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Rubber-mortar composites: Effect of composition on properties

N. SEGRE, I. JOEKES*
Instituto de Química, Universidade Estadual de Campinas, Caixa Postal 6154,
CEP 13084-971, Campinas-SP, Brazil
E-mail: ines@iqm.unicamp.br

A. D. GALVES, J. A. RODRIGUES
Departamento de Engenharia de Materiais, Universidade Federal de São Carlos,
Via Washington Luis km 235, CEP 13565-905, São Carlos-SP, Brazil

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The Weibull modulus of mortar specimens containing 35% (w/w of cement content) of NaOH-treated rubber particles was calculated showing a value of 9.1 for the control and 9.4 for the specimens with rubber, indicating that the incorporation of a high amount of rubber does not change the casting reproducibility. Since the flexural strength of these rubber-containing specimens was reduced by 43%, new composites were prepared using 10% of rubber as addition or aggregate. Water sorption by immersion, resistance to acid attack, flexural strength and freeze-thaw experiments were performed. Transport properties were improved for the addition-rubber-containing composites; the best results were obtained with the aggregate-rubber-containing composites. A reduction of 15% in flexural strength was observed for addition-rubber-containing composites and 25% for the aggregate-rubber-containing composites, roughly as expected if the flexural strength varies linearly with the rubber content. Furthermore, after 60 freezing and thawing cycles, a reduction of 75% in flexural strength was observed for the control specimens and only 20% for the addition-rubber-containing specimens. © *2004 Kluwer Academic Publishers*

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1. Introduction

The ever-increasing volume of rubber waste in landfills from the disposal of used tires has grown into a serious environmental problem. For both environmental and economic reasons, there is renewed interest in developing alternatives to disposal. The major application of scrap rubber, particularly as crumb, is outside the conventional rubber industry. More than half of the scrap is burned for its fuel value for generation of electricity and as a component in cement production. The utilization in extension of asphalt in road construction is now recognized to provide superior road performance and reduced cost. Although the use of recycled tire rubber in asphalt pavements was emphasized in several publications, not much attention has been given to the use of rubber from scrap tires in cement materials. However, large benefits can result from the use of this rubber in cement-based materials, especially in circumstances where properties like lower density, increased toughness and ductility are desired. The use of tire rubber in cement composites would not only make good use of a waste material but can also improves certain properties for particular applications [1–14].

The use of tire rubber in sand-cement mortar was studied in our previous research when an ultimate amount of NaOH-treated tire rubber [15], which represents 35% (w/w) of the cement content, was added to the mortar [16]. Flexural strength was reduced by 43% with the incorporation of this amount of rubber. On the other hand, advantageous effects were observed on the transport properties of this rubber-containing mortar. Sorptivity coefficient was reduced from 0.29 (control) to 0.06 mm/min$^{1/2}$. By immersion, the amount of water absorbed by the specimens with rubber was reduced by 16%. Both results are consistent with SEM observations, which showed an increased amount of closed pores in the specimens with rubber. A significant decrease in the rate of weight loss by acid attack was observed for specimens with rubber. These results showed that NaOH-treated tire rubber particles improve some mortar properties even when used in a high proportion.

In this work, complementary characterization of this initial rubber-containing composition was made as the calculation of the Weibull modulus, which is a measure of the variability of the strength of a material. The second part of this work embraces the optimization of the rubber-mortar composite. To this effect, new compositions were prepared reducing the amount of rubber used in two ways: as addition or aggregate.

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*Author to whom all correspondence should be addressed.

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2. Methods

Borcol Industria de Borracha Ltda. (Sorocaba/SP, Brazil) supplied the samples of powdered tire rubber from bus and truck tires (a mixture of styrene-butadiene rubber (SBR), natural rubber, polybutadiene, oils, curatives, antioxidants, and carbon black, among others). The processing steps to obtain these particles are as follows: after removing the tread of the tires, the resulting scrap is ground in a series of knife mills, where cyclone and suck pumping separate metal particles and synthetic fibers. Mills have an outflow-sieving device to control the final particle size [17, 18]. The rubber particles, with 200 μm average particle size and density of $1.152 \pm 0.001\ \mathrm{g \cdot cm^{-3}}$, were surface-treated with saturated NaOH aqueous solutions for 20–30 min, at room temperature, whilst stirring. The mixture was filtered and the rubber was rinsed with water until neutral pH was achieved and allowed to dry at room temperature [15].

In order to optimize the rubber-mortar composites, mortar test specimens were prepared with Brazilian slag-modified Portland cement (15 μm average particle size and which contains 6 to 34% of blast-furnace slag), washed natural sand with 2.6 fineness modulus (450 μm average particle size) and distilled water. The mixture composition was water/cement ratio (or water/cement + rubber ratio) = 0.52, sand/cement ratio = 2. For specimens with NaOH-treated rubber incorporated, 10% of the rubber (w/w) was added in two different ways: as addition, when 10% of the cement was replaced by rubber, or as aggregate, when 10% of the sand was replaced by the rubber. These new compositions were denominated as addition-rubber-containing and aggregate-rubber-containing compositions, respectively. It is important to emphasize that for these new compositions, the amount of rubber in aggregate-rubber-containing composite is twice the amount in addition-rubber-containing one, since sand/cement ratio is 2.

