Tire rubber-cement composites: effect of slag on properties

(Compósitos de cimento - borracha de pneus: efeito da escória nas propriedades)

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Abstract

Tire rubber-cement composites prepared with type I and three slag-modified cements were studied. Flexural strength, water sorption and resistance to acid attack of specimens were investigated. A decrease in modulus of rupture (MOR) is observed for all specimens containing rubber, when compared with specimens without rubber (controls). The MOR increases with the increase of the hydraulic activity of the slag upon undistinguishable from specimens prepared with type I cement. This behavior is observed for all slag-cements pastes and for mortars control specimens. For mortar specimens with rubber the MOR is independent of the cement type used. A reduction in water sorption is observed for control and with-rubber mortar specimens prepared with all slag-cements, when compared to type I cement. For mortar specimens with rubber, the lower the basicity of the slag, the lesser the water sorption of the composites. These results denote lower porosity and consequently better rubber-matrix adhesion for these specimens. Also, a smaller rate of water sorption is observed for specimens with rubber, particularly for specimens prepared with the less basic slag cements, when comparing with the controls. Results of acid attack to the slag modified mortars indicate that specimen susceptibility is governed not only by microstructural aspects, like porosity and permeability, but also by chemical aspects as the difference in alkali content or the amount of unreacted slag in the specimens.
Keywords: tire rubber-cement composites, granulated blast-furnace slag, transport properties, mechanical properties.

Resumo

Compósitos de cimento-borracha de pneus preparados com cimentos tipo I e contendo adições de três diferentes escórias foram estudados. Resistência à flexão, absorção de água e resistência ao ataque ácido foram investigadas. Um decréscimo no módulo de ruptura (MOR) foi observado para todos os corpos de prova contendo borracha, quando comparados com os corpos de prova sem borracha (controles). Para as pastas controle e com borracha e argamassas controle, preparadas com cimento com escória, o MOR aumenta com o aumento da atividade hidráulica da escória utilizada, até valores indistinguíveis dos obtidos para as argamassas e pastas preparadas com cimento tipo I. Argamassas com borracha apresentaram valores de MOR independentes do cimento utilizado. Uma redução na sorção de água é observada para corpos de prova controle e contendo borracha, preparados com todos os cimentos contendo adição de escória, quando comparados com os corpos de prova preparados com cimento tipo I. Para corpos de prova de argamassa com borracha, quanto mais baixa é a basicidade da escória, menor é a sorção de água dos compósitos. Estes resultados indicam baixa porosidade e consequentemente uma melhor adesão entre a borracha e a matriz de cimento nestes corpos de prova. Além disso, uma velocidade menor de sorção de água é observada para os corpos de prova com borracha, com destaque para os corpos de prova com cimento que contém a escória menos básica, quando comparados com os controles. Resultados de ataque ácido aos corpos e prova de argamassas, preparadas com os cimentos contendo adição de escória, mostram que a susceptibilidade dos corpos de prova frente à degradação por ácido é governada não somente por aspectos microestruturais, como porosidade e permeabilidade, mas também por aspectos químicos, como diferenças na quantidade de álcalis presentes nas escórias ou quantidade de escória não reagida nos corpos de prova.
Palavras-chave: *compósitos de cimento–borracha de pneus, escória granulada de alto-forno, propriedades de transporte, propriedades mecânicas.*

INTRODUCTION

The manufacture of products from recycled materials has technologic, economic, and environmental advantages that have become attractive in recent years. The ever-increasing amount of waste rubber from disposal of used tires has

grown into a serious environmental problem around the world. One approach to waste tires disposal is to incorporate the rubber into cement-based materials. Research reported in the literature focuses on the mechanical properties of the resulting materials. Some authors suggest that the properties of rubber-cement composites should be improved by prior

surface treatment of the tire rubber particles [1-7].

In a previous work, the addition of 10% of powdered tire rubber (35 mesh maximum size) in ordinary Portland cement pastes was investigated. This rubber was used untreated and after surface–treatment with NaOH saturated aqueous solution. The rubber-matrix adhesion was improved with this treatment as observed by scanning electron microscopy (SEM), rendering abrasion resistance and water sorption results significantly better than in pastes with untreated rubber particles [8].

The cement production industry is an important consumer of carbon-based fuels as a source of heat, releasing huge amounts of CO_2, which is the major greenhouse gas responsible for global warming. A significant reduction in energy requirement and CO_2 emission without reducing performance is obtained by the incorporation of granulated slag, a residue of the iron-making process and also a pollutant, to Portland cement clinker [9]. So, in a number of countries slag cements are replacing ordinary Portland cement. Slag content varies from country to country as slag composition depends on the location of each iron-making industrial unit. Composition differences will reflect in the properties of the resulting slag-modified cements. Considering surface aspects, different cements should show different adhesion between matrix and rubber, changing the performance of rubber-cement-based composites.

The degree of adhesion between the cement matrix and the admixtures is a critical parameter in determining the performance of a composite material. The bonds in cementitious materials must result from some combination of mechanical interlock, van der Waals forces, hydrogen bonds, and even chemical reactions. The presence of polar interactions, for example, a polymer containing groups capable of significant hydrogen bonding or acid-base interactions will improve significantly the capacity of adhesive joint formation [10-12].

Strength is the commonly specified property for cement-based materials. This property depends not only on the characteristics and proportions of the components of cementitious materials, but also on the mechanism of failure. Since failure does tend to occur in the interfacial regions, the way in which the different phases are bonded to each other is important. The interfacial region is often considered to be the weakest part of cement-based materials and the preferential route for the penetration of water or aggressive species from the environment. The interface thus is critical for determining durability of cement-based materials. The aim of this work is to investigate the mechanical and transport behavior of NaOH-treated rubber-cement composites considering the slag origin.

