INTRODUCTION

A functional material named water-swelling rubber (WSR) is composed mainly of elastomeric and hydrophilic polymer, which has excellent elastic sealing and water-swelling properties.\[1\] WSR has wide applications for its convenient operation, high efficiency, and long-term water retention, especially in tunnel engineering and underwater engineering.\[2,3\] The preparation technologies of WSR are divided broadly into two categories: chemical grafting modification and physical blending.\[4,5\] The latter is the most promising way because of its facile production, desirable product properties, and low cost. Hence, multicomponent mechanical blending would be greatly attractive method to prepare water-swelling rubber.

In general, various rubbers such as chlorinated polyethylene,\[6\] styrene-butadiene-styrene block copolymer,\[7\] and poly(dimethylsiloxane) rubber\[8\] have been blended with water-absorbent materials like cross-linking poly(sodium acrylate) (CPNaAA),\[9,10\] poly(vinyl alcohol) (PVA),\[11\] poly(acrylic acid) (PAA),\[12\] and so on, for enhancing the mechanical and water-swelling properties of WSR. But hydrophilic water-absorbent resin or polymer nanofiber cannot disperse well in rubber, so that the hydrophilic components can easily break off from rubber networks due to the poor interface between them.\[13,14\] This will weaken the properties of WSR, such as water-swelling abilities, mechanical properties, water long-term retention, and so on. Therefore, how to improve the miscibility of the water-absorbent resin and rubber becomes a problem.\[15\]
In recent years, compatibilizer was generated to mitigate incompatibility between polymer–polymer.\cite{16} Based on the proximity compatibility principle, the compatibility of hydrophilic dispersion phase and hydrophobic continuous phase is expected to be improved greatly by adding amphiphilic block or graft copolymers, such as poly(vinyl alcohol)-g-poly(butyl acrylate) (PVA-g-PBA), chlorinated polyethylene- g- glycidyl methacrylate (CPE-g-GMA), poly(acrylic acid-co-butyl acrylate) (P(AA-co-BA)), and so on.\cite{17–20} These amphiphilic copolymers can react with rubber and water-absorbent resin to improve the interfacial compatibility of the two phases, through the hydrogen bond or interpenetrating polymer networks and so on. However, the intermolecular force is too weak to absorb the absorbent resin in the rubber firmly, leading to the superior mass loss during the repeated water absorption process.

Maleic anhydride (MAH) has drawn much attention for functionalizing polymer, since maleic anhydride containing unsaturated double bonds can react with –OH, –COOH, –NH$_2$, etc. Therefore, some polymers grafted with MAH are beneficial to increase its compatibility with polar polymers and improve the interaction between fillers and polymers.\cite{21,22} In this study, the P (MMA-co-MAH), synthesized by solution polymerization, was regarded as the compatibilizer applied in WSR system. The WSR was prepared by blending CPE, CPNaAA, P (MMA-co-MAH), and other additives using an internal mixer. The effects of the amount of P (MMA-co-MAH) on mechanical properties and water-swelling behavior were studied. The morphological structure of the fractured surface in WSR was investigated by SEM.

## EXPERIMENTAL

### 2.1 Materials

Chlorinated polyethylene (CPE, 135A, Cl–35%) powder used in this work was supplied by Weifang Yaxing Chemical Co. Ltd., Shandong, China, and dried in an oven at 50°C before use. Methyl methacrylate (MMA), MAH, dibenzoyl peroxide (BPO, AR), polyethylene glycol (PEG-1000), dioctyl phthalate, stearic acid, antioxidant 264, tetrahydrofuran, toluene, and methanol were manufactured by Sinopharm Chemical Reagent Co., Ltd. Dicumyl peroxide was used as a vulcanizing agent and obtained from Sinopharm Chemical Reagent Co., Ltd. Cross-linking poly(sodium acrylate) (CPNaAA, Mesh:100) was supplied by Demi new materials Co., Ltd. (Zhuhai, China). Triallyl isocyanurate was obtained from Nanjing Hand in Hand Chemical Technology Co., Ltd. Fumed silica, magnesium oxide, and the other fillers were all chemical grade and supplied by Aladdin Reagent Co., Ltd (China). All liquid reagents were of analytical grade.