For flexural strength experiments, expressed in terms of modulus of rupture (MOR), prismatic test specimens measuring 150 × 25 × 25 mm and cured for 50 days at room temperature (25°C) and 100% relative humidity were used. A three-point bend test was performed. These measurements were performed in a MTS model 810/TestStar IIs testing machine. A displacement rate of 10 mm/min was used.

Water sorption by immersion was measured using 45 × 30 mm cylindrical specimens cured for 40 days at room temperature (25°C) and 100% relative humidity. The specimens were dried at 50°C until constant weight was achieved, and then immersed in water at room temperature. Weight data of each specimen were obtained after several periods of time, until constant weight was achieved. Quintuplicate specimens were used.

For resistance to acid attack, cylindrical specimens measuring 45 × 30 mm and cured for 40 days at room temperature (25°C) and 100% relative humidity were previously immersed in water until constant weight was achieved and then immersed individually in HCl 5% (1.4 M). Weight data of each specimen were obtained after several periods of time. The residue derived from each specimen was collected using filter paper. The HCl solution was replaced once a day. Triplicate specimens were used.

For freeze-thaw experiments, only the addition-rubber-containing specimens were used. Prismatic test specimens measuring 150 × 25 × 25 mm and cured for 43 days at room temperature (25°C) and 100% relative humidity were used. The specimens were first exposed to 20 and 40 freeze-thaw cycles. In a second experiment, the addition-rubber-containing specimens were exposed to 60 cycles and the control specimens to 30 and 60 cycles. Each cycle corresponds to 12 h at 6°C immersed in water, which is the initial step of the experiment, plus 12 h at –20°C surrounded by air. Micrographs of the specimen surfaces were obtained before and after the freeze-thaw cycles using a stereomicroscope Leica MZ 12.5 equipped with a Sony SSC-C374 video camera. Flexural strength experiments were performed for reference specimens (0 cycles) and for the specimens exposed to the freeze-thaw cycles.

3. Results and discussion

As described before, the use of tire rubber in sand-cement mortar was started to be studied in previous research when 35% (w/w of cement content) of NaOH-treated tire rubber, was added to the mortar, reducing the modulus of rupture by 43%, as shown in Fig. 1 [16].

Loss in mechanical strength was expected, since rubber is a soft material and rubber particles themselves can constitute critical flaws. However, casting reproducibility is also an important parameter for the use of brittle materials. This can be assessed by the Weibull modulus, which is a measure of the variability of the strength of a material. It is based on the "weakest link-hypothesis" which means that the most serious flaw in the specimens will control the strength. The most serious flaw is not necessarily the largest one because its severity also depends on where it is situated. In other words, it depends on the stress value on it [19–21]. The higher is the Weibull modulus the smaller is the failure strengths' scatter. This means that the Weibull modulus assesses also the reproducibility of the sample preparation, an important aspect here. As a complementary characterization of the 35%-rubber-containing composition,the Weibull modulus was calculated. Fig. 2 shows the probability of failure as a function of fracture load for control specimens and with rubber. The Weibull modulus was estimated graphically by the slope of ln ln $[1/(1-F)]$ against ln σ plots, where F symbolizes the failure probability and σ the modulus of rupture, as shown in Fig. 3. A Weibull modulus of 9.1 was obtained for the control specimens and 9.4 for the specimens with rubber, indicating that the incorporation of a high amount of rubber does not change the casting reproducibility, although the rubber changes the rheology and microstructure of the mortar. Note that 9.4 is an excellent Weibull modulus comparing with the 13 usually found for high performance ceramics [22, 23].

Since the flexural strength of this previous rubber-containing mortar composition was highly reduced, compared with a control mortar, new compositions

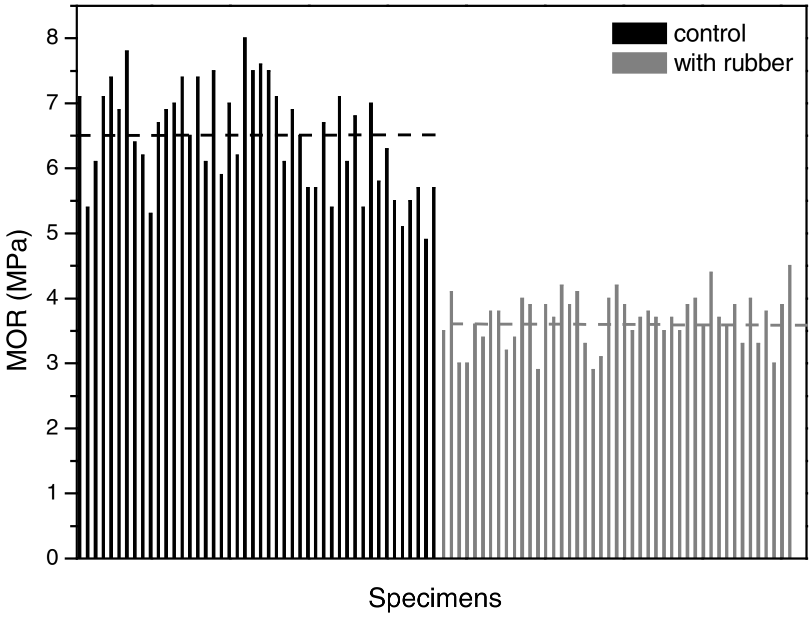

Figure 1 Modulus of rupture for mortar test specimens. In black: control specimens, in gray: specimens with 35% (w/w of the cement content) of NaOH-treated tire rubber particles. Horizontal dashed lines indicate the averages [16].

