength of the final product. Thus, to prevent reducing the strength of the product, more cross-linking is needed in the remaining elastomer, but conversely, a higher cross-link density makes the WSR more rigid and it resists swelling. It is a very important, therefore, to find the right balance between rubber and SAP such that the product has excellent water-absorption property as well as desirable mechanical properties.

#### Applications and Markets

WSRs have created a wide spectrum of applications which makes them effectively unique for use in various forms by particular major industries. They can be used in oil field applications as well as mining and civil engineering; for caulking, sealing of gaps in construction works, cold joints and working joints in concrete, in sewer joints, against slurry walls, and in sheet piling especially with irregular wellbore shapes such as poor hole geometry and corroded casing; for sealing downholes, preventing water leakage from pipe or block connections, preservation of airtightness in machinery and apparatus, isolation of open and cased holes, in underground installations such as culverts, subways and sub-sea tunnels, impounding reservoirs, metros, and retaining dams. One of the advantages of using WSR is that they are re-usable. As an example, for sealing application, in cold seasons, they can absorb the humidity of



**Figure 1.** A schematic presentation of (a) SAP chains before and after swelling<sup>12</sup> and (b) sodium polyacrylate networks.<sup>22</sup>

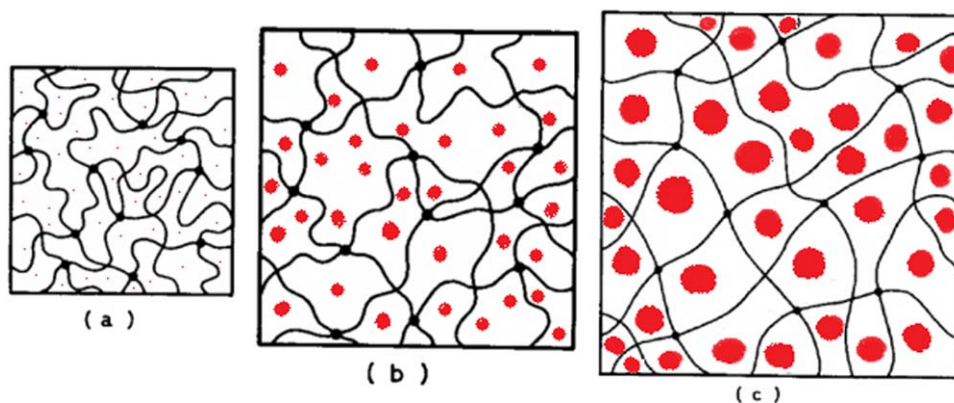
environments and swell and fill the gaps. However, in warm seasons, they can return to their original size and again swell in cold weather for next time. The most commercialized elastomers currently used are NR, NBR, EPDM, SBR, and CR.<sup>13,25–29</sup> Many companies currently use WSR simultaneously as both elastic sealing and water blocking such as Rigzone, Rongwei Rubber, Hebei Kailong Guyite Rubber, Bekina Compounds, Zaoqiang Dacheng Rubber, Qinghe Xinao Rubber Seal, and Martins Rubber. In terms of global marketing, WSRs are currently used in all over the world. However, the regions that have been making the most use of WSR are Africa, Asia (Central and Southern and the Middle East), Europe, and North and Latin America.

Recently, Tendeka company developed a specific strengthening component to reach a significantly improvements of performance for WSR in saline solutions at low temperatures. By optimization of the conditions of swelling test, they successfully characterized WSR to isolate over 10,000 frac stages to date.<sup>30</sup> Similarly, the Halliburton Company currently uses elastomers that can swell when exposed to hydrocarbon products, upon exposure to water or a hybrid of oil and water in a single com-