MATERIALS

Borcol Indústria de Borracha Ltda. (Sorocaba, SP, Brazil) supplied samples of powdered tire rubber from bus and truck tires (a mixture of styrene-butadiene, natural and polybutadiene rubbers, plus oils, curatives, antioxidants, carbon black, and others). The rubber particles, with 200 μm average particle size and density of 1.152 ± 0.001 g.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 [8].

Three different Brazilian slag-modified Portland cements produced with slags from different origins were used, as shown in Table I. The amount of slag was quantified by selective dissolution of all cement components but the slag particles with an EDTA (ethylene diamine tetraacetic acid) and triethanolamine buffered solution [13]. No significant difference in the amount of slag present in the slag-cements is observed, as shown in Table I. Type I Portland cement, consisting essentially of clinker (hydraulic calcium silicates) and roughly 5% of calcium sulfate as an addition was used as reference material.

Blast-furnace slag, a by-product of the iron-making process, is a non-metallic product, consisting essentially of silicates and aluminosilicates of calcium. Granulated blast-furnace, largely glassy, is produced by the rapid quenching of molten blast-furnace slag as it passes through water sprays, followed by water granulation over a spinning drum [9]. The granules are added to the clinker before grinding. Table I also shows chemical indices of Brazilian slags, according to their source [14]. The higher the indices, the higher the basicity and reactivity (or hydraulic activity) of the slag. The constitution of slag can vary over a wide range depending on the nature of the ore, the composition

Table I - Brazilian basic blast-furnace slag sources, amount in the cements and chemical indices.
[Tabela I - Fontes das escórias granuladas de alto-forno brasileiras, quantidade nos cimentos e índices químicos.]

Slag-cement	Slag source designation	Slag amount	Slag	$\dfrac{CaO}{SiO_2}$	$\dfrac{CaO + MgO}{SiO_2}$	$\dfrac{CaO + MgO + Al_2O_3}{SiO_2}$
1	USIMINAS Minas Gerais state	S1	$31 \pm 2\%$	1.24	1.40	1.76
2	CSN Rio de Janeiro state	S2	$29 \pm 2\%$	1.24	1.42	1.89
3	COSIPA São Paulo state	S3	$27 \pm 2\%$	1.25	1.46	1.84

Table II - Chemical composition of Brazilian blast-furnace slags [14].
[Tabela II - Composição química de escórias granuladas de auto-forno brasileiras [14].]

Elements	S1	S2	S3
		(wt.%)	
SiO_2	35.15	32.9	33.85
Al_2O_3	12.79	15.44	13.0
CaO	43.58	40.97	42.22
Fe_2O_3	0.37	0.91	0.68
FeO	0.29	0.43	0.33
MgO	5.48	5.81	7.08
K_2O	0.45	0.73	0.70
Na_2O	0.13	0.19	0.21
TiO_2	0.54	0.49	0.48
Mn_2O_3	0.88	0.86	0.69
SO_3	0.05	-	0.12
S	1.10	1.03	0.67
Fe	0.07	0.25	0.13

of the limestone flux, the coal consumption and the kind of iron being made, as shown in Table II.

METHODS

Sand-cement mortar specimens were prepared using four different cements, washed natural sand with 2.35 fineness modulus (420 µm average particle size) and distilled water. The mixture composition was water/cement ratio = 0.52, sand/cement ratio = 2. For specimens with NaOH-treated rubber, 10% of the rubber (w/w) was added as addition, when rubber replaced 10% of the cement.

Cement paste specimens were also prepared, using the same water/cement ratio and the same rubber replaced amount as for the mortar specimens. Table III shows the sample designations adopted in this work, considering the cement, slag source, and cement-based material types used.

Water sorption by immersion experiments followed ASTM C642-97 (Standard test method for density, absorption, and voids in hardened concrete). Cylindrical specimens measuring 45 mm (in height) x 30 mm (in diameter) were cured for 45 d 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 water saturation. Quintuplicate specimens were used.

Since there is no standard test for resistance to acid attack, cylindrical specimens measuring 45 mm (in height) x 30 mm (in diameter), cured for 45 d at room temperature (25 °C) and 100% relative humidity were previously immersed in water until constant weight was achieved and then immersed in HCl 5% (1.4 mol L^{-1}). Weight data of each specimen were obtained after several periods of time. The HCl solution was replaced once a day. Triplicate specimens were used.

Table III - Sample designation adopted in this work. I: ordinary Portland cement; I-SM: slag-modified Portland cement; R: paste or mortar with rubber included.
[Tabela III - Designação de amostras adotada neste trabalho. I: cimento Portland comum; I-SM: cimento com adição de escória; R: pasta ou argamassa contendo borracha.]

Sample designation	Type of cement-based material	Type of cement [15, 16]	Slag source
P-I or P-I-R	Paste	I	none
P-S1 or P-S1-R	Paste	I-SM	S1
P-S2 or P-S2-R	Paste	I-SM	S2
P-S3 or P-S3-R	Paste	I-SM	S3
M-I or M-I-R	Mortar	I	none
M-S1 or M-S1-R	Mortar	I-SM	S1
M-S2 or M-S2-R	Mortar	I-SM	S2
M-S3 or M-S3-R	Mortar	I-SM	S3

Flexural strength measurements, expressed in terms of modulus of rupture (MOR), were performed based on ASTM D790-90 (Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials) since no standard test for flexural strength measurements of cement-based materials using small specimens is available. Prismatic specimens measuring 150 x 25 x 25 mm, cured for 45 d at room temperature (25 °C) and 100% relative humidity, were used. Three-point bend tests were performed in a MTS model 810/TestStar IIs testing machine, using a displacement rate of 10 mm/min. Quintuplicate specimens were tested.