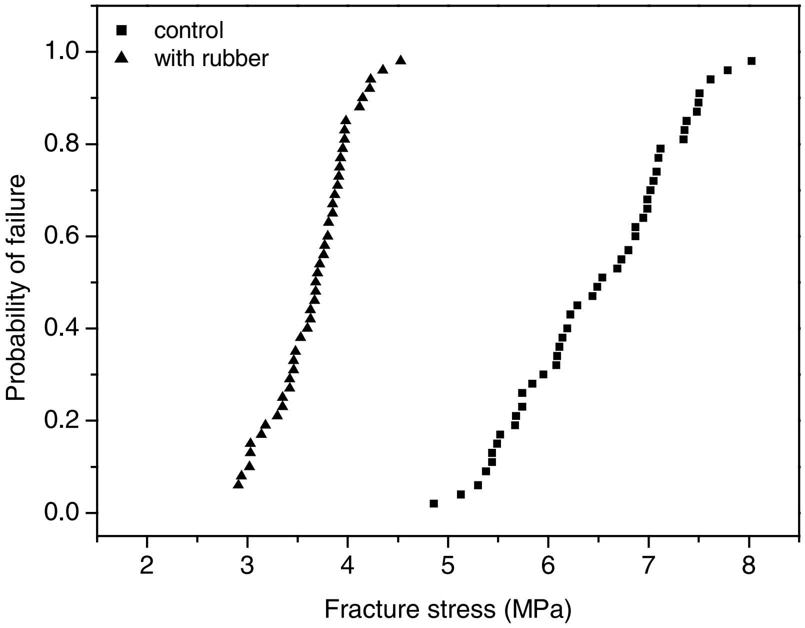

Figure 2 Probability of fracture, F, as a function of fracture stress, σ, for specimens control and with 35% (w/w of the cement content) of NaOH-treated tire rubber particles.

were prepared reducing the amount of rubber. In order to optimize the rubber-containing composite, 10% of rubber was incorporated in mortar, as addition or aggregate, as described in Section 2. The first one is commercially more interesting since cement is the expensive component of the mixture. Fig. 4 shows the results of MOR for these new compositions. The results show a decrease of 15% in MOR for the addition-rubber-containing specimens and a reduction of 25% for the aggregate-rubber-containing specimens. These decreases are justified by the fact that the rubber particles introduce microstructure defects and the absolute density of rubber particles (number of particles per unit volume) is greater in the aggregate-rubber containing type than in the addition-rubber-containing one. For our initial composition, in which the rubber content was 35% (w/w) of the cement content, a decrease of 43% in flexural strength was obtained. In this case, the 35% rubber incorporated corresponds to 25% if as addition or 15% if as aggregate. From these values, and if the reduction of strength is proportional to the amount of rubber added, a reduction of about 18% in MOR would be expected for the addition-rubber-containing composite and 30% for the aggregate-rubber-containing composite. These values are close to those obtained, indicating that the flexural strength of the rubber-cement composites decreases roughly linearly with the rubber content.

The strength of these cement composites is by no means their most important characteristic. Properties

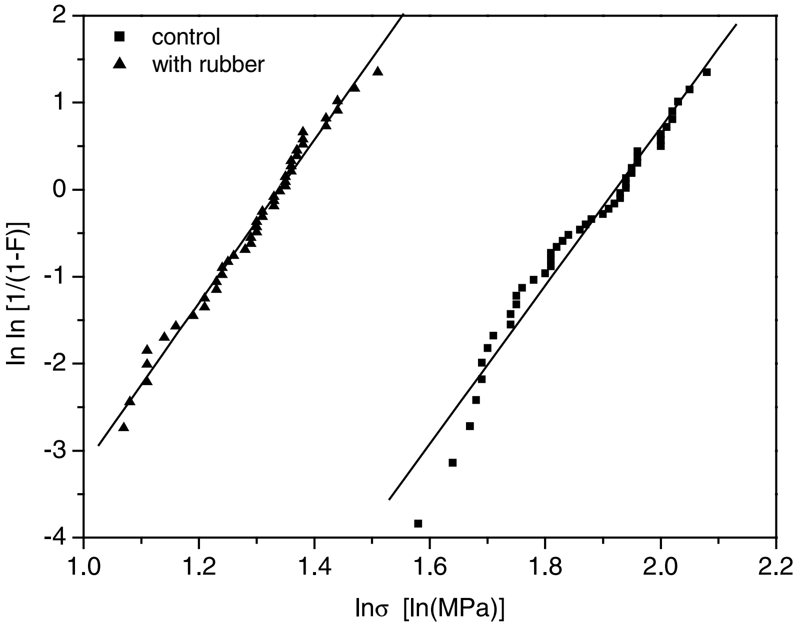

Figure 3 Weibull's plots, using fracture load as the variable, for specimens control and with 35% (w/w of the cement content) of NaOH-treated tire rubber particles.