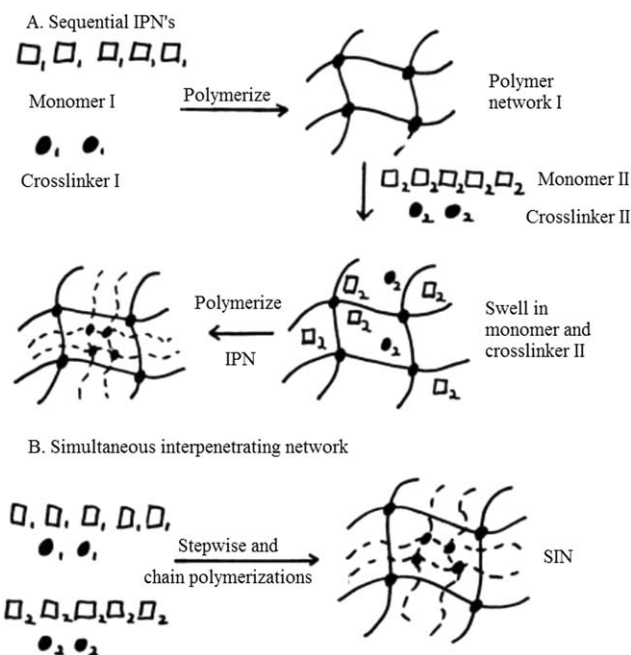
pound. Their products are made by bonding elastomer systems onto oilfield tubulars, with metal end rings installed on each end of the rubber element. The end rings assist in increasing the differential pressure capability and guide the packer when it is run into the hole. They are also can be used for isolating the unwanted zones and resulted in a huge decrease in water cut from 25% to 0.3%.<sup>31</sup> In heavy oil wells, WSR can be installed which use steam to heat the reservoir, causing oil to flow. The high-temperature water swellable packer currently has an upper operational limit of 575°F (302°C).<sup>32</sup> The most common types of elastomers were using in this field includes NBR, HNBR, NBR/polyvinyl chloride (PVC), acrylic rubber, co-polymer fluorocarbon (FKM), and terpolymer FKM.<sup>33</sup>

### SYNTHESIS AND MANUFACTURING PROCESS

The properties of WSR depend on two structural parameters: sufficient interfacial tension to create a small phase for dispersing the ingredients uniformly, and strong interface adhesion to assimilate stresses and strains without any disruption of the established morphology.<sup>34,35</sup> These criteria can be met in different applicable ways such as by increasing the interfacial area by



**Figure 2.** Schematic illustration of swelling mechanism of WSR (a) SAP particles (red dots) between cross-linked chains of rubbers, (b) water molecules penetrate to the chains, causing to increase the volume of SAP, and (c) the network of WSR is extensively swollen. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 3.** Two synthetic methods for preparing interpenetrating polymer networks. (a) sequential IPNs, and (b) simultaneous IPNs.<sup>36</sup>

modifying one or two phases or changing the mixing parameters, to transfer applied stress effectively between phases. Blending techniques have been used successfully for the past decades in blend systems to form homogeneous WSRs. Based on the application of WSR, the cost of final product and the environmental condition for using these kind of composites, the processing method should be properly selected. For example, for natural rubber (NR) due to the need of high shear rate to mix the ingredients, the most common process is using two-roll mill. However, for RTV rubbers such as silicon rubbers, casting or using internal mixer is more preferable.<sup>2,4</sup> Manufacturing methods can be classified in two major groups, physical and chemical, as detailed in the following.

#### Physical Methods

Mechanical dispersion is one of the most common methods for preparing WSR.<sup>3</sup> For example, internal mixing, Banbury, and two-roll milling are batch mixers. Mixing with an extruder in continuous mixing is a common method for dispersing SAP (powder or resin) into the rubber. A vulcanizing agent and a vulcanization accelerator are mixed during the mixing procedure and other ingredients such as filler, plasticizer, antioxidant, or colorants may be incorporated. As in the conventional method, the mixture is then heated until it becomes fully vulcanized, after which it is hot pressed by a compression moulding machine in different moulds, depending on its intended application, to form WSR.<sup>5</sup>

#### Chemical Methods

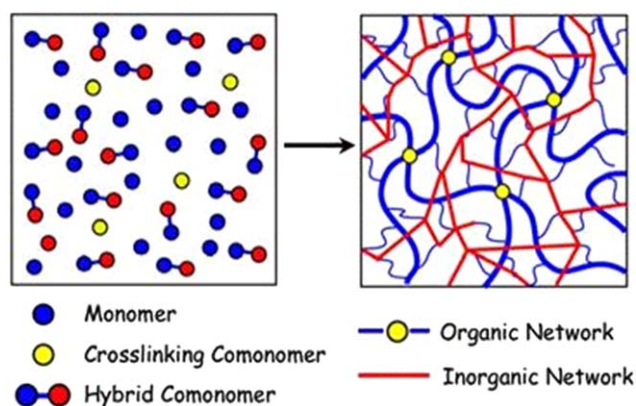
Without the assistance of chemicals, physical methods cannot provide sufficient adhesion between ingredients due to the marked differences in polarity between rubber and SAP. Therefore, chemical blending techniques have been used to overcome this problem. Using chemical modifications such as interpenetrating

polymer network (IPN) technology, grafting, and compatibilizers have been found effective for improving the properties of the final WSR.

