

Study of Rubber-Filled Cementitious Composites

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ABSTRACT: A possible method for recycling automobile and truck tires is to comminute them and incorporate the rubber particles in to cementitious mixtures for nonstructural applications. It was found that addition of rubber granules led to a decrease in compressive and flexural strengths of the mortar. The fracture behavior of cementitious paste containing untreated rubber particles showed particulate pull out characteristics and weak interface. The interfacial strength of rubber-cementitious composite can be improved upon chemical treatment of rubber by gamma mercapto trimethoxy silane coupling agent (GMPTS). The extent of interfacial bonding of rubber and cement was measured by peel strength analysis. The increased interfacial strength of the composite was found to play an important role in the ability of the composite to withstand postpeak loading and postpeak displacement. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 934–942, 2000

Key words: rubber; composite; interface; cementitious material; coupling agent

INTRODUCTION

Rubber tires pose a major disposal problem to the global environment. Across the United States of America, over 250 million tires are discarded each year, with another 2 billion already stockpiled in open areas and landfills.¹ Disposing of tires in open areas is not only illegal, but tires in open areas are major breeding grounds for mosquitoes since they hold water. Moreover, stockpiling of tires in a tire disposal site is dangerous because tires are flammable polymers. When a tire catches fire, it causes significant air, land, and water pollution, and a high cost is associated with the cleanup of the site. Disposing of tires in landfills is no longer a practical alternative because of shrinking landfill space and the maintenance cost of landfill. New methods for recycling or reusing or reducing tires could help alleviate the rubber disposal problem.

Among proposed alternatives to disposal are recycling tires as fuel for cement kilns, as feedstock for producing carbon black, as reefs in a marine environment, and as paving material in asphalt.^{2–4} These alternatives have shown promise, but there are some concerns regarding the wider use of rubber for the aforementioned applications.^{5–8} Even if these issues are addressed satisfactorily, recent estimates suggest that the proposed alternatives (e.g., rubber-containing asphalt) can possibly absorb only a fraction of the scrap tires generated.⁹ Hence, the need for development of alternative recycling methods using scrap tires. A possible method for recycling used tires is to comminute them and incorporate the rubber particles into cementitious materials for nonstructural uses, such as highway pavement overlays, sidewalks, medians, sound barriers, and other transportation structures in which high strength is not a prime consideration.

In an earlier study, we examined the influence of the shape of rubber particles on mechanical properties, workability, and chemical stability of rubber-filled cementitious composites.¹⁰ An en-

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couraging finding was that composite with rubber shreds was able to bridge the crack and prevent catastrophic failure of the specimen, while the composite with granular rubber particles was unable to bridge the crack. The pull out characteristic of granular rubber particles from the matrix is consistent with poor interfacial bonding. In this study, we provide evidence to show that adhesion of granular rubber particles and cement paste can be improved by treating rubber with bifunctional silane-coupling agent, such as gamma mercapto trimethoxy silane coupling agent (GMPTS).

BACKGROUND

During the past few years, efforts have been made to develop rubber-filled cementitious composites.^{10–22} Most of the research results on the use of rubber in cementitious material have shown that the rubber–cement interface is weak. Several attempts have been made to strengthen the interface by washing the rubber particles.^{15,17,20–22} Eldin and Senouci²⁰ by washing the rubber particles with water, cleaned the rubber particle to promote adhesion. Rostami et al.²² also showed that washing the rubber particles with water and carbon tetrachloride, and water and latex admixture improved the adhesion of rubber-filled cementitious composite.