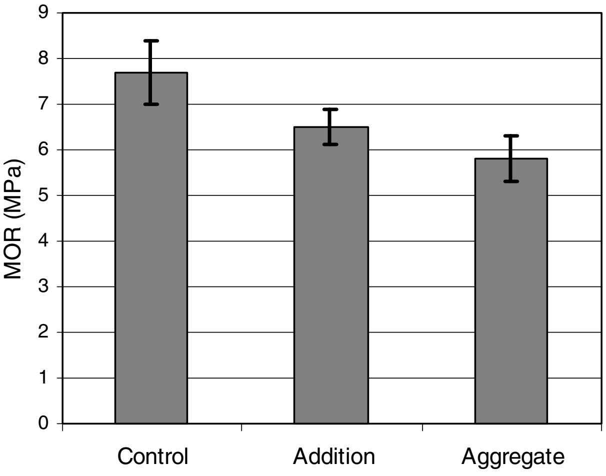

Figure 4 Modulus of rupture for mortar test specimens control and with NaOH-treated tire rubber particles (as addition or aggregate). Control: sand-cement mortar. Results of a set of ten specimens for each composition.

such as elastic modulus, impermeability, and resistance to weathering agents including aggressive waters, are directly related to durability. Water take up is related to porosity and gives a picture of internal microstructure. Fig. 5 shows results of the sorption of water by immersion, which is related to the open porosity of the specimens tested. The behavior of the addition-rubber-containing composites is similar to that of the control, which is better than expected; since the water/cement ratio is higher for this composition than for the control, higher porosity is inevitable, meaning that the rubber is acting as closed pores.

In addition to a smaller rate of water absorption, a significant reduction in the amount of water absorbed is found for the aggregate-rubber-containing specimens, meaning that they have fewer pores or that fewer pores are reachable by the water. In this case, the water/cement ratio is the same as for the control, indicating that the rubber is responsible for these results.

The durability of a cement-based material relates to its service life under given environmental conditions. The hydrated cement paste is alkaline and, therefore, acidic waters are expected to be particularly harmful to these materials. Deleterious chemical effects of this acidic attack include leaching of the calcium hydroxide. Acidic fluids will also increase the porosity, thus making the material more vulnerable. Under these conditions, impermeability becomes a primary factor in determining durability [24, 25].

The effect of the use of rubber as addition or aggregate on the acid resistance was also investigated. Results displayed in Fig. 6 show that the rubber particles have a positive effect on the acid resistance, even when used in a reduced amount. Acid attack progresses from the surface to the bulk, releasing the sand and the rubber. In Fig. 7 the weight of sand and rubber lost during the acid attack is displayed, showing again an excellent performance for the aggregate-rubber-containing composite. Note that the reproducibility of the data obtained with these composites is significantly higher than that of the addition-rubber-containing composites, which must be related with their higher rubber content. This result is consistent with the water adsorption data. On the other hand, the addition-rubber-containing composites were expected to be less resistant than the controls: the amount of rubber and sand lost should be higher, since their cement content is lower, and cement is the binding material.

Water in the pores of cement materials expands upon freezing. If the required volume is greater than the space available, the pressure of expansion drives off the excess water. The magnitude of this hydraulic pressure depends on the permeability of the cement material, the degree of saturation, the distance to the nearest unfilled void, and the rate of freezing. If the pressure exceeds the