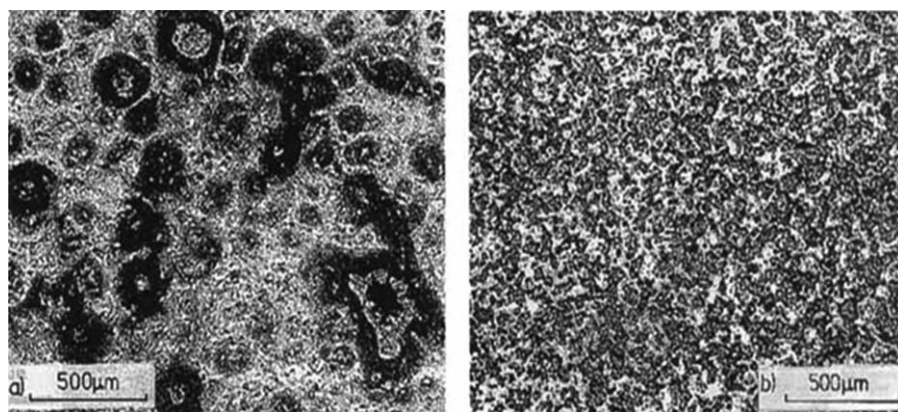
**IPN Technology.** IPNs are defined as combinations of two or more networks form polymeric components, with at least one of the polymers being polymerized and/or cross-linked immediately in the presence of the other polymer(s). The networks interpenetrate each other without any chemical bonds. In synthesizing IPNs, two methods of cross-linking are normally used: sequential and simultaneous, as shown in Figure 3.<sup>36</sup> In sequential cross-linking, an initial mixture consisting of monomer, cross-linking agent, and catalyst/initiator is polymerized to form a network; a second combination of monomer and cross-linking agent is then added to that network. Causing the first network to swell, the second network is polymerized within the first network and an IPN will be formed. Reactive polymer chains with initiator or catalyst can also be used instead of monomers to synthesize the networks.

In simultaneous IPN, the polymerizing of two networks is done in a single step. Different monomers or different polymer chains with appropriate cross-linking agents are polymerized together. The advantage of this process is that the two components are cross-linked by reactions and will not interfere with one another,<sup>37</sup> such as when a condensation reaction occurs polymerizing one network while the other network is formed by a free radical reaction. Figure 4 shows a schematic mechanism of IPNs. This new technology has become widespread, being used in a variety of materials with different purposes such as sheet-moulding compounds (SMCs), membranes, ion-exchange resins, sound damping, dental fillings, artificial joints, tough rubber and plastic materials, and also WSR. It should be noted that IPN can still be considered an expensive technology requiring professional experts and that it highly evolves chemical wastes.

One of the practical ways to prepare a high performance nanocomposite is using nanoparticles into polymer matrix by introducing simultaneous interpenetrating polymer network. For example, simultaneous IPN is developed for polyimide matrix using PI/POSS with lower dielectric constant. Enhanced in glass transition temperatures and uniformly embedding of POSS



**Figure 4.** A schematic mechanism of interpenetrating polymer networks.<sup>38</sup> [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 5.** Micrographs of films of SAP/rubber in ratio 30/100 (a) dispersion from the mixing chamber of a Brabender and (b) dispersion from a two-roll mill.<sup>46</sup>

particles with sizes of approximately 50–60 nm of into polyimide matrices shown by SEM.<sup>39</sup> In similar study, the graft-mode of simultaneous IPN method was used to obtain the controlled domains on a nanometer scale between two phases.<sup>40</sup> This method is one of the potential ways to fabricate WSRs with multi-functionalities introduced by nanoparticles. There are two structures for IPN networks: open cell and closed cell. Open cell structure is softer and less dense with air pockets within the cell structure. Closed cell structure differs in that its cell structure is closed and packed tightly together making it much denser and hard to the touch. Because it is so rigid, closed cell can actually improve the structural stability. Based on application both methods can be used, however, in case of durability (e.g., using WSR in harsh environments), closed cell is more preferable.