### 2.2 Synthesis and purification of P (MMA-co-MAH) copolymer

Maleic anhydride, regarded as reaction monomer, was mixed with BPO (initiator, 0.4 wt% of reaction monomer.), tetrahydrofuran, and methylbenzene (solvent) in a round-bottom flask of 250 ml capacity. The MMA, resolved in tetrahydrofuran, was added into aforementioned mixing solution by constant pressure funnel at 80°C for 8 hr, and the reaction was protected by N$_2$. At the end of the reaction, the white floc was obtained by quickly stirring with a large amount of methanol. Then, the white floc was washed with methanol for three times. After filtration, the product was dried in vacuum at 50°C and crude products were obtained. The crude product was soaked in toluene for 24 hr, and polymethyl methacrylate (PMMA) homopolymer was extracted. Then, the sediments was dried to obtain pure P (MMA-co-MAH) copolymer. (The molar ratio of MMA/MAH was 1:1 and initiator accounted for 0.4%.) The reaction equation of grafting MAH onto MMA is shown in Figure 1.

### 2.3 Preparation of WSR

Magnesium oxide, PEG-1000, stearic acid, antioxidant 264, dicumyl peroxide, triallyl isocyanurate, fumed silica, CPNaAA, and P (MMA-co-MAH) were masticated in an internal mixer at 25°C for 2–3 min, and then, dioctyl phthalate was added as the plasticizer. CPE was added and blended continuously; vulcanizing agent and co-vulcanizing agent were fed into quickly when the blending system reached a

![Figure 1](image-url) The reaction equation of grafting maleic anhydride onto methyl methacrylate
constant torque. After 0.5 min of mixing time, the mixtures were removed from the mixer and fed to a double-roller blending rolls mill and masticated for 5–7 times; the blended compound was put in a 150 × 150 × 2 mm mold, preheated for 5 min, and cured for 30 min at 160°C in a 15 MPa press vulcanize for vulcanization. After that, the mold was taken out and cooled to room temperature. The sheets of WSR were obtained. The concentrations for the CPE system are expressed in parts per hundred CPE by weight (phr), and the concrete formulations are shown in Table 1.

2.4 | Characterization

The chemical structure of the copolymer was investigated by Fourier transform infrared (FTIR) spectroscopy and proton nuclear magnetic resonance spectroscopy (1H-NMR). FTIR spectra were collected by using a Perkin-Elmer Spectrum One Spectrometer at range of 450–4,000 cm⁻¹. The 1H-NMR spectra were obtained by using a Varian Inova 600 with dissolution in deuterated chloroform (CDCl₃). Tetramethylsilane was used as an internal standard material. Thermal behavior of P (MMA-co-MAH) copolymer was investigated by thermogravimetric analysis (TGA; TGA-60, Shimadzu); the sample was set inside alumina pans and hanged in the heating furnace. The weight of the remaining material was recorded, while the furnace was heating from 50 to 500°C at a rate of 10°C/min. N₂ was fed into the furnace as a purge gas. The micro morphology of WSR was performed on a JEOL-JSM6510LV scanning electron microscope.

In order to measure the tensile properties, dumbbell-shaped specimens were prepared according to GB/T528-1998. Tensile strength, tensile stress at 100% (100%Se), and elongation at break were performed on a universal testing machine (CMT 4104; Shenzhen Sans Material Testing Co., Ltd., Shenzhen, China). Tests were run at room temperature and v = 500 mm/min crosshead speed and the related stress–strain curves were registered. Shore A hardness (Shore A) was measured using Shore A hardness tester according to the GB/T531-1999. The mechanical tests were conducted on samples both before and after water immersion, in which the samples were dipped in deionized water for equilibrium. Five samples for each composite were tested, and the median value was regarded as the final value. The mechanical properties of the materials were determined by a tensile test.