RESULTS AND DISCUSSION

The main purpose of this study is to compare the effect of type I and three different slag-modified cements on the properties of rubber-cement composites considering the slag origin. It is known [17, 18] that the drying shrinkage, a cement-based material deformation that often leads to cracking due to segregation and to volume changes during setting and hydration, is a paste property. According to Mindess and Young [17] the shrinkage in cement paste is twice as high as in mortar. Sand particles tend to restrain shrinkage because of their higher elastic modulus, conferring to mortar a better mechanical behavior. Based on the literature, it can assumed that the cement paste specimens will inevitably develop more cracks than the mortars, considering the experimental procedures adopted in this work. Since the presence of sand in the rubber-mortar composites is expected to have high influence, paste specimens were used in this work to weigh out the sand influence.

Flexural strength

Fig. 1 shows a box plot of MOR results for the specimens prepared with the different cements. A box plot is an effective
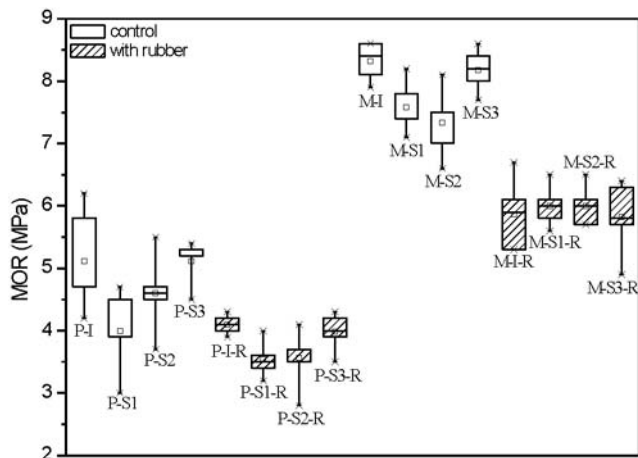
Figure 1: Box plots of modulus of rupture for paste (P) and mortar (M) test specimens, prepared with different cements (I, S1, S2 and S3). In white: control specimens, in hatch: specimens with 10% (w/w of the cement content) of NaOH-treated tire rubber particles (R). Results of quintuplicate specimens.

[Figura 1: Diagrama de blocos do módulo de ruptura de corpos de prova de pasta (P) e argamassa (M), preparados com os diferentes cimentos (I, S1, S2 e S3). Em branco: corpos de prova controle; hachurado: corpos de prova com 10% (m/m em relação à massa de cimento) de partículas de borracha de pneu tratadas com NaOH (R). Médias de quintuplicatas de amostras.]

visual representation of both central tendency and dispersion. Box shows 50% of the data, the small square indicates the average, the median is shown as a line across the box (or on its horizontal bounds) and the vertical line contains the other 50% of the data and the minimum and maximum data values on its edges. The length of the vertical line indicates visually how far from the middle of the distribution the extreme values are.

As expected, lower values of MOR are observed for paste specimens when compared to mortars. A decrease in MOR was observed for all specimens with rubber. According to the Griffith equation, $\sigma = Y(2E\gamma/\pi c)^{1/2}$, the tensile cracking stress (σ) of a brittle material is related to a critical length of defects (c), which may be closed pores or flaws. Both the Young´s modulus (E) and surface energy (γ) were taken as material constants [19]. Loss in mechanical properties for specimens with rubber may be due to the presence of large voids, which are frequently undetected by conventional pore analysis methods since pores can be either effectively closed or out of size range to be measured [20].

The difference between the Young's modulus of the components used in the specimens could also be used to explain the loss in mechanical properties for rubber-cement composites. Roughly, the Young's modulus (E) for the cement-rubber composite can be estimated as equation (A)

$$E_{composite} = (f_{paste} \times E_{paste}) + (f_{rubber} \times E_{rubber}) \qquad (A)$$

where f is the volume fraction of the component in the composite. Considering E = 20 GPa for the paste and 5 MPa for rubber [20, 21], $E_{composite}$ = 18 GPa. Using Griffith law and

considering c and γ as constants, a reduction of 5% in MOR for paste specimens with 10% of rubber should be expected. The results show a higher reduction in MOR for pastes with rubber, which means that the difference of modulus of the components does not interfere significantly when rubber is added in small proportions. In this case, it is believed that the presence of critical flaws is the major responsible for the reduction of MOR in the specimens with rubber.

The reactivity of slag is slower than that of clinker, in the absence of a slag-activator. According to Lumley, the percentage of the slag reacting in pastes of water/solid ratios of 0.4 to 0.6, cured at 20 °C for 28 d, is typically 30-55% and 45-75% at 1-2 y [22]. Since brief cure periods were used, the presence of anhydrous slag is probably responsible for the lower values of MOR obtained for the control specimens prepared with S1 and S2 slag-cements, when compared with the type I-cement specimens. Nevertheless, the specimens prepared with S3 slag-cement showed similar MOR behavior as the type I cement specimens. The cement composition does not seem to influence the strength of mortar specimens with rubber, for which almost indistinguishable MOR values are observed, considering the experimental errors. On the other hand, the boxes obtained for specimens M-S1, M-S2 and M-S3 are significantly reduced when compared to M-I box, which means less scattered or more reproducible values of MOR for the slag-cements materials. The box position also indicates a tendency to higher values of MOR for rubber-mortar composites prepared with slag-cements.

The higher the chemical indices values the higher the basicity. According to Table I, the basicity of the slags follows the order S3 > S2 > S1, considering mainly the $(CaO + MgO)/ SiO_2$ index. In general, the more basic slag has the greater hydraulic activity and higher is the strength of the slag cement-material. This effect could explain the increase in MOR observed for the specimens with S3 slag-cement when compared with the S1 slag-cement specimens. However, there is not a universally agreed definition about the correlation between the hydraulic modulus and the mechanical strength [9]. According to Glasser [23], strength gain depends on other factors besides slag composition, such as the specific nature of the activator used and, for cements, their alkali content, as well as the freshness of the slag, since ground-slag reactivity drops even during dry storage. However, Lumley [22] observed that for slag-modified cement, the composition of the Portland cement has no significant effect on the extent of reaction at ages from 28 d to 1 y, even with inclusion of 5% additional gypsum in the blend. In this way, differences in MOR should be attributed to slag nature, only.

