EFFECT OF ADDING CRUMB TIRE RUBBER PARTICLES ON THE MECHANICAL PROPERTIES OF DCPD-MODIFIED SULFUR POLYMER MORTARS

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HAMED MARAGHECHI, IMAN FOTOVAT AHMADI AND SIAMAK MOTAHARI

Sulfur polymer mortars are composite materials in which modified sulfur is the binder while sand and other fillers are used as aggregates. Sulfur-based composite materials are characterized by their high chemical and mechanical properties along with fast setting behavior. However, sulfur modification is essential in order to achieve sulfur mortars with enhanced characteristics. In this study, incorporation of crumb tire rubber in dicyclopentadiene-modified sulfur-based mortars, as some replacement of sand, is evaluated. Use of crumb tire rubber influences the compressive stress-strain behavior of the mortars significantly. While the compressive strength of the rubber-added mortars is reduced dramatically, the postpeak response of the mortars is of the great interest. Use of a reactive-mixing method improves the compressive strength of rubber-added sulfur polymer mortars up to approximately 25%. Scanning electron microscopy observations confirm better adhesion between the rubber particles and sulfur polymer matrix via reactive mixing. Furthermore, it is clarified that the crumb tire rubber type and presence of a curing agent during the mortar preparation process affect the mechanical properties of the sulfur mortar.

1. Introduction

Large amounts of sulfur are produced annually in some countries, from the mining of sulfur deposits and as a byproduct of oil and gas refining in the petroleum industry. Nowadays sulfur is known as a prominent candidate for certain applications in construction industries. As an alternative to cement concrete, sulfur concretes have found their way among other construction materials. Sulfur concrete is obtained by mixing modified sulfur melt as the binder and preheated stone, sand, and filler as aggregates. Solidification of the fresh mix occurs rapidly and the concrete gains its strength shortly. High mechanical strength, fast setting, low permeability, and high chemical resistance against strong acids and saline environments are some of the remarkable characteristics of sulfur concrete [Abdel-Jawad and Al-Qudah 1994]. In many specialized construction and transportation applications in which conventional materials like Portland cement are unable to endure the operational conditions, sulfur concretes would be an appropriate substituent option. These conditions could include pipes or tiles for handling acidic sewer waters, airfield runways and aircraft parking, flooring material for industrial plants, and tanks for holding corrosive substances [Yue et al. 2006; Mohamed and El Gamal 2007; 2009].

Sulfur concrete with unmodified sulfur binder lacks durability and stability. During solidification from melt, pure or unmodified sulfur crystallizes to the monoclinic allotropic (S$_\beta$), which is stable between the melting point of sulfur and 95°C. On further cooling to ambient temperature, the monoclinic allotropic reverts to the denser orthorhombic allotropic (S$_\alpha$), which has a different crystalline structure. This transition takes approximately a day to complete. As a result of the distinct densities and structures

*Keywords:* sulfur polymer mortar, modified sulfur binder, crumb tire rubber, ductile behavior, allotropic transformation.
of these two allotropes, large shrinkage and residual internal stresses are induced within the bulk of the sulfur. In addition, when using unmodified sulfur as the binder in composite materials or concretes, microcrystals of orthorhombic sulfur start to grow and change into macrocrystals of orthorhombic sulfur. This makes the composite brittle and impractical for most applications, due to loss of durability. Chemical modification of sulfur overcomes these problems, particularly concerning the changes in crystallinity. Frequently, polysulfides, or some commercial materials such as SRX™ (Starcrete™ Technologies Inc.), are used in order to modify and control the crystallization of sulfur [Blight et al. 1978; Bordoloi and Pearce 1978]. Other chemicals, such as dicyclopentadiene (DCPD), its oligomers, and bitumen have also been employed [McBee and Sullivan 1982; Mohamed et al. 2006]. The reaction products of these components are mostly mixtures of various polysulfides and unreacted sulfur. The reactions of sulfur with dicyclopentadiene have been investigated by several researchers [Blight et al. 1978; Bordoloi and Pearce 1978; Mohamed and El Gamal 2007]. While sulfur-modified concrete is a promising alternative material in specialized applications, its high initial fabrication costs and relatively low melting temperature comparing to Portland cement restrict its utilization in large-scale ordinary constructions.