For measuring the water-swelling equilibrium of WSR, the vulcanized strips of the WSR were cut into sheets with dimensions of 20 × 10 × 2 mm, weighted accurately, and soaked in distilled water at room temperature. At regular intervals, the sample was got 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, the samples were dried at 50°C until constant weight. The swelling equilibrium ratio by mass (Sₑ) and the percentage loss by mass (Lₑ) were measured according to the following equations:

\[
Sₑ = \frac{W₂ - W₁}{W₁} \times 100\%
\]

(1)

\[
Lₑ = \frac{W₁ - W₃}{W₁} \times 100\%
\]

(2)

where \(W₁\) and \(W₂\) were the weights of the unswelled and swelled with water, respectively. Experiments were carried out three times and they were averaged; where \(W₃\) was the weight of the dried swollen sample.

For testing the water-swelling rate of WSR at equilibrium when absorbing water at 24 hr, a formula of swelling rate was designed:

\[
v = \frac{SRₑ}{SRₑ^{24}}
\]

(3)

where \(SRₑ\) and \(SRₑ^{24}\) were the water-swelling ratio and water-swelling equilibrium when absorbing 24 hr, respectively.

3 | RESULTS AND DISCUSSION

3.1 | Characterization of P (MMA-co-MAH) copolymer

The chemical structure of copolymer samples was analyzed with FTIR spectroscopy. Figure 2a shows the peaks at 1,730 and 1,198 cm⁻¹ are ascribed to the asymmetric stretching vibration peaks of the carbonyl (O=C=O) and the ether bond (C–O–C) on the MMA, respectively. The peak at 1,447 cm⁻¹ is the vibration absorption peak of –CO–O–CH₃, and the peak at 2,850–3,000 cm⁻¹ is the general saturated alkane.
The peaks at 951 cm\(^{-1}\) are for cyclic anhydrides (O=C−O−C=O) and at 1,240 and 1,148 cm\(^{-1}\) for C−O−C. Those specific bands, known as 1,852 and 1,782 cm\(^{-1}\), are the special absorption peaks of the symmetric and asymmetric expansion vibration of C=O in the five-member anhydride ring. The disappearance of C=C double bonds at 1,637 cm\(^{-1}\) indicated that the copolymerization of MMA and MAH occurred.

With deuterated chloroform (CDCl\(_3\)) as the solvent, the structure of P (MMA-co-MAH) was further confirmed by \(^1\)H-NMR. As shown in Figure 2b, 3.469–3.877 ppm is the proton peak of methyl hydrogen on –COOCH\(_3\) in the MMA structural unit, and 0.760–1.552 ppm is the proton peak of methyl hydrogen in MMA structural unit. The proton peaks of the methylene hydrogen on –CH\(_2\)C− in the MMA structural unit are showed in 1.748–2.178, and 2.599–3.211 ppm is the proton peak of –CHCH in MAH structural unit, indicating that MMA is copolymerized with MAH, and the copolymers have formed with two corresponding monomer units.\(^{[23,24]}\) In addition, 6.41, 6, and 5.47 ppm have disappeared in the \(^1\)H-NMR spectrum of the copolymer, which are regarded as the proton peak of hydrogen on the unsaturated bond in raw MMA and MAH, respectively. It is considered that the basic reaction of the double bonds of MMA and MAH in the product is complete. 2.355, 7.075, and 7.124 ppm in the copolymer \(^1\)H-NMR atlas are the proton absorption peaks of toluene solvent which are not removed in the product. Combined with FTIR and \(^1\)H-NMR analysis, it can be considered that MMA and MAH have copolymerized to form P (MMA-co-MAH).
The TGA curve of P (MMA-co-MAH) copolymer is shown in Figure 3. The weight loss 5\% of the copolymer was defined as the initial decomposition temperature. Figure 3 shows that the peak temperature of degradation for of P (MMA-co-MAH) copolymer was 192.9°C; the fastest degradation temperature was 335.6°C. The AB segment in the TG curve was the degradation of side chain in P (MMA-co-MAH) copolymer, and the CD section was the thermal decomposition of polymer, which is the degradation of main chain, and the decomposition temperature is about 335.6°C. While the fastest degradation temperature of PMMA is at 293.1°C,\cite{25} it is obvious that P (MMA-co-MAH) has good thermal resistance. This is the interactions among five-membered ring of anhydride occurred in P (MMA-co-MAH) copolymer increase the rigidity of the molecular chain.