Water sorption

Water sorption was the method used in this work to evaluate the influence of cement concerning the transport properties of the specimens. The experiment of water sorption by immersion accomplishes only the open porosity of the specimens tested and cannot be used as a total porosity
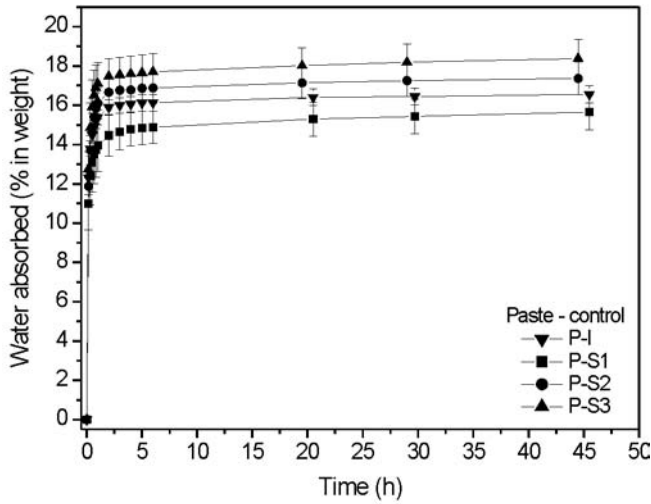
Figure 2: Water sorption by immersion, at room temperature, as a function of time for paste control specimens prepared with different cements. Results of quintuplicate specimens.
[Figura 2: Sorção de água por imersão, a temperatura ambiente, em função do tempo, para corpos de prova de pasta controle preparados com os diferentes cimentos. Médias de quintuplicatas de amostras.]
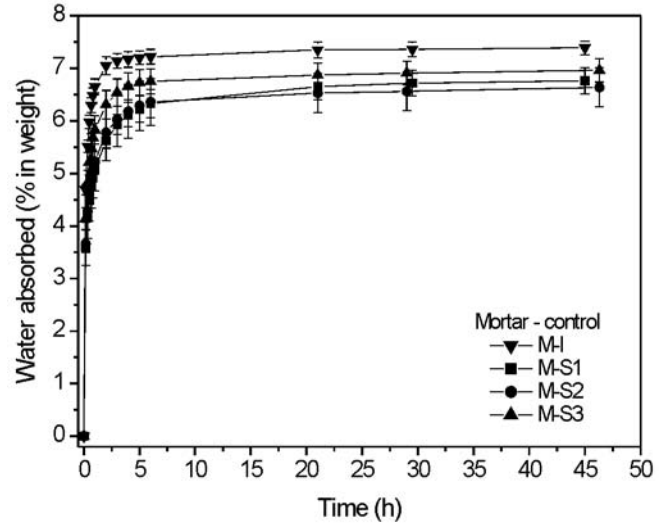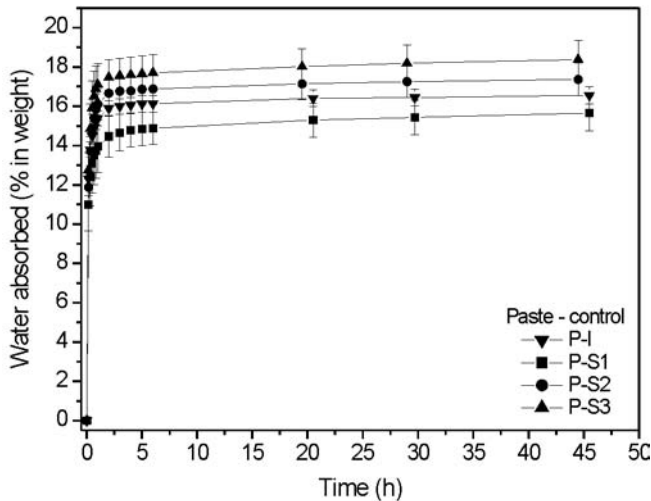

Figure 4: Water sorption by immersion, at room temperature, as a function of time for mortar control specimens prepared with different cements. Results of quintuplicate specimens.
[Figura 4: Sorção de água por imersão, a temperatura ambiente, em função do tempo, para corpos de prova de argamassa controle preparados com os diferentes cimentos. Médias de quintuplicatas de amostras.]

Figure 3: Water sorption by immersion, at room temperature, as a function of time for paste specimens with 10% (w/w of the cement content) of NaOH-treated tire rubber particles, prepared with different cements. Results of quintuplicate specimens.
[Figura 3: Sorção de água por imersão, a temperatura ambiente, em função do tempo, para corpos de prova de pasta contendo 10% (m/m em relação à massa de cimento) de partículas de borracha tratadas com NaOH, preparados com os diferentes cimentos. Médias de quintuplicatas de amostras.]
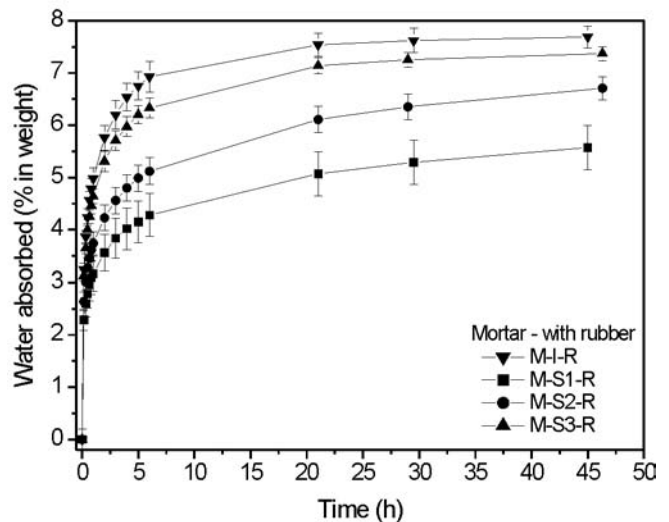

Figure 5: Water sorption by immersion, at room temperature, as a function of time for mortar specimens with 10% (w/w of the cement content) of NaOH-treated tire rubber particles, prepared with different cements. Results of quintuplicate specimens.
[Figura 5: Sorção de água por imersão, a temperatura ambiente, em função do tempo, para corpos de prova de argamassa contendo 10% (m/m em relação à massa de cimento) de partículas de borracha tratadas com NaOH, preparados com os diferentes cimentos. Médias de quintuplicatas de amostras.]

parameter. Figs. 2 to 5 show the results of water sorption by immersion as a function of time for the control paste specimens, paste specimens with rubber, control mortar specimens and mortar specimens with rubber, respectively, prepared with the different cements.