The increasing volume of used tires in landfills has caused serious environmental problems. Since waste rubber is not easily biodegradable even after a long period of landfill treatment, material and energy recovery are alternatives to disposal. Thus, many studies have been carried out in recent decades looking for applications of waste rubber in construction materials, especially in Portland cement concretes. Researchers have endeavored to enhance some mechanical properties of concrete, such as toughness and energy absorption, by incorporating scrap tire rubber of various shapes and sizes: crumb, milled tire rubber, slit, and shredded or chipped tires [Topçu and Avcular 1997; Khatib and Bayomy 1999; Segre and Joekes 2000; Bennazzouk et al. 2003; Albano et al. 2005; Bignozzi and Sandrolini 2006]. Tantala et al. [1996] examined the energy absorption capacity of rubberized Portland cement concrete (rubcrete) mixtures made by replacing 5% to 10% of coarse aggregate by volume with scrap rubber, and reported that the toughness of rubcretes is higher than that of the control concrete mixture. Low-density concrete mixtures, made using crumb rubber to replace up to 30% by weight of coarse and fine aggregate, have shown improved crack and chemical resistance [Sukontasukkul and Chaikaew 2006]. According to [Siddique and Naik 2004], on the use of scrap tire rubber in concrete, the compressive strengths of rubber modified concretes are less than those of unmodified concretes; however, toughness and impact strength improve. Moreover, it was observed that the use of coarse scrap tire rubber affects the properties more negatively than the use of fine particles [Eldin and Senouci 1993]. Analyzing the fracture mechanisms in rubber modified concretes indicated that the bonds between cement and rubber particles were weak. Bond strength augmentation between rubber and cement is the key parameter in overcoming the defects of rubber modified concrete [Topçu and Avcular 1997].

This paper presents the results of a study on the use of crumb tire rubber as a feasible toughness enhancer in sulfur polymer mortars. The effect of rubber content on stress-strain behavior, compressive strength, density, and elastic modulus is investigated and compared with Portland cement mortars. Furthermore, reactive mixing and ordinary mixing procedures and their influence on the compressive strength of the prepared samples are evaluated. As a result, the effect of the presence of crumb rubber particles during the copolymerization of sulfur with dicyclopentadiene (DCPD) is determined. Finally, the influence of rubber type — tread or sidewall tire rubber — and the availability of traditional rubber-curing agents during mortar mixing on the mechanical properties of the sulfur polymer mortar is studied.
2. Experimental

Materials. Elemental sulfur (99.9% purity) was obtained from the Tehran Refinery Complex, Iran. Dicyclopentadiene (DCPD) was supplied by Merck with 99.9% purity. Stearic acid, zinc oxide, and accelerator CZ (N-cyclohexyl benzothiazole-2-sulfenamide) were supplied by Issatiss (Yazd Tire Co.) and used as curing agents. Crumb tire rubber selected from tread and sidewall sections of car tires was supplied by Issatiss (Yazd Tire Co.), with maximum particle size of approximately 0.4 mm and densities of $1.15 \pm 0.02 \, \text{g/cm}^3$ and $1.09 \pm 0.02 \, \text{g/cm}^3$, respectively. The composition of tire tread and sidewall rubber are presented in Table 1. Ordinary Portland cement type II was provided by the Abeyek Company, Iran. Washed natural river sand with density of $2.60 \, \text{g/cm}^3$ was used as fine aggregate in sulfur and Portland cement mortar mixtures. The sand was kept in a $140^\circ \text{C}$ oven for twelve hours to dry and heat up. The maximum size of sand in sulfur-based mortars is 2.4 mm and the stone dust was used as filler. Cumulative grain size distribution of the crumb tire rubber and sand particles are shown in Figure 1.

Procedures. As a binder of mortars, modified sulfur was produced by a copolymerization reaction of sulfur melt with 10% (w/w) dicyclopentadiene uniformly mixed for three hours at $140^\circ \text{C}$ using a mechanical stirrer. The progress of the reaction was followed carefully by temperature and viscosity variation.