3.2 Effect of P (MMA-co-MAH) content on the water-swelling properties of WSR

Generally, the water-absorbent resins were usually selected to blend with rubber or elastomer for improving the water-swelling ability of WSR. Cross-linking poly(sodium acrylate) (CPNaAA) was chosen as a super water-absorbent resin to strengthen the mechanical, water-swelling, and morphological properties of WSR. The water-swelling ability had been extensively enhanced, and the mass loss ratio of WSR was decreased. Meanwhile, phase separation was clear between the phases of water-swellable rubber due to the poor compatibility between rubber and CPNaAA. In order to overcome the problem of inhomogeneity between CPE and CPNaAA in their blends, a trial was made by introducing the obtained P (MMA-co-MAH) as a compatibilizer. The effect of P (MMA-co-MAH) dosage on water-absorbent properties of WSR is exhibited in Table 2, the equilibrium water absorption and the water absorption ratio increased slightly with the increase in P (MMA-co-MAH) content. The equilibrium water absorption ratio of the WSRs increased from 337\% (with 0 phr P (MMA-co-MAH)) to 368\% (with 8 phr P (MMA-co-MAH)). The water absorption rate increased from 0.66 to 0.76 when the P (MMA-co-MAH) content was increased from 0 to 8 phr. All of these results indicated that the effect of the introduction of P (MMA-co-MAH) on the water-swelling rate was small. This phenomenon can be explained as follows: The water absorption rate and the equilibrium water absorption ratio of WSRs are mainly depended on the amount and distribution of CPNaAA in WSRs.\cite{6,20} In the formulations, the water absorption component CPNaAA was fixed at 40 phr, and when changing the amount of P (MMA-co-MAH), the distribution of CPNaAA in WSRs was also changed. With the increase in P (MMA-co-MAH) up to 8 phr, CPNaAA dispersed well in the CPE substance and resulted in maximum equilibrium water absorption ratio and the speed of water absorption of WSR. When too much P (MMA-co-MAH) was added, the water-swelling ratio in the equilibrium and the water absorption rate decreased slightly due to the hindrance of P (MMA-co-MAH).

Interestingly, the mass loss ratio decreased remarkably from 7.2\% to 3.0\% when the P (MMA-co-MAH) content was increased from 0 to 10 phr. The more the P (MMA-co-MAH) content, the more CPNaAA is restricted in the CPE matrix, which results in a decrease in $L_w$. Recently, Lang et al.\cite{1} prepared a novel PVC/CPNaAA/CPE water-swellable rubber by blending PVC/CPE, water-swellable resin (CPNaAA), and other fillers. The new composites showed 10 wt\% $L_w$ when the amount of CPNaAA was 40 phr, and the value of $L_w$ increased with the increase in CPNaAA. With the increase in CPNaAA content in WSR, the proportion of CPNaAA also increased gradually. However, the poor

<table>
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<tr>
<th>Property</th>
<th>The content of P (MMA-co-MAH) (phr)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Equilibrium water absorption</td>
<td>337</td>
</tr>
<tr>
<td>(SR,%)</td>
<td></td>
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<tr>
<td>Water absorption rate (V)</td>
<td>0.66</td>
</tr>
<tr>
<td>Mass loss ratio ($L_w,%$)</td>
<td>7.2</td>
</tr>
</tbody>
</table>