The results show that the sorption of water by paste specimens is twice that of the mortar specimens. This result

is expected, since mortar specimens contain sand, which does not sorb water. For paste specimens, no significant reduction on ultimate water sorption is observed between control and with rubber specimens.

A reduction in ultimate water sorption is observed for mortar specimens control and with rubber, prepared with all slag-cements, when compared to type I cement (Figs. 4 and

5). This effect is partly observed for paste specimens but, again, cracks formed on paste specimens during drying can disguise this tendency. Slag grains are reported to hydrate leaving a porous core. Thus the structure of connecting pores, which is present initially, changes to a structure of closed pores, and lowered permeability arises as a consequence of this pore-space redistribution [23].

No significant difference in water sorption is observed among the mortar control specimens prepared with the slag-cements (Fig. 4). On the other hand, for mortar specimens with rubber, Fig. 5, specimens M-S1 absorbed 20% less water than specimens M-S2 that absorbed 10% less water than specimens M-S3. In general, specimens prepared with the S1 slag-cement tend to absorb less water. As described before, the basicity order of the slags is S3 > S2 > S1. The NaOH-treated rubber surface is basic [24] and a better interaction with the less basic slag should be considered since acid-base interactions has the capacity to improve adhesive joint formation leading to a reduction in water sorption.

Compared to the controls, a smaller rate of water sorption is observed for specimens with rubber, particularly for specimens prepared with S1 and S2 slag-cements (the less basic slags), when compared to the type I and S3 slag cements. These results indicate lower or smaller permeability and consequently, better adhesion for these specimens.

Acid attack

Regarding durability of the specimens against aggressive agents, acid attack experiments were performed. Figs. 6 to 9 display the results of weight loss due to acid attack as a function of time for control paste specimens, paste specimens with rubber, control mortar specimens and mortar specimens with rubber, respectively, prepared with the different cements.

The results show that the weight loss for paste specimens, after 4 d of immersion, is considerably higher than for mortar specimens. The initial cracking of the paste specimens, formed on drying, must be taken into consideration again to explain this behavior, since this initial cracking makes the material more vulnerable to the acid attack. For paste specimens with rubber (Fig. 7), the cements used do not seem to influence the resistance to acid attack. Fig. 10 shows representative photographs of specimens before the immersion in acid. Figs. 11 and 12 shows photographs of the specimens after 4 d of acid attack. Intense cracking and flaking is observed for the paste control specimens. Specimens as P-S1 go through a very aggressive attack, loosing their original form (Fig. 11). Cracking is also observed for paste specimens with rubber (Fig. 12) but much less intense than paste control specimens. Mortar specimens show leached surfaces after 4 d of acid exposure but no cracking is observed. Mortar specimens with rubber, Fig. 12, show lesser-leached surfaces when compared to mortar controls.

The resistance of cement-based materials to chemical attack is mainly determined by their permeability, alkalinity, and the chemical composition of the cement paste. Cement

paste degradation is induced by a combination of diffusion-transport effects and chemical reactions. The degradation kinetics in the paste depend thus upon the kinetics of each of these two phenomena. [25]

Cement materials degradation by acid attack is caused by the reaction of the acid with the cement hydration products forming soluble salts, mostly with calcium, as shown in
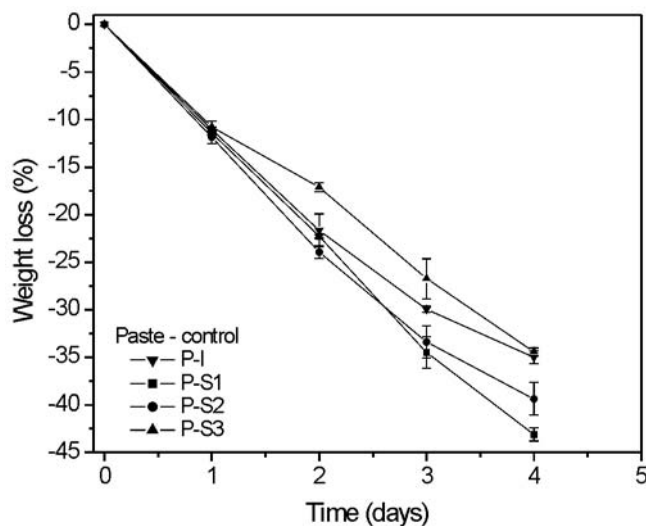

Figure 6: Weight loss due to acid attack as a function of time, for paste control specimens prepared with different cements. Results of triplicate specimens.
[Figura 6: Perda de massa por ação de ataque ácido em função do tempo, para corpos de prova de pasta controle preparados com os diferentes cimentos. Médias de triplicatas de amostras.]
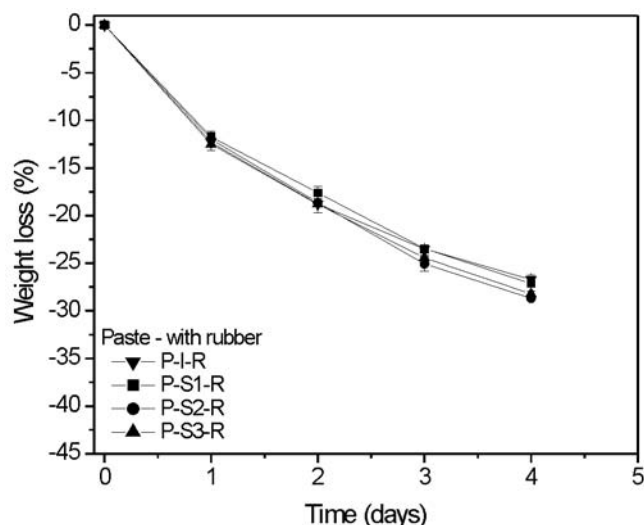