**Compatibilizing and Grafting.** Most polymer blends are immiscible with each other and have inadequate properties for most end uses. Suitable functional additives called compatibilizers have been used to improve the miscibility of polymers. Compatibilizers can be either block or graft copolymers which include segments of similar structure or solubility parameters to the polymers being mixed (typically at 5–7 wt %). Compatibilizers are used for verification of polymers such as polymer blends, alloys, melts, and solutions.<sup>41</sup> The general principles of compatibilization are reduction the interfacial tension between two polymers and finer dispersion to stabilize the morphology against high stresses during the formation and to increase adhesion between the phases.<sup>42</sup> Recently, we report the compatibilizer (aminopropyltriethoxysilane) and neutralizer (sodium hydroxide) effects on the conventional poly(acrylic acid) (PAA)/poly(dimethylsiloxane) WSRs and find that the water swelling ability and durability of the WSR increased by virtue of the synergistic effects of compatibilizer and neutralizer.<sup>43</sup>

Grafting is one of the prime techniques for polymer modification which combines a variety of functional components in a single material. Chemical and radiation techniques are the most applicable pathways for performing grafting reactions. Chemical routes are classified in three groups: (1) redox reaction in which using redox reagents, radicals can be generated to form a polymer and grafting reaction occurs; (2) living radical formation, which

avoids the chain termination step either by increasing the rate of initiation without changing the rate of propagation or by eliminating chain termination and transfer reactions. Therefore, polymer chains grow in a constant rate with similar chain lengths which provides polymers capable to grow whenever an additional monomer is supplied; (3) enzymatic technique that expressing the graft reactions can be featured with assistance of enzymes.<sup>44</sup>

### PROPERTIES OF WSR COMPOSITES

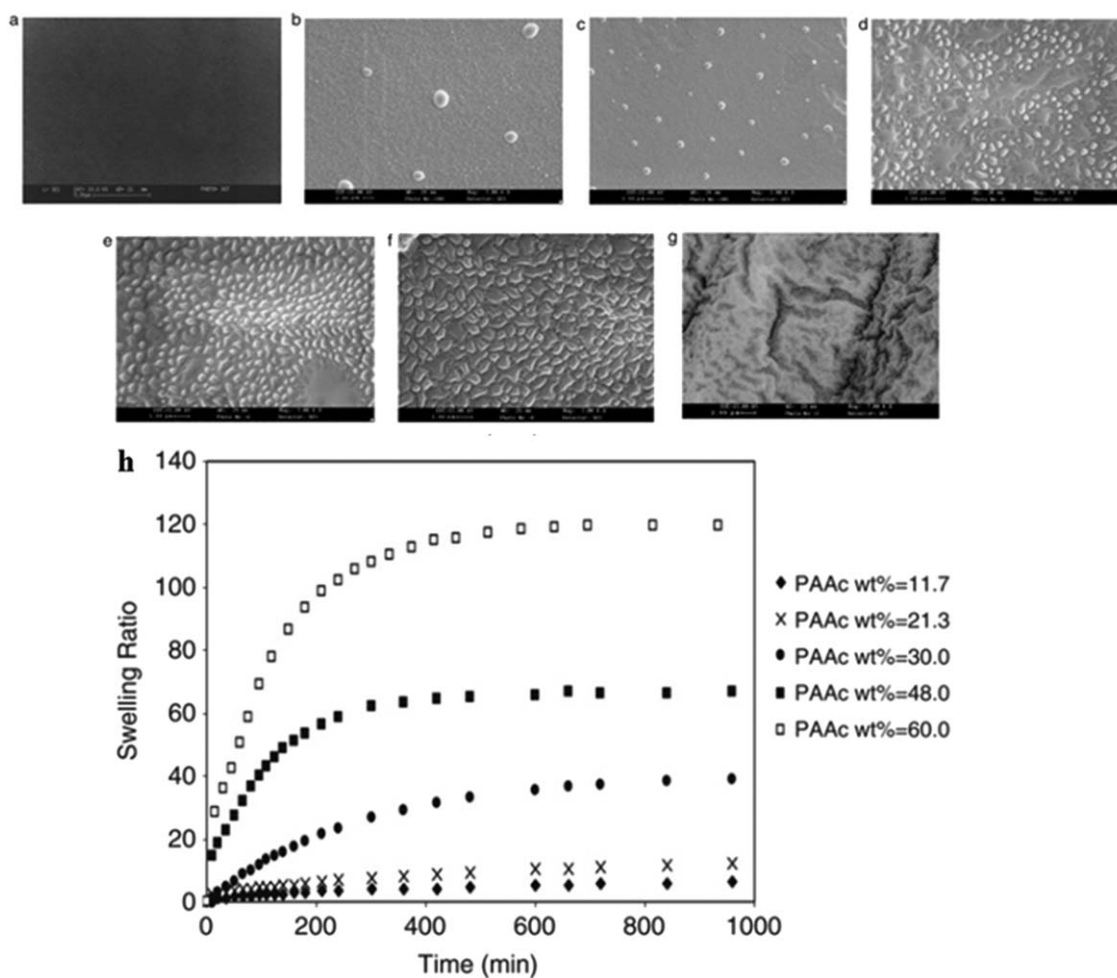
Depending on different factors, the properties of WSR can be changed. The properties most often investigated for such materials are water swellability, water expansion rate, mechanical properties (e.g., tensile and impact results), and morphological characterization of composites.