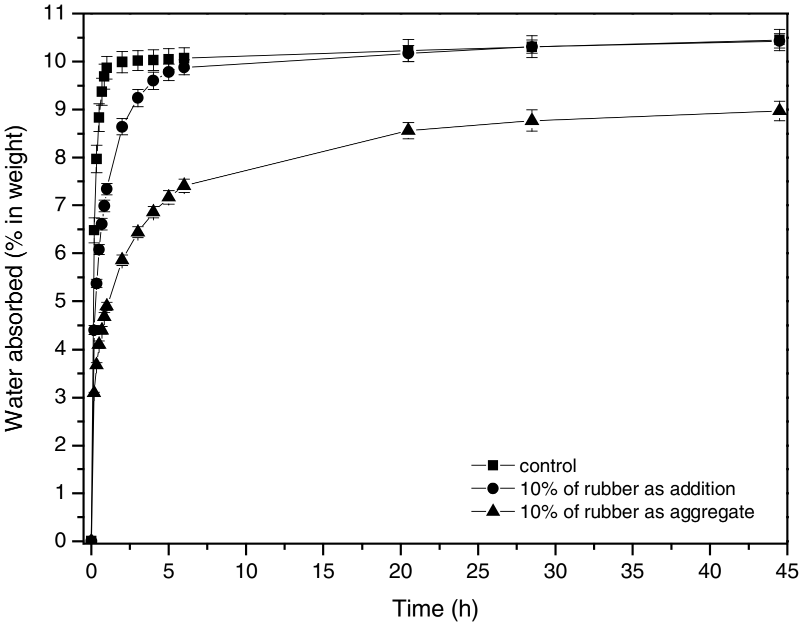

Figure 5 Water sorption by immersion, at room temperature, as a function of time for mortar test specimens with 10% (as addition or aggregate) of NaOH-treated tire rubber particles. Control: sand-cement mortar. Results of quintuplicate specimens.

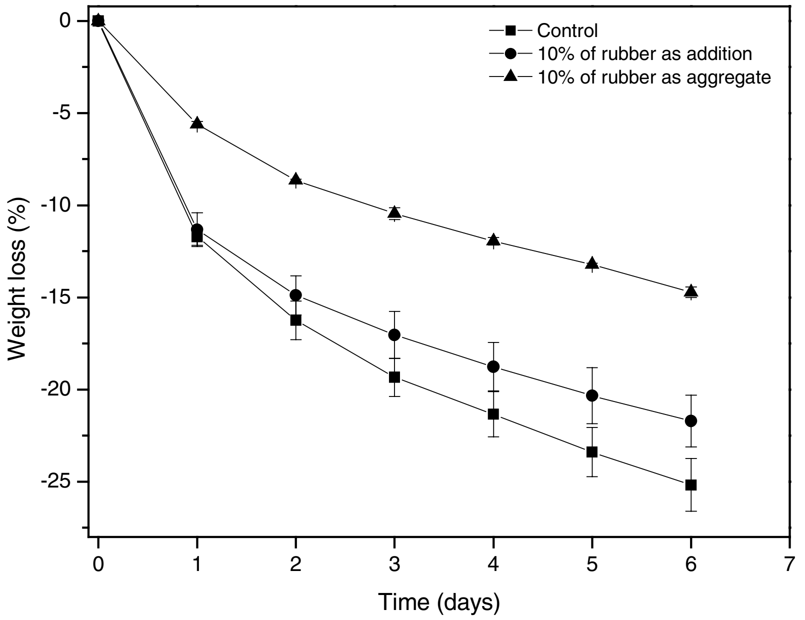

Figure 6 Weight loss due acid attack, as a function of time, for mortar test specimens with 10% (as addition or aggregate) of NaOH-treated tire rubber particles. Control: sand-cement mortar. Results of triplicate specimens.

tensile strength of the material at any point, it will cause local cracking. The frost damage in cementitious materials can take several forms, the most common being cracking and spalling. Cement materials slabs exposed to freezing and thawing in the presence of moisture and de-icing chemicals are susceptible to scaling (i.e., the finished surface flakes or peels off) [24, 26].

The pore structure of the system (size, number, and continuity of pores) is one of the factors that control the resistance to freezing and thawing. The addition-rubber-containing composite behaved similar to the control for the ultimate water absorption, as shown in Fig. 5. Since their open porosity is considered the same, the content of hydraulic pressure escape frontiers can also be considered the same for addition-rubber-containing composites and control. In this case, both systems were used to evaluate the effect of the rubber particles in freeze-thaw stresses. Figs 8 and 9 show micrographs of controls and addition-rubber-containing composites surfaces after 0, 20 and 40 freeze-thaw cycles, respectively. After 20 cycles, no significant surface damage was observed. After 40 cycles, intense cracking and flaking is observed on the controls; conversely, the surface damage is less intense for the specimens with rubber. The results of 30 and 60 cycles were obtained in a second experiment, as described in Section 2, and these specimen surfaces show bright white spots and some flaking instead of cracking, as shown in Fig. 10.

Fig. 11 shows the results of modulus of rupture for the specimens after the freeze-thaw cycles. A pronounced decrease in MOR is observed for control specimens as