Figure 7: Weight loss due to acid attack as a function of time, for paste specimens with 10% (w/w of the cement content) of NaOH-treated tire rubber particles, prepared with different cements. Results of triplicate specimens.
[Figura 7: Perda de massa por ação de ataque ácido em função do tempo, para corpos de prova de pasta contendo 10% (m/m em relação à massa de cimento) de partículas de borracha tratadas com NaOH, preparados com os diferentes cimentos. Médias de triplicatas de amostras.]

equations B and C. The weight loss is caused by leaching of these soluble products. Also, the formation of this double salts produces expansion and gives rise to disintegrating stresses in the specimens, which fall apart. The acid attack starts on the surface, diffusing to a much greater extent by
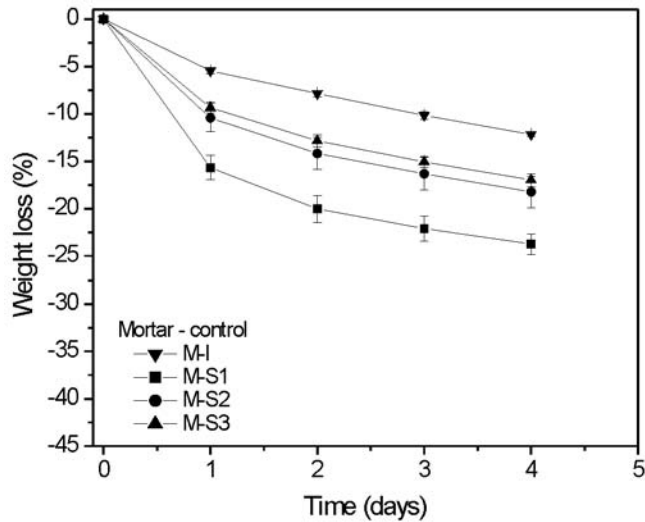

Figure 8: Weight loss due to acid attack, as a function of time for mortar control specimens prepared with different cements. Results of triplicate specimens.
[Figura 8: Perda de massa por ação de ataque ácido em função do tempo, para corpos de prova de argamassa controle preparados com os diferentes cimentos. Médias de triplicatas de amostras.].
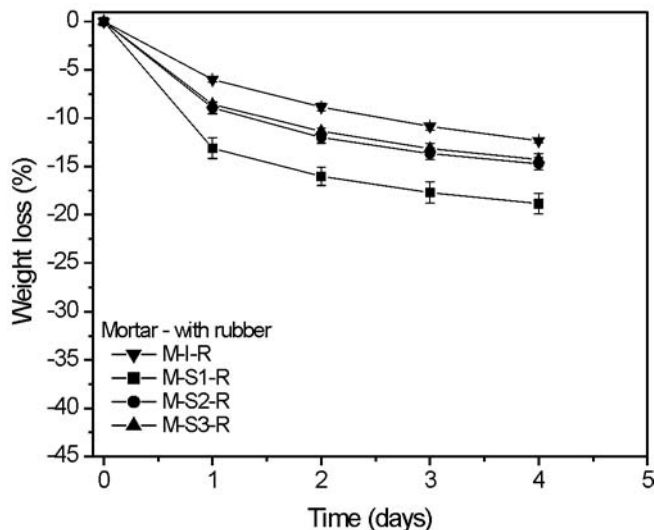

Figure 9: Weight loss due to acid attack, as a function of time for mortar specimens with 10% (w/w of the cement content) of NaOH-treated tire rubber particles, prepared with different cements. Results of triplicate specimens.
[Figura 9: Perda de massa por ação de ataque ácido em função do tempo, para corpos de prova de argamassa contendo 10% (m/m em relação à massa de cimento) de partículas de borracha tratadas com NaOH, preparados com os diferentes cimentos. Médias de triplicatas de amostras.]
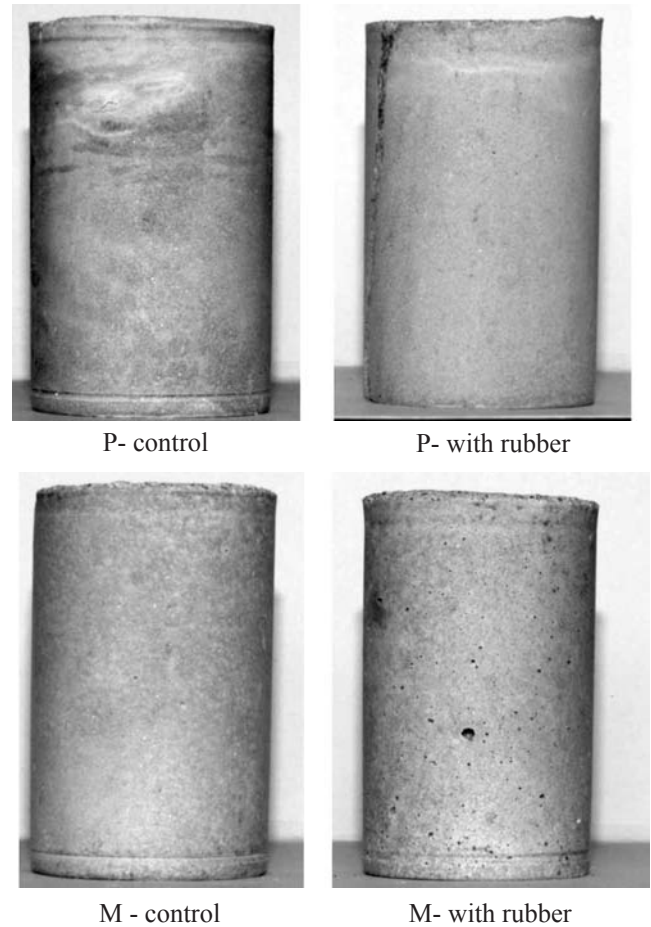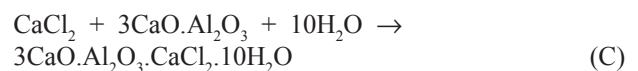