#### Effect of Mechanical Mixing

Processing techniques and mixing parameters can affect the swellability, phase morphology, distribution, and dispersion of SAP into rubber and influence the mechanical properties of the resultant WSR composites. A comprehensive summary of processing methods for different kinds of composites of WSRs which have been successfully produced is listed in Table I. In mechanical mixing, by varying the mixing time, speed, and temperature, the properties of WSR composites can be optimized. For instance, Zhang *et al.* reported that if the size of SAP grains is within the range of 74–840 nm the dispersion is not homogeneous. After the resultant WSR was immersed in water the SAPs easily dropped out of the rubber matrix. They suggested that fine SAP powder below 20 nm gave better dispersion.<sup>5</sup> This can be achieved by increasing the high shear rate during the mixing process. Figure 5 illustrates the importance of choosing an appropriate mechanical method for the dispersion of SAP into the rubber, with comparison images of samples prepared by (a) Brabender and (b) two-roll mill.

#### Effect of IPN Networks

The morphology of immiscible polymer blends is usually unstable due to high interfacial tension between the phases, which leads to poor physical and chemical interactions across the phase boundaries. IPNs can control the phase morphology of immiscible polymer blends (like interfacial agents) by sharing load between the components without transferring stress across



**Figure 6.** SEM micrographs obtained from cross-sections of (a) (magnification  $\times 7000$ ) unmodified PDMS, and PDMS/PAA IPNs having a PAA contents of (b) (magnification  $\times 7000$ ) 20 wt %, (c) (magnification  $\times 3000$ ) 20 wt %, (d) (magnification  $\times 7000$ ) 30 wt %, (e) (magnification  $\times 7000$ ) 40 wt %, (f) (magnification  $\times 7000$ ) 50 wt %, (g) (magnification  $\times 7000$ ) 60 wt %, and (h) swelling behavior of PDMS/PAA IPNs.<sup>45</sup>

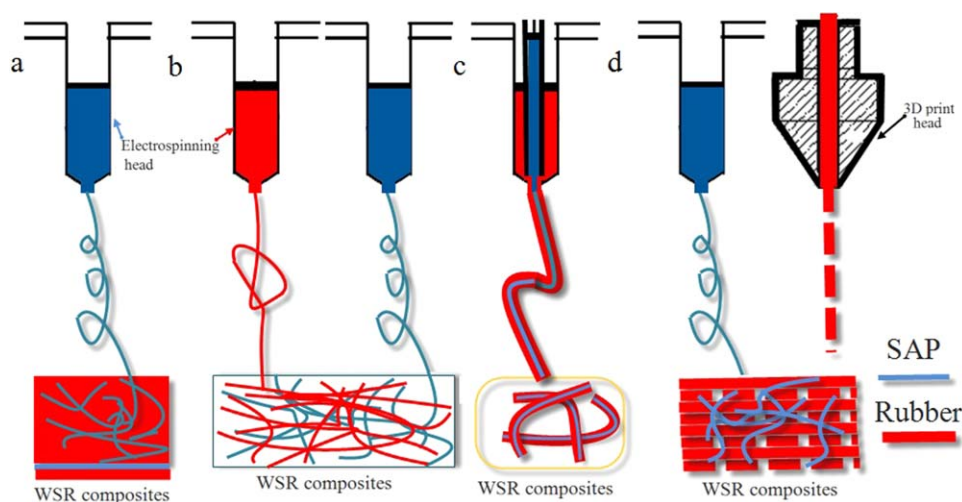
the phase boundaries.<sup>3</sup> This new technology has opened a wide range of variations in the preparation of WSR which can customize the properties to the specific needs of many different applications. Yoo *et al.* prepared PDMS interpenetrating networks of two different molecular weight PDMS, and the swelling, mechanical property, and toughness results proved that the load was effectively transferred between the networks.<sup>48</sup> It has been proposed that selected combinations of two networks could provide synergistic performance which could maximize useful properties and minimize unwanted properties.<sup>49</sup> As an example, Jalili *et al.* proved that the addition of 20 wt % PAA to PDMS with IPNs technology produced the dispersed phase as fine particles, resulting in synergistic effects in the new composites. Their observations are explained in Figure 6, with visible morphological changes in scanning electron microscope (SEM) results, and with changes in swelling properties.<sup>45</sup> Figure 6 shows the variation of swelling with time for the IPNs with different PAA concentrations. This plot exhibits two distinct slopes, with a higher slope at concentrations of PAA greater than 25%. Jalili *et al.* also observed that in the case of IPNs in the solid state, phase inversion occurred at PAA concentrations

of about 60 wt %, but in the swollen state, PAA acted together with the absorbed water as a single phase.<sup>45</sup>