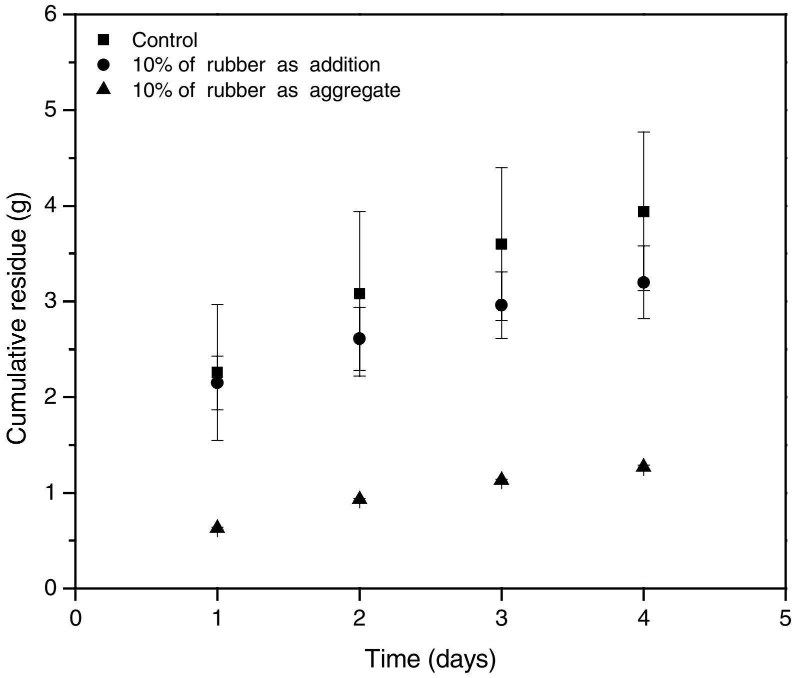

Figure 7 Cumulative residue draw from acid attack, as a function of time, for mortar test specimens with 10% (as addition or aggregate) of NaOH-treated tire rubber particles. Control: sand-cement mortar. Results of triplicate specimens.

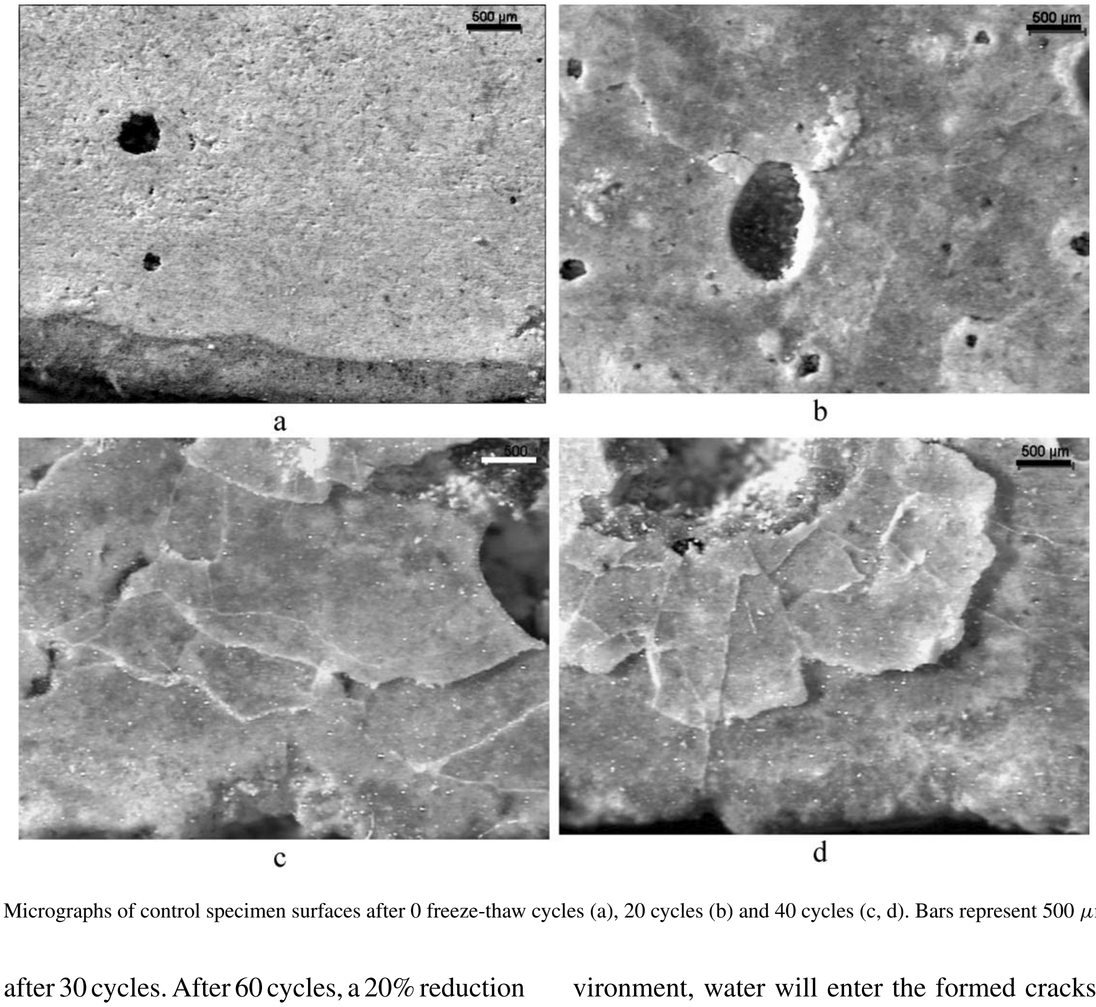

Figure 8 Micrographs of control specimen surfaces after 0 freeze-thaw cycles (a), 20 cycles (b) and 40 cycles (c, d). Bars represent 500 μm.