| P- control | P- with rubber |

| M - control | M- with rubber |

Figure 10: Photographs of pastes (P) and mortars (M) control and with rubber specimens, prepared with type I cement, before the immersion in acid.
[Figura 10: Fotografias de corpos de prova de pastas (P) e argamassas (M) controle e contendo borracha, preparados com cimento tipo I, antes da imersão em ácido.]

reacting with the cementitious matrix [26-28].

$$Ca(OH)_2 + HCl \rightarrow CaCl_2 \qquad (B)$$

$$CaCl_2 + 3CaO.Al_2O_3 + 10H_2O \rightarrow$$
$$3CaO.Al_2O_3.CaCl_2.10H_2O \qquad (C)$$

According to the literature, the degree of leaching, expressed in this case by calcium dissolution, is proportional to the square root of time (nonsteady-state diffusion) since the diffusion kinetics slows down with time, and, after a transitory time, the conditions for local chemical equilibrium are achieved inside the specimen. Due to the high solubility of its surface layer, the cement specimen will have a high surface dissolution rate, and, after a relatively short time the kinetics of degradation will follow a t $^{1/2}$ law [25, 29].

All mortar specimens prepared with slag-cements showed higher weight loss when compared with the mortar specimens prepared with type I cement. This result is unexpected, since cured type I cement contains more free $Ca(OH)_2$ than the cured slag-modified cements.

P-I - control   P-S1 - control   P-S2 - control   P-S3 - control

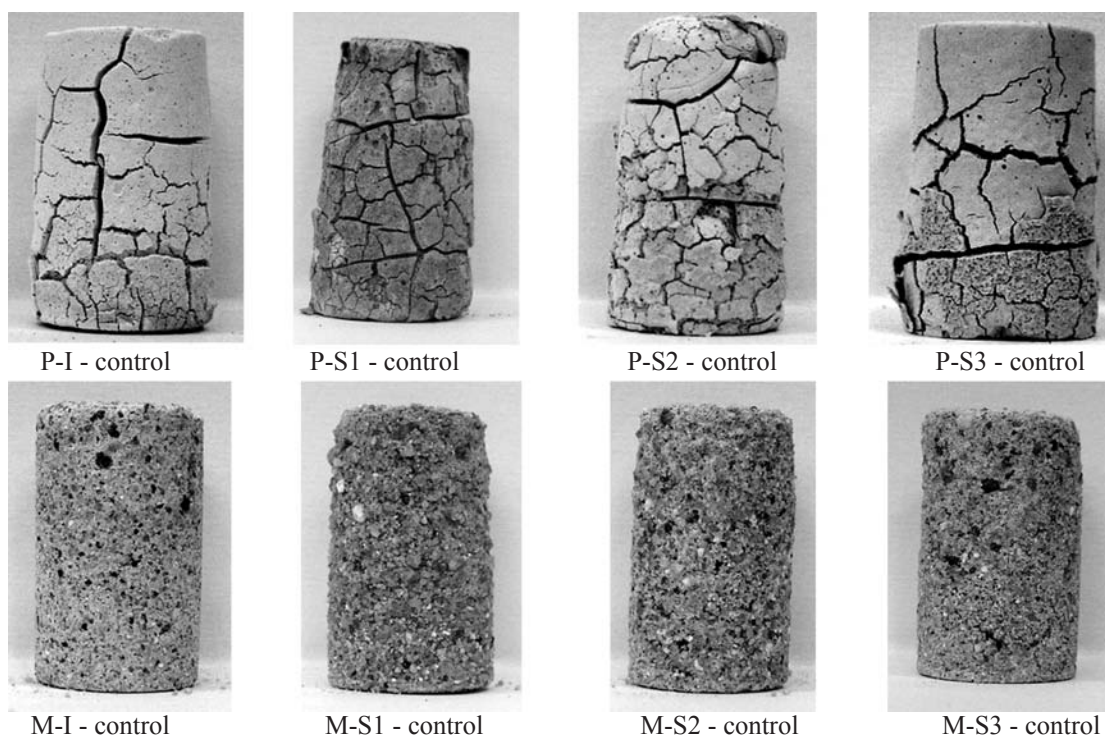M-I - control   M-S1 - control   M-S2 - control   M-S3 - control

Figure 11: Photographs of paste (P) and mortar (M) control specimens, prepared with different cements (I, S1, S2 and S3) after four d of immersion in acid.
[Figura 11: Fotografias de corpos de prova de pastas (P) e argamassas (M) controle, preparadas com os diferentes cimentos (I, S1, S2 e S3) após quatro dias de imersão em ácido.]