In an attempt to improve the rubber–cement interface, several surface modification approaches using chemicals, such as dilute nitric acid and sulfuric acid, have also been investigated. The treatment of rubber with nitric acid was expected to chemically oxidize rubber and introduce polar groups so as to improve the adhesion of the rubber particles with cement matrix. Contrary to expectation, nitric acid was found to decrease the strength of the composite.¹⁵ On the other hand, Lepore and Tantala²¹ observed improvement in the adhesion of rubber to concrete when the rubber particle was treated with sulfuric acid. It is probable that pretreatment of rubber with some surface modifiers may improve the adhesion of rubber to the cement matrix. The primary objective of the present research is to investigate the role of bifunctional silane-coupling agent as surface modifiers in strengthening the interface of rubber-filled cementitious composites.

As expected, the present study confirmed the findings of previous work that rubber addition decreases the compressive and flexural strengths of the mortar and produces a weak interface of rubber and cement. This observation may be explained as the result of the addition of low-mod-

ulus rubber material to a very high-modulus cementitious paste and/or the weak rubber–cement interface. In this study, we are addressing the weak rubber–cement interface by pretreating rubber with coupling agent so that the interfacial adhesion of rubber to cement can be improved. For this exploratory study, we choose to study cement paste, rubber, and silane-coupling agent, and, later, we plan to extend the work to include mortar and concrete. This is because it is easier to understand the adhesion of rubber and cement paste with and without coupling agent in the absence of aggregate. The degree of adhesion between GMPTS-modified rubber, and cement paste is expressed as peel strength.

EXPERIMENTAL

Compressive and Flexural Strength Determination of Mortar Specimens with Untreated Rubber

Mortar batches were prepared, as described in ASTM C109.²³ The mass ratios of sand-to-cement and water-to-cement were 2.75 and 0.485, respectively. Depending on the specimen, the cement-to-rubber ratio ranged from infinity to 5. In the preparation of the mixtures, the untreated rubber was added at the end of the mixing of the sand, cement, and water. The specimens for strength measurements were cured at 100% relative humidity (RH) for 24 h at room temperature ($23 \pm 2^\circ\text{C}$). Upon removing the samples from the curing chamber, the samples were stored in lime-water for 7 days before testing for compressive and flexural strengths.

The specimens for compressive strength measurements were 75 mm diameter \times 150 mm long cylinders, and the specimens for flexural strength were $25 \times 25 \times 279$ mm rectangular beams. For compressive strength, the cylindrical specimens were capped by neoprene caps and tested according to ASTM C39,²⁴ while the flexural strength of the specimens was measured using one-third point loading, as described in ASTM C 78.²⁵

Measurement of Peel Strength

To determine the bonding of rubber and cement paste in the presence and absence of coupling agent, experiments were conducted on cement paste instead of mortar. Rectangular rubber strips of the dimensions of 152 mm length \times 25 mm breadth \times 3.2 mm thickness, obtained from

Goodyear Tire Company (Akron, OH), was placed on top of the cement paste specimen. (*Note:* Certain supplier names and the names of instruments and materials are identified in the article to adequately describe the experimental procedure. In no case does such identification imply recommendation or endorsement by Howard University, nor does it necessarily imply that the items are best available for the purpose.) Since it is difficult to analyze the coatings on individual cement grains, flat surfaces of 24-h-cured cement paste specimens were prepared for the current study. One mL of 25 vol % solution of coupling agent (25 mL of GMPTS + 75 mL of toluene, ethanol, butanol, and distilled water mixture) was prepared and placed on 8200 mm² of cement paste block. The rubber strip was immediately placed on the top of cement block. The entire configuration was heated to 150°C and maintained at 150°C for 1 h at 3000 psi, using a Carver Press compression unit. After the specimen had cooled to room temperature, the peel strengths of the rubber-cement-coupling agent and the rubber-cement specimen were determined using an Instron tensile tester. A strain rate of 1 mm s⁻¹ was used to avoid premature failure at the interface. The rubber was separated from the cement at an angle of 180°, and the separation was continued for sufficient distance to determine the peel strength value.