TABLE 2 Effect of the content of P (MMA-co-MAH) on water-absorbent properties of water-swelling rubber
interfacial compatibility between CPNaAA and CPE resulted in CPNaAA falling off from WSR easily during repeated water absorption; thus, the more CPNaAA, the higher \( L_w \). Zhang et al. [17] obtained a kind of WSR by multicomponent blend method, which took the chlorohydrin rubber (CHR) as rubber, cross-linked polycrylate (CPA) as water-swelling resin, and poly(ethylene glycol)-g-poly(butyl acrylate) (PVA-g-PBA) as compatibilizer. The \( L_w \) was 18.82% when CPA in the WSR was 70 phr in the absence of PVA-g-PBA. However, with the introduction of PVA-g-PBA, the mass loss of WSR was decreased. When the PVA-g-PBA was 10 phr, the \( L_w \) was 16.72%. Obviously, this is because the PVA-g-PBA could reduce the interfacial tension and improve the dispersion of CPA in CHR. Therefore, the addition of compatibilizer PVA-g-PBA could decrease \( L_w \).

In this work, when all the raw materials were masticated in an internal mixer, the –C=C– and –COO– of P (MMA-co-MAH) can be cross-linked with CPE, which can form cross-linked network from CPE and improve the distribution of CPNaAA. With the reaction of P (MMA-co-MAH) between CPE and CPNaAA, CPNaAA was wrapped in CPE matrix, causing a stable and less mobile interface that can resist the loss of hydrophilic compounds.

### 3.3 Effect of P (MMA-co-MAH) content on the mechanical properties of WSR

The properties of multiple component polymer materials, especially the mechanical behavior, are related to content and components of the blends. Figure 4a,b shows that the tensile strength and elongation at break of WSR in dry state and wet state changed with the alteration of P (MMA-co-MAH). The maximum value of tensile strength of dry-state WSR was 11.3 MPa when the P (MMA-co-MAH) was 5 phr, which increased with the increase in P (MMA-co-MAH) content, but when P (MMA-co-MAH) amount was over 5 phr, tensile strength decreased. Obviously, the tensile strength of WSR in wet state was better than that of WSR in dry state. This is because that in the wet state, water can fill in the gap through permeating in the WSR blends. Due to the “bridge” effect of water, the stress transport was improved, so the tensile strength of wet-state WSR was increased, [19] but the WSR in wet state showed higher elongation at break than that of WSR in dry state. Figure 4c,d shows the effect of the P (MMA-co-MAH) content on the tensile stress at 100% and Shore A hardness of the blends in dry state and wet state.
state, respectively. P (MMA-co-MAH) could efficiently improve the tensile stress at 100% and Shore A hardness regardless of dry state or wet state. When too much P (MMA-co-MAH) was added, there was a tendency that the tensile strength and elongation at break performance of WSR in wet and dry states were lost. It is worthy to notice that the WSR sample containing 40 phr of CPNaAA and 10 phr of P (MMA-co-MAH) with 100 phr of CPE had satisfactory tensile strength, about 11.3 MPa. The value is much better than that of CPE/PNaAA WSR\[^{[1]}\], CR/PNaAA WSR,\[^{[4]}\] NBR/CSPSPAA/Na/P(AA-co-BA) WSR\[^{[20]}\] with similar formulations, and so on. It should be noted that adding P (MMA-co-MAH) to blends could result in some chemical bonding between the two phases (CPNaAA and CPE), which could enlarge the contact area of two phases and increase phase homogeneity of blends. In addition, P (MMA-co-MAH) has played a role as a reinforcing agent, so that it can disperse evenly in all directions. The compatibilization role of P (MMA-co-MAH) can be attributed to the presence of polar groups in MAH chain and backbone chains, which can reduce the superfacial tension of CPNaAA and the superfacial tension of CPE elastomer, respectively. Thus, the usage of P (MMA-co-MAH) has weakened the interfacial tension and ameliorates the compatibility, which improved the performance of WSR.\[^{[19]}\]