soon as after 30 cycles. After 60 cycles, a 20% reduction in MOR is observed for the addition-rubber-containing specimens, whereas for control specimens a 75% reduction is observed. Since flaking and cracking was intense in the controls, it can be inferred that their porosity increased, rendering a poorer mechanical strength. In repeated cycles of freezing and thawing in a wet environment, water will enter the formed cracks during the thawing portion of the cycle only to freeze again later, and there will be progressive deterioration of the macro and microstructure with each cycle. Since rubber is a soft material, and since the freeze-thaw experiments were conducted above its −60°C glass transition temperature [27], it absorbs the expansion energy

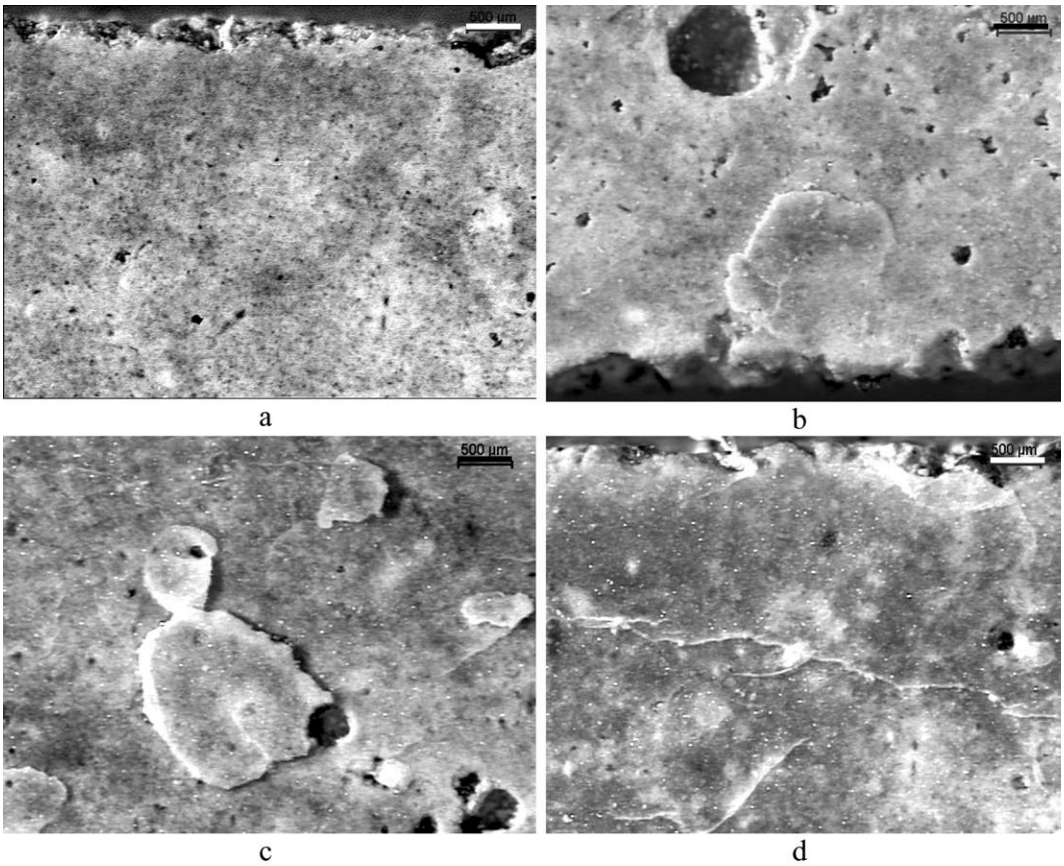

Figure 9 Micrographs of 10%-addition-rubber-containing specimen surfaces after 0 freeze-thaw cycles (a), 20 cycles (b) and 40 cycles (c, d). Bars represent 500 μm.