Fracture Behavior of Bonded Specimens

Cement paste and rubber-filled cement paste were prepared by maintaining a constant water-to-cement ratio (0.35) and rubber-to-cement ratio (0.2). The same ratios of rubber, cement, and water were used for bonded specimens. Pulverized rubber supplied by Goodyear Tire Co. was used for the current study. For preparing bonded specimens, a 1 vol % solution of coupling agent (prepared by acid hydrolysis of GMPTS in water) was added to the rubber, which was added to the cement paste at the end of standard mixing cycle. The entire mixture was mixed for an additional 2 min. The specimens for strength measurements were cast in cylindrical molds of the dimensions of 254 mm (diameter) × 508 mm (length). Pastes were cast into molds and consolidated for approximately 2 min, followed by 24 h curing in a 100% RH chamber at room temperature. One set of demolded specimens was cured for an additional 28 days in the curing chamber, and the other set of demolded specimens was autoclaved. Autoclav-

ing was performed on some specimens at 150°C for 24 h, while some other specimens were autoclaved at 170°C for 24 h in saturated steam. The autoclaved samples were allowed to attain room temperature. All the cylindrical specimens were capped with bonded sulfur caps and tested in compression at a rate of 0.003 mm s⁻¹ to observe the fracture behavior of the specimens.

RESULTS AND DISCUSSION

Strength of Untreated Rubber-Filled Mortar

Figure 1 shows the compressive strength of the cylindrical mortar specimens as a function of weight percent of rubber in the composite. A water-to-cement ratio of 0.485 was initially chosen, and control specimens with no rubber were prepared. No replicate batches were included in these tests. The within-batch coefficients of variations ranged from 1.5 to 4.5%. The compressive strength of mortar cylinders decreased with the increased content of granular rubber in the specimen. Several researchers have noticed a similar trend and proposed a weak rubber-matrix interface as one of the causes for the failure of the composite.^{13,19,21}

Figure 2 shows the flexural strengths of the mortar beams as a function of mass percent of rubber in the composite. The within-batch coefficient of variation was around 4%. Replicate batches were included in these tests. The flexural strength of the mortar beams decreased with the addition of rubber. The reduction of strength of mortar-containing rubber is either due to the replacement of load carry material by the low modulus of elasticity rubber aggregate material or the weak rubber-cement interface or their combined effect.

Figure 3 is a light micrograph of a fracture surface of untreated rubber-filled mortar. We notice the rubber granules are dispersed in the cement paste matrix, and they vary in diameter and shape. The geometry of the rubber granules varies considerably, depending on the grinding process and the source and origin of rubber tire.²⁶ Observation of the specimen showed that a fracture occurred at the rubber-to-cement interface. The pullout characteristics of the rubber particles from the mortar are consistent with poor interfacial bonding. This confirms our earlier observation that the rubber-cement interface is weak.¹⁰