#### Effect of Fillers

Fillers are commonly used to reinforce composites by improving properties such as hardness, tensile strength, tear resistance, and abrasion resistance. Compared to other techniques currently used to enhance the efficiency of WSR, the use of reinforcement fillers is one of the most convenient ways to achieve this goal. In WSR, a common reinforcement filler is silica. It is highly polar due to the existence of numerous silanol groups on its surface which can improve not only the mechanical properties but also the water-absorbent properties of the WSR.<sup>8</sup>

Zhang and co-workers found that when CPA grains were dispersed into CHR, the SAP grains were isolated from others by a rubber phase and could not give full play to the water-absorbing ability. However, with the addition of PEG into the system, some water-absorbing routes between water-absorbent grains were built. In other words, the PEG created a bridge between SAPs to transfer the water among them and make the composite swell. By increasing the PEG content, the number of



**Figure 7.** Schematic drawings of (a) electrospinning SAP fibers/mats to rubber layers, (b) multi-layering electrospinning of SAP and rubber, (c) co-electrospinning of SAP and rubber, and (d) hybrid 3D printing with electrospinning of rubber and SAP to form WSR composites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

water-absorbing routes within rubber was increased and the water-absorption rate was also increased.<sup>7</sup>

The amount of filler plays an important role in compatibilizing WSR.<sup>4-6</sup> With the appropriate amount, the water-absorption properties and the mechanical properties of composites both increase; but if more compatibilizer is added, those properties decrease due to a decrement in the size of the cross-linked networks, limiting the expansion of WSR and its absorption of

water and also affecting tensile properties such as elongation at break and strength at break. Table II shows the use of different reinforcement fillers as compatibilizers and the use of coupling agents for improving specific properties of samples.

#### Effect of Grafting

Graft copolymerization can make the blend system more compatible by reducing the interfacial tension between two phases and increasing the cohesive force between them. Zhang *et al.*

**Table I.** Summary of WSR Composites with Their Corresponding Manufacturing Methods

Polymer	Other substances	Methods	Ref
Chlorohydrin rubber (CHR)	PVA-g-PBA (compatibilizer); Cross-linked polyacrylate (SAP)	Grafting	5
CHR	PVA-g-PBA (compatibilizer) Polyethylene glycol (PEG) Precipitated silica (PSA)	Grafting	7
CHR	Precipitated silica reinforcing filler Cross-linked sodium polyacrylate (CSP); Poly(ethylene oxide) (PEO)	Grafting	8
CHR	PVA-g-PBA and cross-linked polyacrylate (CPA)	Grafting	10
Chlorobutadiene rubber (CR)	CSP; reactive clay; P(AA-co-BA)/CR	IPN	3
Polydimethylsiloxane (PDMS)	PAA	IPN	45
Natural rubber (NR)	Sodium polyacrylate	Internal mixer	9
CR	CSP; PEO; PSA	Banbury mixer	1
NR	PEO- <i>b</i> -PBA; CSP; PSA	Open mill	4
NR	PEO; Trimethylpropane trimethacrylate	Open mill	2
NR	SAP; carbon black (reinforcing agent); TBBS (accelerator)	Open mill	27
NR; Chlorobutyl rubber; Ethylene propylene diene (EPDM)	Polyacrylamide (PAM)	Open mill	46
Styrene Butadiene Rubber (SBR)	Cellulose nanocrystals (CNC)	Solution Casting	47
Styrene Butadiene Rubber (SBR)	Cellulose nanocrystals (CNC)	Compression molding	47