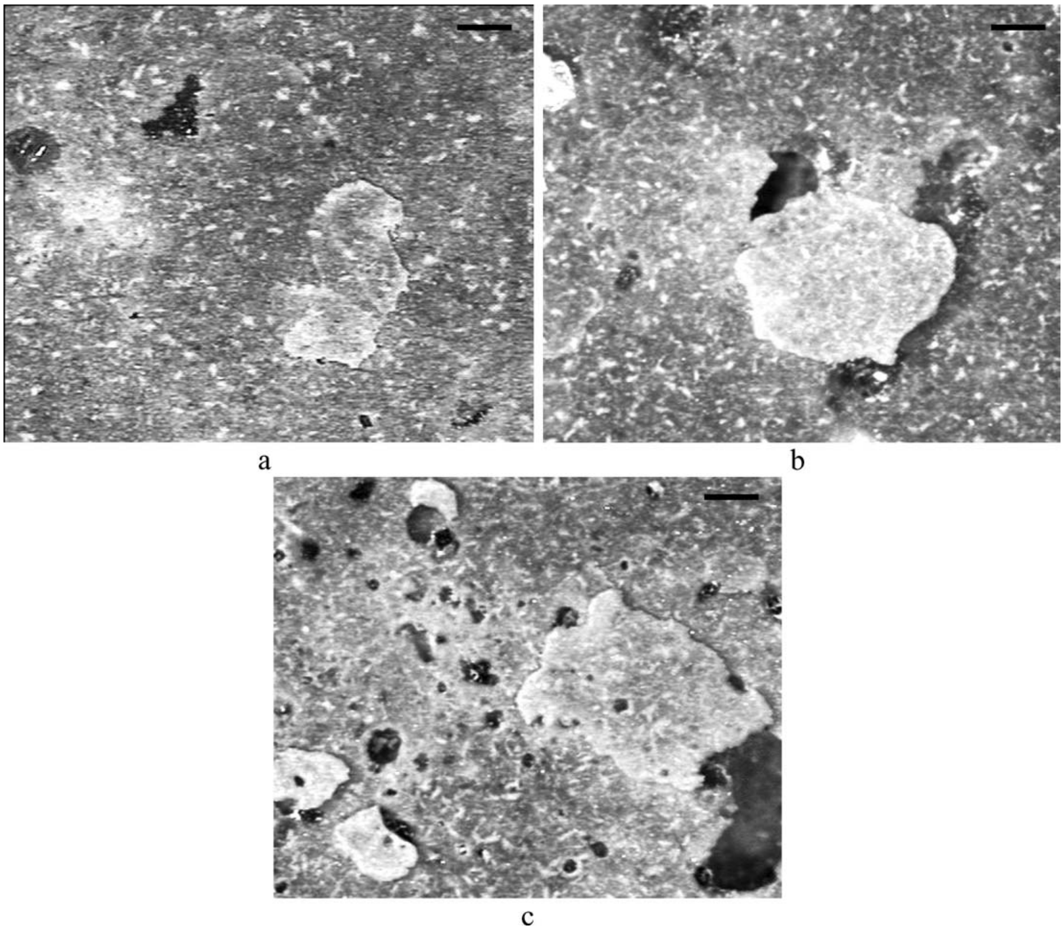

Figure 10 Micrographs of control specimen surfaces after 30 freeze-thaw cycles (a) and 60 cycles (b) and a micrograph of 10%-addition-rubber-containing specimen surface after 60 cycles (c). Bars represent 500 μm.

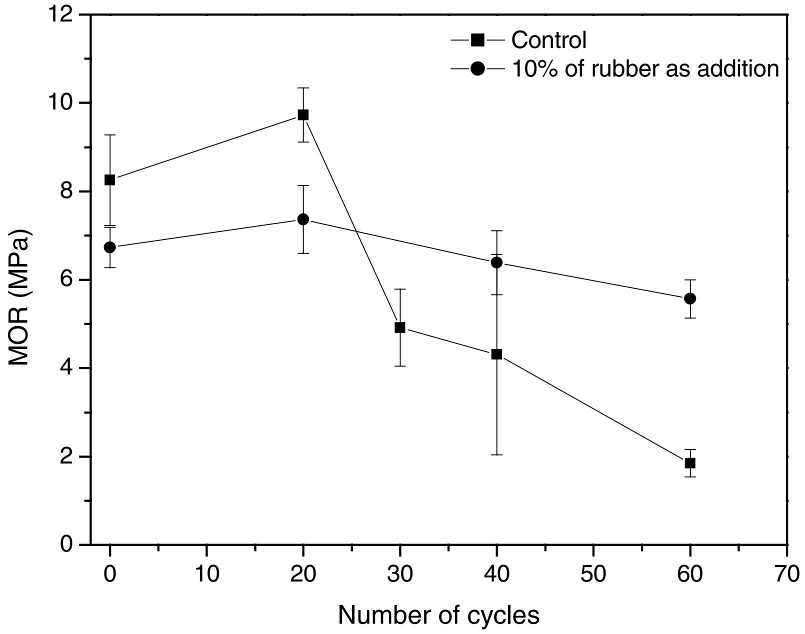

Figure 11 Modulus of rupture for control and 10%-addition-rubber-containing mortar test specimens as a function of the number of freeze-thaw cycles. Results of quintuplicate specimens.

caused by water freezing and, in this way, avoids structure failure.

Another interesting point is the suitability of 3-point bending test to investigate the freeze-thaw damage in mortars. Although the damage is limited to an outer shell of the treated body, its consequence is revealed well by the high sensitivity to surface condition of 3-point bending arrangement.

4. Conclusions

As a complementary characterization of the 35%-rubber-containing composition, the Weibull modulus was calculated and showed that the incorporation of a high amount of rubber does not change the casting reproducibility, although the rubber changes the rheology and microstructure of the mortar. In order to optimize the tire rubber-mortar composition, the amount of rubber was reduced and incorporated in two different ways: as addition, when 10% of cement was replaced by the rubber particles, and as aggregate when 10% of the sand was replaced by the rubber. The flexural strength of these new compositions was reduced in relation to the control, almost linearly with the rubber content. On the other hand, the transport properties were improved for the addition-rubber-containing composites since the water absorption was supposed to be higher with the reduction of cement content. The best results on transport properties were obtained with the aggregate-rubber-containing composites. The excellent results obtained for the resistance to freezing and thawing cycles show that this is a promising durability property to be explored in order to make the tire rubber-mortar composite suitable for engineering purposes.

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