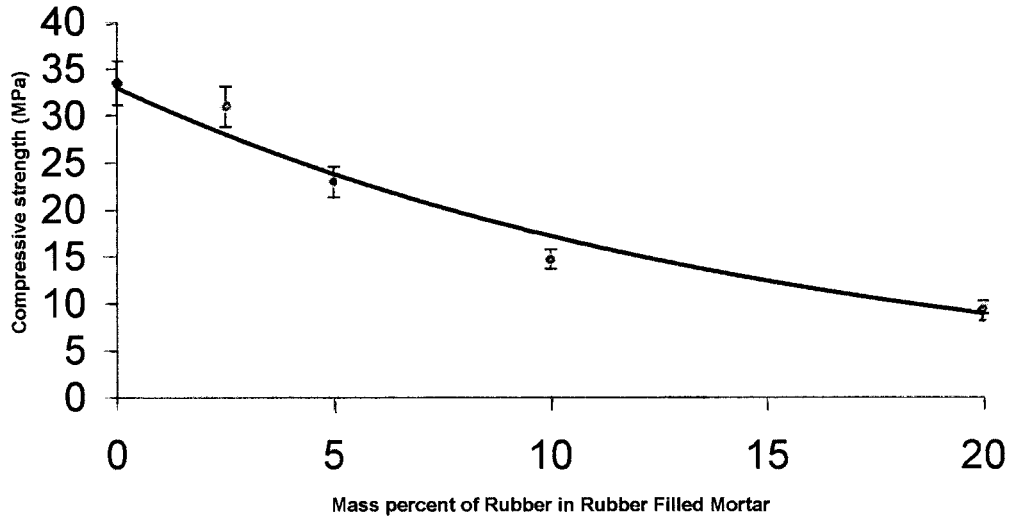


Figure 1 Compressive strength of untreated, rubber-filled mortar as a function of the mass percent of rubber loading.

Because of the low modulus of elasticity of rubber and poor adhesion of rubber to cement paste, the addition of untreated rubber results in the strength reduction of the mortar. Lepore and Tantal²¹ showed that the chemical treatment of rubber granules could improve the adhesion of rubber and cement paste.

Adhesion of Rubber-Filled Cement Paste

In an attempt to develop an understanding of adhesion between rubber and cement, peel experiments were conducted on rubber-cement paste instead of a rubber-mortar mixture. To improve

the adhesion of the rubber granules to the cement paste, the rubber granules were treated with GMPTS as the coupling agent. Upon acid hydrolysis, the GMPTS coupling agent forms methanol and trihydroxy silane derivative. At room temperature, the hydroxyl group of the GMPTS bonds with the hydroxyl groups of the cement surface to form siloxane bonds. Upon hydrolysis, Portland cement form gelatinous calcium silicate hydrate and calcium hydroxide of high specific surface area. At elevated temperatures, we also expect the functionalities of GMPTS to react with rubber.

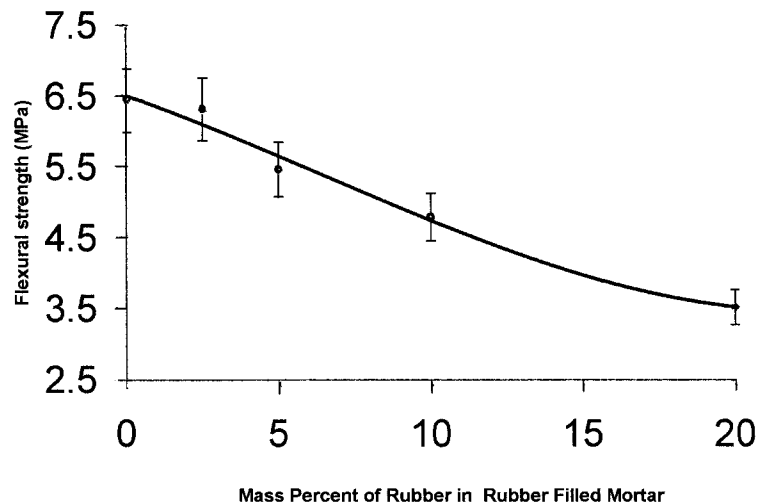


Figure 2 Flexural strength of untreated, rubber-filled mortar as a function of the mass percent of rubber loading.