**Table II.** Effect of Different Kinds of Fillers on Water Swelling Ratio and Mechanical Properties of WSRs

WSR	Fillers	Ws (%)	TS and EB	Ref.
	PEO: 5–30 phr;	550–700	-	1
CR + CSP	Precipitated silica: 10–50 phr	800–500		
NR	PEO: 10 phr;	200 (14 days)	TS <sup>a</sup> = 11.1 ± 0.2	2
	Trimethylpropane trimethacrylate: 2 phr		EB <sup>a</sup> = 642 ± 6	
			TS <sup>b</sup> = 8.0 ± 0.1	
			EB <sup>b</sup> = 702 ± 6	
CR + CSP	Reactive clay: 30 phr;	350	TS <sup>a</sup> = 7.7	3
	P(AA-co-BA): 30 wt %		EB <sup>a</sup> = 1530	
			TS <sup>b</sup> = 2.8	
			EB <sup>b</sup> = 1730	
NR + CSP	PEO- <i>b</i> -PBA (36% grafting): 5 phr	1200 (10 days)	-	4
	Precipitated silica			
	PEG: 10–20 phr			
CHR + SAP	PVA- <i>g</i> -PBA: 10 phr	568		5
	PEG 40: phr	-	-	
	PSA: 40 phr	-	-	
CHR + SAP	PVA- <i>g</i> -PBA: 10 phr;	-		7
	PEG: 40 phr;	474	-	
	Precipitated silica: 40 phr	545		
CHR + SAP	Precipitated silica: 15–50 phr;	-	TS <sup>a</sup> = 9.0	8
	PEO: 10 phr		EB <sup>a</sup> = 1070	
			TS <sup>b</sup> = 0.55	
			EB <sup>b</sup> = 350	
CHR + cross-linked CPA	PVA- <i>g</i> -PBA (340.4% grafting): 5 phr	550 (for 80 hrs)	TS <sup>a</sup> = 3.09	10
			EB <sup>a</sup> = 136.27	
			TS <sup>b</sup> = 0.31	
			EB <sup>b</sup> = 92.48	
NR + SAP	Carbon black: 10 phr;	500 (40 phr SAP for 91 days)	TS <sup>b</sup> ≈ 3.5	27
	ZnO: 3 phr		EB <sup>b</sup> ≈ 580	
	S: 0.5 phr			
	TBBS: 1 phr			
PDMS+SAP	Aminopropyltriethoxysilane:0.036 g;	250 (40 phr SAP for 1000 hrs)	TS <sup>a</sup> = 2.29	43
	Sodium hydroxide: 5 g		EB <sup>a</sup> = 171.5	
			TS <sup>b</sup> = 0.09	
			EB <sup>b</sup> = 66.3	

Note: tensile strength (TS, MPa); elongation at break (EB, %).

<sup>a</sup> Before swelling.

<sup>b</sup> After swelling.

showed that the properties of polyvinyl alcohol (PVA) were greatly improved by grafting poly(butyl acrylate) (PBA) with good elasticity due to its long soft side-chains and relatively low glass-transition temperature ( $-49^{\circ}\text{C}$ ) onto PVA. At the same time, the branched chains were hydrophobic, and were used as backbone. PBA can serve between hydrophobic rubber and hydrophilic PVA as an amphiphilic graft copolymer.<sup>5</sup> As a result, the water-absorption and water swelling abilities are enhanced. However, when a large amount of graft polymer is added into

the mixture, the branched chains of PBA agglomerate by themselves and form a thin layer of continuous paste which can obstruct the passage of water molecules through the rubber to reach the SAPs.<sup>6</sup> Thus, the amount of grafted polymer should be optimized to ensure better properties. In a similar experiment, Zhang *et al.* found that the incorporation of PVA-*g*-PBA into chlorohydrin rubber significantly enhanced not only the water swelling behavior but also the mechanical properties of WSR before and after water swelling. The blend consisted of 5



phr PVA-g-PBA with a grafting percentage of 340.4%, and the tensile strength increased from 1.87 to 3.09 MPa and 0.27 to 0.31 before and after water swelling, respectively.<sup>10</sup>

### Other Methods

For fabrication of WSR, some other methods which are not as common as above-mentioned techniques can be used. As an example, aqueous suspensions of absorbent polymer are mixed with rubber to make a homogenous solution. The resulting mixtures are then cast into the glass mould and placed into oven till solvent is completely evaporated. Furthermore, the resulting WSR films can be compressed with optimized conditions to obtain non-shrinking, free-standing films for investigating properties.<sup>47</sup>

### FUTURE OF WSR

The main goal of processing WSR is to achieve a high swelling rate in every contact with water without any drop-out from the rubber, with considerable mechanical strength. One of the main disadvantages of common WSRs is that the costs involved in their processing for specific applications are quite high. Complex technologies such as the use of IPNs to improve the properties can increase the cost of the final product. Therefore, utilization of such technologies on a large scale is not economical. Moreover, they are not generally reusable, and their disposal after use can impact on the environment. Based on the research to date, one of the best ways to enhance the swelling kinetics of WSR is the use of reinforcement fillers which prevent migration of SAP particles from the rubber to the water phase.