**FIGURE 5** The SEM images of water-swelling rubbers with different amount of P (MMA-co-MAH) (a) 0 phr; (b) 5 phr; (c) 10 phr. MAH: maleic anhydride; MMA: methyl methacrylate

**FIGURE 6** The schematic diagram of compatibilization mechanism of P (MMA-co-MAH) in water-swelling rubber. MAH: maleic anhydride; MMA: methyl methacrylate
3.4 Effect of P (MMA-co-MAH) content on the morphologies of WSRs

Figure 5a–c shows the SEM images of WSR containing 0, 5, and 10 phr P (MMA-co-MAH), respectively. As shown in Figure 5a, the WSR has a distinct two-phase structure without adding P (MMA-co-MAH), and the dispersed phase formed a deformed cavity on the cross section. The phase domain of the dispersed phase is larger and inhomogeneous, indicating poor interfacial adhesion between phases. After the P (MMA-co-MAH) was added into the WSR, there were obvious changes in fracture surface of reactive blends. As shown in Figure 5b, with the addition of 5phr P (MMA-co-MAH), the size of dispersive microdomain of CPNaAA and surface pores became smaller and the fracture surface became rough. This indicates an enhancement of the interfacial compatibility. With the increase in the amount of P (MMA-co-MAH), the interface and holes become vaguer (in Figure 5c), and this phenomenon shows the better improvement of compatibility between CPNaAA and CPE. This is because the anhydride group in the molecular chain of the P (MMA-co-MAH) copolymer can react with the carboxyl group in the chain of CPNaAA, forming the cross-linking structure. In the meantime, the compatibility between the two phases of the rubber and the water absorption component were enhanced with the polarity of the MAH group and the Cl atom in CPE.[20]

3.5 The compatibilization mechanism of P (MMA-co-MAH) in WSR

To understand the effect of compatibilizer P (MMA-co-MAH) in WSR, we proposed a possible mechanism. As shown in Figure 6, the water-absorbent resin could not disperse evenly in WSR due to the polarity effects. With the addition of P (MMA-co-MAH), polar hydrophilic anhydride group of P (MMA-co-MAH) could increase the ionic strength of the absorbent resin and improve the affinity of polymer network to water. And the double bonds and –COO– can be chemically cross-linked with rubber during vulcanization process, which can improve the dispersion of water-absorbent resin particles in the rubber matrix, reduce the precipitation, and cause a certain coupling effect. Accordingly, the P (MMA-co-MAH) could enhance the water-absorbent abilities and mechanical properties of WSR.

4 CONCLUSIONS

The P (MMA-co-MAH) copolymer was successfully prepared and blended with CPE, CPNaAA, and other ingredients to construct WSR. Morphological observation of the fracture surface of WSR before and after water swelling demonstrated that P (MMA-co-MAH) decreased the interfacial tension between the rubber and the water-absorbent resin and increased the cohesive force between CPE and CPNaAA. Mechanical properties before and after water swelling were greatly improved by P (MMA-co-MAH). The changes are more distinct in the blend with the addition of P (MMA-co-MAH). The stress–strain curves of the dynamically vulcanized WSR exhibited an elastomeric behavior. The increase in P (MMA-co-MAH) content in WSR led to the distinct increase in hardness, tensile strength, water absorption speed, and water-swelling equilibrium ratio, whereas the weight loss and elongation at break were decreased. The optimum amount of P (MMA-co-MAH) was 8 phr, and tensile strength, elongation at break, water-swelling equilibrium ratio, water absorption speed, Shore A, and percentage loss of the WSR were 11 MPa, 393%, 368%, 0.76%, 81%, and 3.3%, respectively.

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