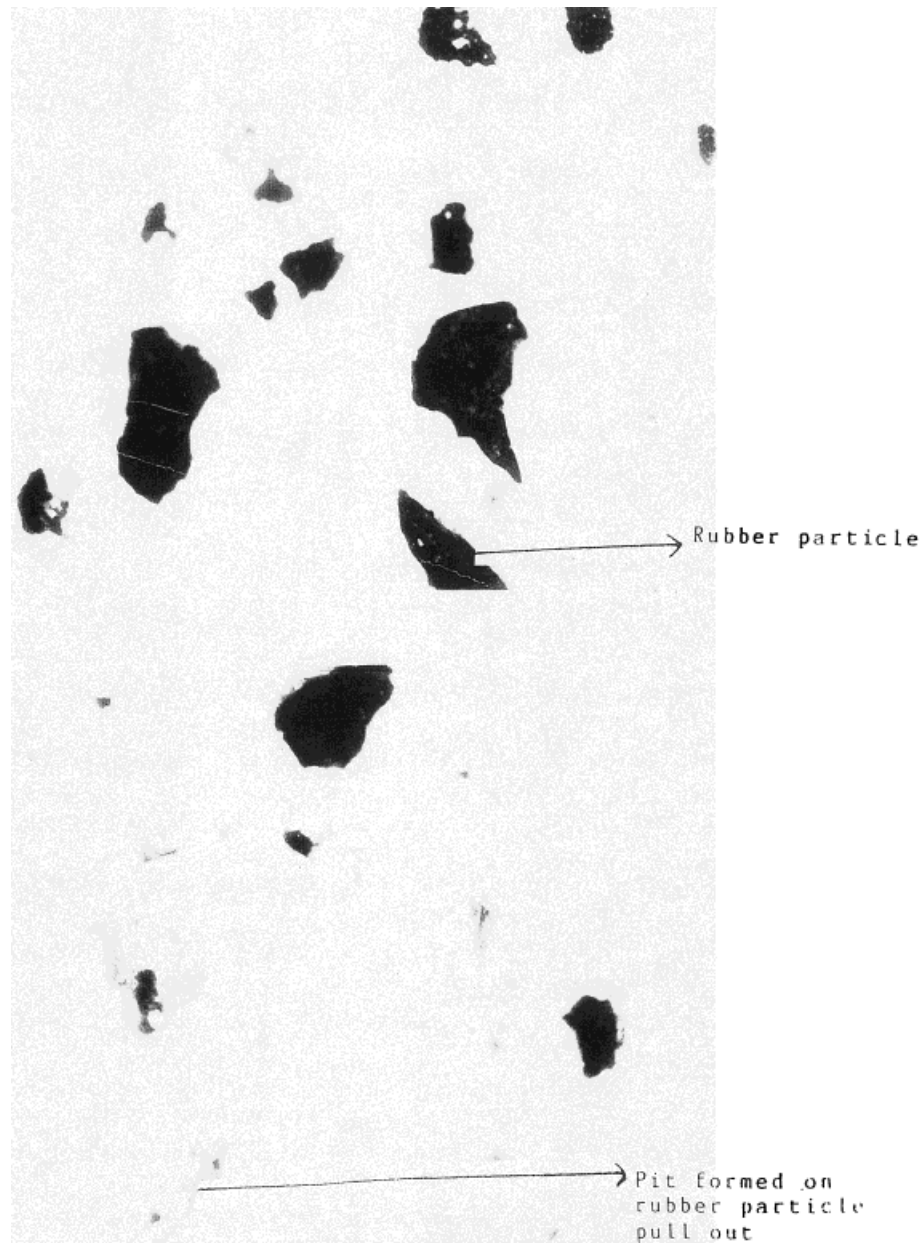


Figure 3 Photomicrograph of a fracture surface of untreated, rubber-filled mortar.

In the range of the mass of the coupling agent studied, the adhesion between the rubber and the cement increased with the mass of the coupling agent. In the absence of coupling agent, the composite showed such poor bonding that it could not be tested for peel strength using the current test method. Similarly, we noticed poor bonding for composite specimens with coupling agent that were compression-molded at room temperature. As expected, it appears that the coupling agent did not react with rubber at room temperature.