<table>
<thead>
<tr>
<th>Components</th>
<th>Tire tread</th>
<th>Tire sidewall</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural rubber</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Synthetic rubber</td>
<td>50 (SBR)</td>
<td>45 (BR)</td>
</tr>
<tr>
<td>Carbon black</td>
<td>45</td>
<td>50</td>
</tr>
<tr>
<td>Naphthenic oil</td>
<td>9</td>
<td>7</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Sulfur</td>
<td>1.5</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 1. Chemical compositions of tire tread and sidewall tire (parts per hundred of rubber).

Figure 1. Cumulative grain-size distribution of crumb rubber and sand particles.
Since the reaction was exothermic, accurate temperature control was essential to make sure the reaction temperature did not exceed 145°C; otherwise the viscosity would rise abruptly and unstable sulfur would form. The reaction product, which hereafter is called modified sulfur binder, was a mixture of polysulfide and unreacted sulfur.

Portland cement and pristine and modified sulfur polymer mortar proportions are reported in Table 2, so that their characteristics can be assessed and compared with each other by performing the proposed analyses. The mixtures marked with “P” and “S” are the formulations in which Portland cement and pristine sulfur, respectively, are used as the binder. The symbol “MS” represents the mortars containing modified sulfur binder. MS0, MS5, MS10, and MS15 mixtures are those in which 0, 5, 10, and 15% (v/v) of sand are replaced by crumb tire rubber with identical particle size, respectively. Portland cement mortars were prepared by mixing the components shown in Table 1 with a water/cement ratio of 0.48. Specimens were cured at 20°C and 100% relative humidity for 28 days prior to testing. In order to make fresh sulfur polymer mortars comprising crumb tire rubber particles, initially prefabricated modified sulfur binder was melt mixed with the specified amounts of rubber particles for 5 minutes mechanically so that homogeneous mixtures in which modified sulfur binder wetted the rubber particles utterly were obtained. Subsequently, sand and filler particles that were preheated up to 140°C were added to the mixture according to their volume percentages in Table 2 under strict temperature control. After a homogeneous mixture was attained, prepared mortars were cast in cubic preheated steel molds (130°C) with dimensions of 50×50×50 mm. They were then compacted by a vibrator for 30 s. The samples were permitted to cool down to ambient temperature and demolded after 24 hours. All tests were implemented one week after mixing.

In one set of experiments, in order to evaluate the increase in adhesion between rubber particles and sulfur polymer matrix, reactive mixing and ordinary mixing procedures were studied. In the former procedure, crumb rubber particles were added to the reaction mixture of sulfur/DCPD from the beginning of the copolymerization, while in latter the rubber particles were added after the copolymerization of sulfur with DCPD.

**Testing techniques.** Differential scanning calorimetry (DSC) was performed by Dupont 2000 V4.0B equipment to examine the influence of different DCPD percentages on the allotropic phase transformation of the sulfur as a result of thermal variation. Three different sulfur mixtures with 5, 8, and 10 wt% DCPD were analyzed after being stored for a week; the heating rate was 10°C/min.

<table>
<thead>
<tr>
<th>Components</th>
<th>P</th>
<th>S</th>
<th>MS0</th>
<th>MS5</th>
<th>MS10</th>
<th>MS15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur</td>
<td>0</td>
<td>35</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Portland cement</td>
<td>35</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Modified sulfur</td>
<td>0</td>
<td>0</td>
<td>35</td>
<td>35</td>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td>Sand</td>
<td>55</td>
<td>55</td>
<td>55</td>
<td>50</td>
<td>45</td>
<td>40</td>
</tr>
<tr>
<td>Filler</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Crumb rubber</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>5</td>
<td>10</td>
<td>15</td>
</tr>
</tbody>
</table>

**Table 2.** Mix design of Portland cement and sulfur polymer mortars with and without crumb tire rubber (volume %).
Mechanical properties of the prepared samples were determined one week after molding as average value of three samples for each mixture by a Zwick 1494 (Germany) testing machine on 50 × 50 × 50 mm cubic sulfur polymer mortar with a constant deflection rate of 5 mm/min.

In order to investigate the interface adhesion between the rubber particles and modified sulfur binder qualitatively, microstructure observations were carried out by scanning electron microscopy (CamScan, MV2300, operated at 20 kV) on the fracture surface resulting from compressive strength tests after samples were sputtered with silver layer.