P-I - rubber   P-S1 - rubber   P-S2 - rubber   P-S3 - rubber

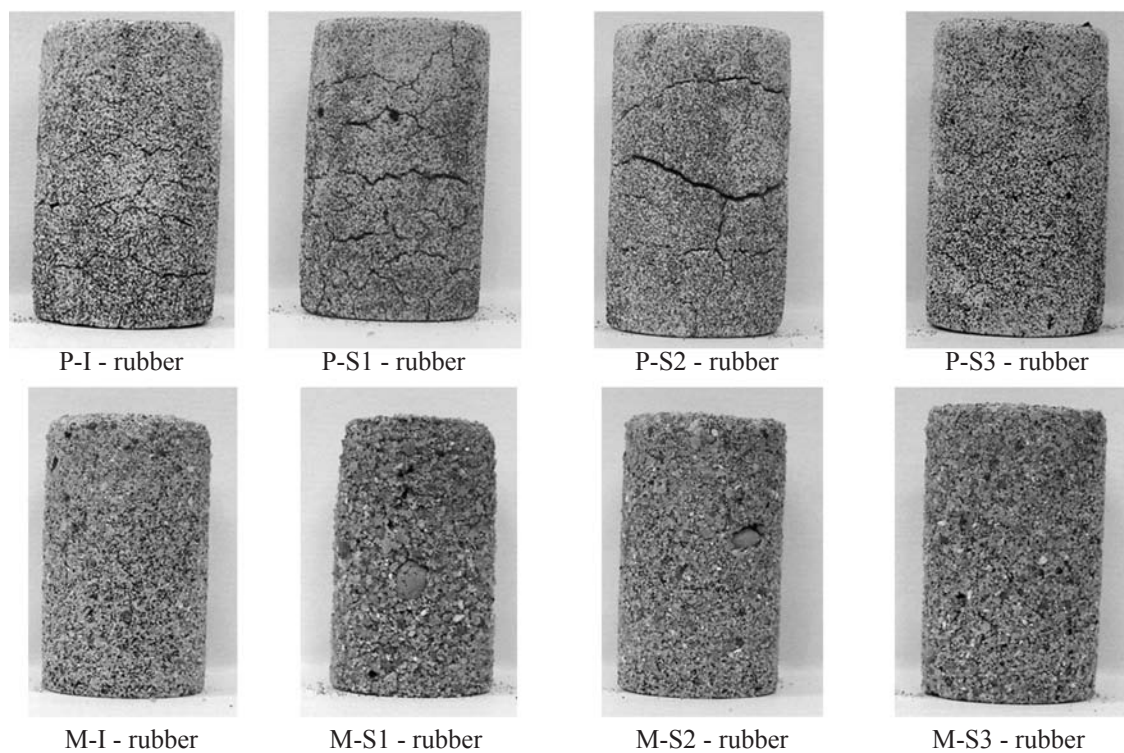M-I - rubber   M-S1 - rubber   M-S2 - rubber   M-S3 - rubber

Figure 12: Photographs of paste (P) and mortar (M) specimens with 10% (w/w of the cement content) of NaOH-treated tire rubber particles, prepared with different cements (I, S1, S2 and S3) after four d of immersion in acid.
[Figura 12: Fotografias de corpos de prova de pastas (P) e argamassas (M) com 10% (m/m em relação à massa de cimento) de partículas de borracha tratadas com NaOH, preparadas com os diferentes cimentos (I, S1, S2 e S3) após quatro dias de imersão em ácido.]

The comparison of types I and slag-modified cements performance face to acid attack is limited in literature but in general slag-cement materials are more resistant [30-35]. However, factors as type of cement-based material, type and concentration of the acid, specimen age and acid exposure time and replacement seems to influence the chemical process involved on acid attack [32]. DeCeukelaire [33] evaluated the effect of 1% hydrochloric acid on 28 d-old mortar specimens prepared with type I and slag cements after 2 y of acid exposure. After long periods the slag-cement mortars showed the best results. On the other hand, the author pointed that the literature also describes that the resistance of mortar to HCl short time exposure is irrespective of cement type. Hobbs [36] pointed that the resistance to acid attack is dependent upon the concrete quality and is little influenced by cement type. DeBelie [30] observed that mass loss of 60 d-old concrete specimens immersed in a pH 5.5 lactic and acetic acid solution after 4 d of exposure showed higher amount of mass loss for the specimens prepared with slag-cement when compared to type I cement specimens.

Differences in acid attack are observed among the slag-cements materials. The alkalinity of blended cements is dominated in practice by their soluble alkali contents and $Ca(OH)_2$ solubility is greatly depressed in the presence of alkali hydroxides such as NaOH and KOH [23]. In this case, the higher the amount of Na_2O and K_2O, the lower the solubility of $Ca(OH)_2$ which leads to a lower alkalinity of the cement paste. The lower the alkalinity the lesser the acid attack. The composition of slags S2 and S3 show the same amount of Na_2O and K_2O and the specimens prepared with these slag-cements behave the same way face to acid attack. On the other hand, a prominent higher weight loss was observed for specimens prepared with the S1 slag-cement, which slag composition contains the lower Na_2O and K_2O amounts.

It is well known that the $Ca(OH)_2$ contained in the cement matrix is one of the activators responsible for slag hydration. The hydration of slag consumes $Ca(OH)_2$ decreasing its amount and consequently decreasing susceptibility to acid attack. Brief cure periods were used, leaving unreacted slag in all specimens. Since the less basic slag has the lower reactivity, the S1 slag-cement specimens should contain more unreacted slag, leaving more $Ca(OH)_2$ available to acid attack.

No difference in weight loss was observed between control and with-rubber mortar specimens prepared with the type I cement. However, for the slag-cements mortar specimens, a reduction of roughly 20% in weigh loss is observed for specimens with rubber, probably as a consequence of the permeability reduction of these composites.

CONCLUSIONS

Concerning mechanical properties, the specimens prepared with the S3 slag-cement behave similarly to the type I cement specimens, even at early ages. This result indicates that type I cement can be replaced by S3 slag-

cement without reducing performance. For rubber-mortar composites, the type or composition of the cement used has no influence in the performance of the material.

Specimens prepared with S1and S2 slag-cements absorb less water, probably as a consequence that the less basic slags should interact more effectively with the rubber, forming a better adhesive joint and leading to a reduction in water sorption.

Results of acid attack to the slag modified mortars indicate that specimen susceptibility is governed not only by microstructural aspects, like porosity and permeability, but also by chemical aspects as the difference in alkali content or the amount of unreacted slag in the specimens.

ACKNOWLEDGMENTS

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