As we have discussed, fillers can modify composite properties such as swelling behavior, strength, impact, and solvent resistance. However, fillers with low aspect ratios cannot create a major improvement from the properties of unfilled WSR. When the aspect ratio between the longest and the shortest dimension of the filler is greater than a certain amount, the filler (known as fiber) significantly affects the properties of the composite. Electrospinning enables the manufacture of nanofibers in the form of sheet or membrane-type products with virtually any functional polymer, using known and established formulations. Meanwhile, considering their length, fibers can act as routes for the transfer of water between isolated SAP particles within the rubber matrix, increasing the swellability of WSR. Moreover, with the provision of good bonding between fiber and polymer components (both rubber and SAP), strength in the fiber direction is significantly increased. By bonding to SAP particles, fibers also prevent the migration of SAP from the rubber, with the result that better water swellability can be achieved.

Recently, we reported the improved water absorption property and stability of WSR obtained using electrospun multi-scale hybrid fiber mats of cross-linked PAA nanocomposites as water channels, as shown in Figure 7(a). Electrospinning of various superabsorbent fibers with hyperbranched polymer (HB) and/or graphene oxide (GO) having nano- and submicro-diameter fiber sizes was performed. With hybrid fillers (HB and GO) added into the PAA, spun fiber mats showed the increased water swelling ability due to the presence of spiderweb-like multi-scale structures and enhanced specific surface areas. The

spun fiber mats were added into conventional WSR and the resultant rubber composites showed enhanced water swelling ability. The electrospun fibers acted as internal multi-scale water channels to bridge isolated PAA particles wrapped in hydrophobic rubber together and link the internal PAA with the composite surface to enhance the short- and long-term water swelling ability of rubber composites.<sup>50</sup>

Conversely, further potential for cost-effective seals using simple methods and environmentally friendly processes can arise from innovations in manufacture, especially 3D printing technology and electrospinning methods. Complex technologies such as the use of IPNs to improve printing technology and electrospinning methods are now being used. One of the potential ways to improve the characteristics and performance of WSR is electrospinning of rubber and SAP at the same time, as shown in the probable schematic in Figure 7(b,c) with SAP and rubber.<sup>51</sup> In this technique, different types of polymers are electrospinning either multilayering [Figure 7(b)] or simultaneously together mixed [Figure 7(c)] to make a mixed fiber mesh. In simultaneously mixing process, two different polymers are electrospun from different syringes at the same time on the same target collector. In the multilayering system, after the first polymer is electrospun, the second polymer is sequentially electrospinning on the same collector to form a hierarchically ordered structure of different kinds of polymer (here SAP/rubber).

The other promising technique is 3D printing (layer-by layer) rubber and SAP together, inspired by ideas from Compton and Lewis<sup>52</sup> and Tumbleston *et al.*<sup>53</sup> regarding lightweight cellular composites and continuous liquid interface production by 3D printing. To achieve controlled composition, geometric shape, function, and complexity, 3D printing method is much effective rather than traditional manufacturing procedures. Moreover, to generate composites (especially immiscible blends such as rubber and SAP) with controlled structure and adequate physical properties, advanced fabrication techniques are being used. Hybrid of 3D printing and electrospinning is a good example of such a technique.<sup>54,55</sup> This new method can be further considered to simplify the fabrication of novel WSR composites with value-added performance by incorporating of 3D printing with electrospinning process, as shown in Figure 7(d).

### CONCLUDING REMARKS

The use of WSR has been investigated in great depth by many researchers during recent decades. The methods (physical and chemical) used for processing have a huge effect on the properties of WSR. Indeed, modifications of this new kind of polymer constitute another direction of development in this area, involving features such as reinforcement fillers, compatibilizers, or coupling agents, with the aim of imparting specific desirable properties. This approach to tailor-made materials has been successfully applied to synthetic and natural rubbers. Interfacial interaction promotes adhesion of hydrophobic rubber to hydrophilic substrate and, as a result, great increments in water-absorption ratio have been observed relative to unmodified WSRs. We expect that, with the introduction of

hydrophilic fibers into the WSR as internal water channels as well as reinforcement, greater absorption properties in combination with considerable mechanical strength should be achieved. With the further development of electrospinning and 3D printing technologies, WSR composites with desirable properties can be fabricated in a cost-effective and environmentally friendly manner.

## ACKNOWLEDGMENTS

Y. Tang is grateful for the support of the Australian Research Council with a Discovery Early Career Research Award Grant (DE120102784) for the research work.

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