3. Results and discussion

**DSC characterization of modified sulfur.** In order to be assured of the copolymerization reaction between the sulfur and the modifier, DSC diagrams for pure sulfur and sulfur with three different DCPD loading percentages are depicted in Figure 2. It was mentioned before that the advantage of sulfur modification is that the crystalline phase transformation during cooling down of the molten sulfur to ambient temperature would be retarded. Hence, less orthorhombic structures are formed due to the presence of polysulfides. Sulfur and modified sulfur samples prepared from the molten state were analyzed with DSC after proper storage time under ambient conditions. The storage period is to ensure enough time for the phase transformation from $S_\beta$ to $S_\alpha$ to be complete. In the DSC heating diagram corresponding to pure sulfur (Figure 2a), two separated endothermic peaks are observed. The first peak at around 102°C is attributed to the crystalline phase transformation of orthorhombic ($S_\alpha$) to monoclinic ($S_\beta$) structures during temperature increase. The second peak is associated with the melting of sulfur monoclinic structures.

![DSC diagrams](image)

**Figure 2.** DSC diagrams of (a) pristine sulfur, (b) 5 wt% DCPD and sulfur, (c) 8 wt% DCPD and sulfur, and (d) 10 wt% DCPD and sulfur.
which obviously require more heating energy. However, it is observed that by addition of DCPD to pure sulfur the first peak gradually broadens and becomes the shoulder of the second peak as the percentage loading of the modifier increases (Figures 2b and 2c) and then when 10 wt% DCPD is used the second peak is mostly diminished (Figure 2d). A similar observation was reported in [Lui et al. 2008], a study on sulfur coated urea. The modified sulfur is a mixture of polysulfides and unreacted sulfur. In fact, polysulfides hinder the crystallization of free unreacted sulfur in the modified sulfur binder substantially. Thus, the unpleasant mechanical behavior of pristine sulfur concrete as well as its volume shrinkage is avoided via modification process since the modified sulfur does not undergo the allotropic transformation during thermal alteration.

**Effect of the addition and replacement methods.** The compressive strength of two sulfur polymer mortar mixtures, with the same formulation as MS10, yet prepared through different approaches — addition and replacement — was compared. In the addition method sand grains were replaced by rubber particles indiscriminately, while in the replacement method sand aggregates were replaced with crumb rubber tire of a similar grain size. The results indicate that using the replacement method the compressive strength grows by approximately %5, reaching 18.96 MPa, relative to 17.98 MPa for the sample prepared via the addition method. As a consequence of volumetric substitution of the similar size sand with crumb rubber particles in the replacement method, it is observed that sulfur polymer mortar with higher compressive strength and fluidity is achieved. This is mainly because in the addition method, sand particles are replaced by rubber grains with a larger total surface area for the same bulk volume. Thus the resulting mortar has a higher interface area between sulfur paste and rubber grains, relative to mortar prepared via the replacement method. Since the sulfur-rubber bond is weaker than the sulfur-sand bond, reduction in strength and workability is observed in the case of the addition method. Similarly, replacing the sand by rubber based on mass percentage would result in a severe slump and strength reduction. Therefore, all mortars in this study are prepared through the replacement method, in which sand particles are replaced by similar-sized rubber grains.

**Effect of rubber particles on physical and mechanical properties of mortar.** The physical and mechanical properties of the mortars described in Table 2 are listed in Table 3. Preliminary observations of all fresh mortars showed relatively good flowability, as a result of the high volume fraction of binder. During the preparation of the sulfur polymer mortars, it was observed that the workability of the fresh mixtures decreases with an increase in the rubber content. According to [Eldin and Senouci 1994], on

<table>
<thead>
<tr>
<th>Composition</th>
<th>Hardened unit weight (g/cm³)</th>
<th>Compressive strength (MPa)</th>
<th>Elastic modulus (GPa)</th>
<th>Failure strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>2.45</td>
<td>32.48</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>S</td>
<td>2.43</td>
<td>39.54</td>
<td>18.34</td>
<td>0.221</td>
</tr>
<tr>
<td>MS0</td>
<td>2.40</td>
<td>48.87</td>
<td>21.68</td>
<td>0.229</td>
</tr>
<tr>
<td>MS5</td>
<td>2.34</td>
<td>31.62</td>
<td>17.36</td>
<td>0.242</td>
</tr>
<tr>
<td>MS10</td>
<td>2.25</td>
<td>18.96</td>
<td>9.31</td>
<td>0.254</td>
</tr>
<tr>
<td>MS15</td>
<td>2.19</td>
<td>15.51</td>
<td>6.86</td>
<td>0.313</td>
</tr>
</tbody>
</table>

Table 3. Physical and mechanical properties of the samples.
rubberized concrete, this observation is attributed to the interlocking structure of tire chips, which lessens the flowability of concrete. It is also claimed that this behavior could be related to the reduced density of the concrete as well as the high friction between the rubber particles and the mixture due to the rough surface of the rubber aggregate particles [Nehdi and Khan 2001; Cairns et al. 2004].

All prepared sulfur polymer mortars possess lower density than the Portland cement mortar. Logically, replacement of natural sand with rubber particles reduces the density of the sulfur polymer mortars, as a result of the inherent lower density of rubber particles compared to sand. Unit weight results indicate that increasing the crumb rubber content decreases the sulfur polymer mortar density, resulting in lighter mortars (Table 3). For instance, the MS15 sample exhibited lighter weight, with density decreased approximately 8.7% as compared to sulfur polymer mortar without rubber particles (MS0).

According to Table 3, the compressive strength of the pristine sulfur mortar (S) is almost 21% higher than that of Portland cement mortar. It is also observed that sulfur polymer mortar (MS0) has higher compressive strength and elastic modulus than pristine sulfur mortar. This is due to the fact that polysulfides retard the unfavorable crystallization transformation and thus less shrinkage occurs upon cooling and less residual stresses are developed within mortar. This leads to higher mechanical properties in comparison with unmodified mortar. Introduction of rubber particles in sulfur polymer mortars leads to a general decreasing of mechanical properties. Considerable reduction in compressive strength is observed for sulfur polymer mortars in which sand grains are replaced by rubber particles. The more sand grains substituted by rubber particles, the less the compressive strength of the mortar. In mortars with 5% rubber, a decrease of approximately 35% in compressive strength is observed in comparison with MS0, while the approximate reductions in compressive strength of the mortars with 10% and 15% rubber content are 61% and 68% respectively. That an increase in volume percentage of rubber particles in the mortar from 10 to 15% reduces the compressive strength at a slower rate has also been observed and reported by other authors [Eldin and Senouci 1994]. Reduction in compressive strength and modulus was anticipated because rubber particles have lower modulus and higher resiliency in comparison with sand grains. This results in the formation of cracks within the mortar, particularly along the boundary of separated phases, upon loading and also in failure of sulfur polymer mortar. In fact, weak adhesion between the surface of rubber particles and the modified sulfur binder causes the mortars to fail at lower stresses as a result of debonding between the rubber and the binder. Similar findings have been made by other researchers while using scrap tire rubber in Portland cement concretes. The reduction of the compressive strength is attributed to the weak rubber/binder adhesion [Eldin and Senouci 1994; Bignozzi and Sandrolini 2006]. It can also be assumed that since crumb rubber particles have a low elasticity modulus they act as void in concrete, and hence they are not able to withstand the applied external load. However, it is found that the enhancement of the adhesion between the rubber and binder through pretreatment of the rubber particles improves its ultimate mechanical strength [Nehdi and Khan 2001]. The comparison between the compressive strength of rubber-added sulfur polymer mortar and that of Portland cement mortar reveals that although with incorporation of crumb rubber in sulfur polymer mortar composition the mechanical strength is decreased, the obtained values may still be acceptable for some nonstructural applications.

Stress-strain curves for pristine sulfur mortar and sulfur polymer mortars, with and without rubber particles, are presented in Figure 3. As observed in the left part of the figure, pure sulfur mortar exhibits completely brittle behavior and after its peak stress, the mortar fractures and collapses abruptly. Modification of sulfur by DCPD has generated a binder system with slightly ductile characteristics;
therefore the MS0 sample shows improved behavior in comparison with mortar S, resulting from the inhibition of allotrope conversion, as discussed before. Despite the unfavorable effect of rubber particles on compressive strength, the increase in rubber content improves postpeak response of the mortars. It can be inferred from Figure 3, right, that rubber-added sulfur polymer mortars sustain their integrity and withstand deformations better than mortars without rubber. As a matter of fact, various cracks are generated within samples under compression loads due to stress concentration on the interface of rubber particles and binder, which leads to failure of the sample; however, rubber particles lessen the crack propagation rate and hence delay the failure of samples containing crumb rubber tire. Figure 4 shows photographs of an MS15 sample during postpeak deformation and after its failure. The picture in part (a) is taken at a stress of 7 MPa and strain of 0.66%, and as it is seen the sample has withstood large plastic deformation without full disintegration and has kept its unity after undergoing remarkable displacement.

Figure 3. Left: Stress-strain curves for pristine sulfur mortar (S) and sulfur polymer mortar (MS0) samples. Right: Stress-strain curves for mortar samples containing different percentages of crumb rubber particles.

Figure 4. Behavior of MS15 mortar (a) during postpeak deformation and (b) after failure.
Such a behavior of the rubber-added mortars is not observed in mortars without rubber particles. With an increase in the rubber content, samples reveal more ductile behavior and the deformability of the sulfur polymer mortar is enhanced. The displacement of strain at peak toward higher values for rubber-added mortars confirms the above-mentioned behavior transition. Similar behavior was reported in [Yue et al. 2006] by increasing the rubber content in sulfur rubber concrete. This is mainly because rubber particles serve as crack stabilizers and toughness enhancers in sulfur polymer mortars. Moreover, it can be seen in Table 3 that the elastic modulus declines with increasing rubber content in sulfur polymer mortar, which is associated with the formation of a less rigid mortar.

**Comparison of ordinary mixing and reactive mixing procedures.** As mentioned before, the weak adhesion of the rubber and modified sulfur binder results in significant strength loss in rubber-added mortars. Hence, promoting affinity by means of chemical interaction between the rubber particles and the modified sulfur binder can improve the mechanical properties. To this end, favorable conditions for the reaction between the surface of the rubber particles and the modified sulfur binder are achieved through the inclusion of the rubber particles in the sulfur modification reactor during copolymerization by DCPD. This procedure is called reactive mixing, due to the simultaneous presence of DCPD, sulfur, and rubber particles in the reactor, while in the ordinary method rubber particles are added after the copolymerization of sulfur with DCPD. It is evident that the sulfur radicals serve to substitute allylic hydrogen sites present in elastomer chains to form crosslinked structures. Noting the possibility of the existence of double bonds on the surface of cured rubber particles, pristine sulfur or DCPD-modified sulfur could react with rubber unsaturated bonds at 140°C for 3 hours, and further vulcanization of rubber particles and interaction with the sulfur would form during reactive mixing. According to Table 4, the compressive strengths of the samples prepared through reactive mixing indicate more than 20% growth. Although increase in the rubber content decreases the compressive strength of sulfur polymer mortars, the growth rate of the compressive strength of the samples prepared via reactive mixing in comparison with that of samples prepared by the ordinary mixing method is enhanced with increase in rubber content. In other words, the compressive strength of MS5, MS10, and MS15 improve by approximately 21%, 24%, and 25%, respectively, which shows enhanced interactions between sulfur and rubber in the case of reactive mixing.

In order to visualize the enhanced interaction and adhesion between rubber and sulfur phases, SEM micrographs of the fracture surfaces of rubber-added sulfur polymer mortar (MS10) prepared by ordinary and reactive mixing procedures are presented in Figure 5. The images depict the interface of rubber particles and a bulk region of modified sulfur binder phases. Comparing the two micrographs, it is observed that the adhesion of rubber particles and modified sulfur binder is enhanced by the reactive mixing method.

<table>
<thead>
<tr>
<th>Compressive strength (MPa)</th>
<th>Ordinary mixing</th>
<th>Reactive mixing</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS5</td>
<td>31.62</td>
<td>RMS5 38.26</td>
</tr>
<tr>
<td>MS10</td>
<td>18.96</td>
<td>RMS10 23.51</td>
</tr>
<tr>
<td>MS15</td>
<td>15.51</td>
<td>RMS15 19.39</td>
</tr>
</tbody>
</table>

**Table 4.** Comparison of the compressive strengths of samples prepared via reactive mixing and ordinary mixing procedures.
while relatively weaker bonding between components is obtained through ordinary mixing. Figure 5b shows a rubber particle well-adhered to the modified sulfur binder as a result of chemical interaction between them during reactive mixing. The increase in compressive strength of reactively mixed mortars further confirms the improved interactions between the sulfur binder and rubber particles.

**Effect of rubber type and curing agent.** Finally, the effect of utilizing two different rubber types, selected from the treads and sidewalls of tires, on compressive strength of the sulfur polymer mortar is evaluated. The compressive strengths of the MS10 and MS15 formulations comprising the different rubber type are shown in Table 5. The increase in compressive strength as a result of using the sidewalls of tires in comparison with using the tread sections is due to the distinct composition of these sections. The fact that the properties and microstructure of the rubber employed in tread and sidewall sections of tire are different may lead to enhanced strength of sulfur polymer mortar to which sidewall rubber has been added. In the supplied sidewall sections of tires, good resistance against crack propagation and fatigue are the most desirable characteristics, which leads frequently to usage of polybutadiene and natural rubber in this part. On the other hand, styrene butadiene rubber (SBR) accompanied by natural rubber are used extensively in tread sections of supplied tires due to its great abrasion resistance, as presented in Table 1.

<table>
<thead>
<tr>
<th></th>
<th>Sulfur polymer mortar properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unit weight (g/cm³)</td>
</tr>
<tr>
<td>Tread rubber</td>
<td>MS10   2.27</td>
</tr>
<tr>
<td></td>
<td>MS15   2.21</td>
</tr>
<tr>
<td>Sidewall rubber</td>
<td>MS10   2.25</td>
</tr>
<tr>
<td></td>
<td>MS15   2.17</td>
</tr>
</tbody>
</table>

**Table 5.** Comparison of properties of sulfur polymer mortars containing rubber from tread and sidewall tire sections.
Therefore, the selection of appropriate rubber is a key parameter in achieving improved properties. In order to study the effect of conventional rubber-curing agents on improving the adhesion between sulfur and rubber, several agents were added to the sulfur polymer reactor in the reactive mixing procedure, 30 minutes before the end of the polymerization: namely, stearic acid, zinc oxide, and the accelerator known as CZ (N-cyclohexyl-2-benzothiazolesulfenamide). These compounds, which are well-known in rubber industry, are typically added to rubber to accelerate and improve vulcanization by sulfur. The mass ratio of stearic acid, zinc oxide, CZ and rubber was adjusted to 2:10:2:100. Through this approach, the compressive strength of a sulfur polymer mortar mixture including 10% rubber was increased by approximately 7%, which can be attributed to further vulcanization of the surface of rubber particles by sulfur.

4. Conclusions

The overall results in this work reveal that the incorporation of crumb tire rubber particles in sulfur polymer mortars results in a composite material with lower density and more ductile behavior, which maintains its consistency after failure to high strains. However, the lower strength of rubber particles and the poor adhesion between the surface of the rubber and the modified sulfur binder reduce the compressive strength of the mortars. Use of a reactive mixing method causes some chemical interactions between the surface of the rubber particles and the modified sulfur binder which finally improves the compressive strength of the rubber-added sulfur polymer mortars. Also, use of sidewall tire rubber results in a slight improvement in the compressive strength of mortars compared with the use of tread section tire rubber. Furthermore, it is observed that the presence of curing agents during the preparation process of the sulfur polymer mortars enhanced their mechanical properties due to the further vulcanization of the rubber particles. Although compressive strength reduction occurred due to the usage of rubber particles in the sulfur polymer mortar, these mortars still can be utilized in many applications thanks to their generally higher compressive strength as compared to Portland cement mortars, as well as the other features that have been described.

References


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HAMED MARAGHECHI: hym5061@psu.edu
Department of Civil and Environmental Engineering, Pennsylvania State University, 3127 Research Drive, State College, PA, 16803, United States

IMAN FOTOVAT AHMADI: imanfotovat@alumni.ut.ac.ir
Department of Chemical Engineering, College of Engineering, University of Tehran, P.O. Box 11365-4563, Tehran, Iran

SIAMAK MOTAHARI: smotahari@ut.ac.ir
Department of Chemical Engineering, College of Engineering, University of Tehran, P.O. Box 11365-4563, Tehran, Iran
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