For the mercapto functional group of coupling agent to react with unsaturated groups in rubber and establish the bonding, the specimen should be cured at elevated temperature. When a composite specimen with coupling agent was compressed and cured at elevated temperature ($\sim 150^{\circ}\text{C}$ for 1 h), there was a measurable degree of bonding. To establish the bonding between coupling agent and rubber at elevated temperature, X-ray photoelectron spectroscopy (XPS) measurements were performed on the model system (po-

Table I Peel Strength Data of Untreated and Silane-Agent-Treated Rubber-Filled Cement Paste

Type of Specimen	Coupling Agent (%)	Peel Strength (Jm^{-2})
Rubber + cement	0	no adhesion
Rubber + cement + coupling agent	25	182 ± 90
Rubber + cement + coupling agent	100	455 ± 90

lybutadiene and the GMPTS coupling agent). A shift in the S(2p) peak of the coupling agent was noticed when the GMPTS, along with polybutadiene, was allowed to react at an elevated temperature. The shift may be a result of chemical bonding of the thiol group with the unsaturation in polybutadiene. Further XPS measurements on the model system are needed to confirm the observation.

In this study, as previously stated, the degree of bonding between the rubber and the coupling-agent-treated cement paste is expressed as peel strength. Table I is a summary of the peel strength results for various conditions. Reproducibility of the peel strength results was determined by conducting triplicate analyses. On peeling rubber samples from bonded specimens, the peel load–displacement profile shows the two following distinct regions: (1) a linearly increasing region, followed by (2) a plateau region. The load at the plateau region was used in the determination of peel strength. For composite specimens with a layer of undiluted coupling agent (100%), the peel strength was $\sim 455 \text{ Jm}^{-2}$; for composite specimens with a layer of diluted coupling agent (25%), the peel strength was $\sim 182 \text{ Jm}^{-2}$. The data suggests that the peel strength is dependent on the mass of the coupling agent.

Recently, we came across one study that provides further evidence to support our observation in this article. The article is from an investigation by Chung et al., who used a vinyl triethoxy silane coupling agent to chemically bond rubber to aggregates.²⁷ They showed that the interfacial adhesion of rubber and aggregate could be improved when a recipe of rubber, vinyl trimethoxy silane coupling agent, sulfur, and zinc oxide was mixed with an aggregate at 160°C. The vulcanization reaction between the vinyl group of coupling

agent, rubber, and sulfur occurred at 160°C. Similarly, in the present research, GMPTS was used as a coupling agent to promote adhesion between rubber and cementitious material at 150°C. Typically, rubber strips are cured by operating at a test temperatures in the 150 to 180°C range for approximately 60 min.²⁸ The unreacted double bonds in the vulcanized rubber participate in the bond formation with the mercapto group of GMPTS. Because of the reaction between the coupling agent and rubber, as well as the reaction between the coupling agent and cementitious surface, we notice improved adhesion between the rubber and the cement paste.

Fracture Behavior of Silane-Agent-Treated Rubber-Filled Cement Paste

In an attempt to determine whether improvements in adhesion translate to desirable failure of the rubber-filled cement paste, we compared the fracture behavior of rubber-filled cement paste and silane-agent-treated rubber-filled cement paste. Water and cement were mixed in a ratio (w/c) of 0.35 by mass to form a compression-molded specimen. The volume of coupling agent solution was kept constant. A minimum of five samples was tested to obtain reliable stress–strain curves. Figure 4(a) shows the average stress–strain curve of cement paste. As expected, the cement paste had high strength and low failure strain. Cement paste shows minor changes in fracture behavior with preparation conditions (i.e., autoclaving or 28-day curing of the paste specimen). In general, the autoclaved and the 28-day cured specimens showed a brittle fracture behavior (as observed by stress–strain curve). Our results indicate that autoclaving of specimens yielded cement pastes with the strength roughly equivalent to that of 28-day moist cured strength. This is in general agreement with the data reported in the literature for 28 days aerated and autoclaved cementitious specimens.^{29,30}

In the second set of experiments, the mixture was the same as the control, except that 1% of coupling agent solution was added to the mixture. Figure 4(c) shows the average stress–strain curve of coupling agent containing the cement paste system. When coupling agent was added to cement paste, the fracture stress was comparable to that of the cement paste, while the fracture strain improved marginally.

A rubber-filled cement paste was prepared in a similar way to the control mixture, with the wa-

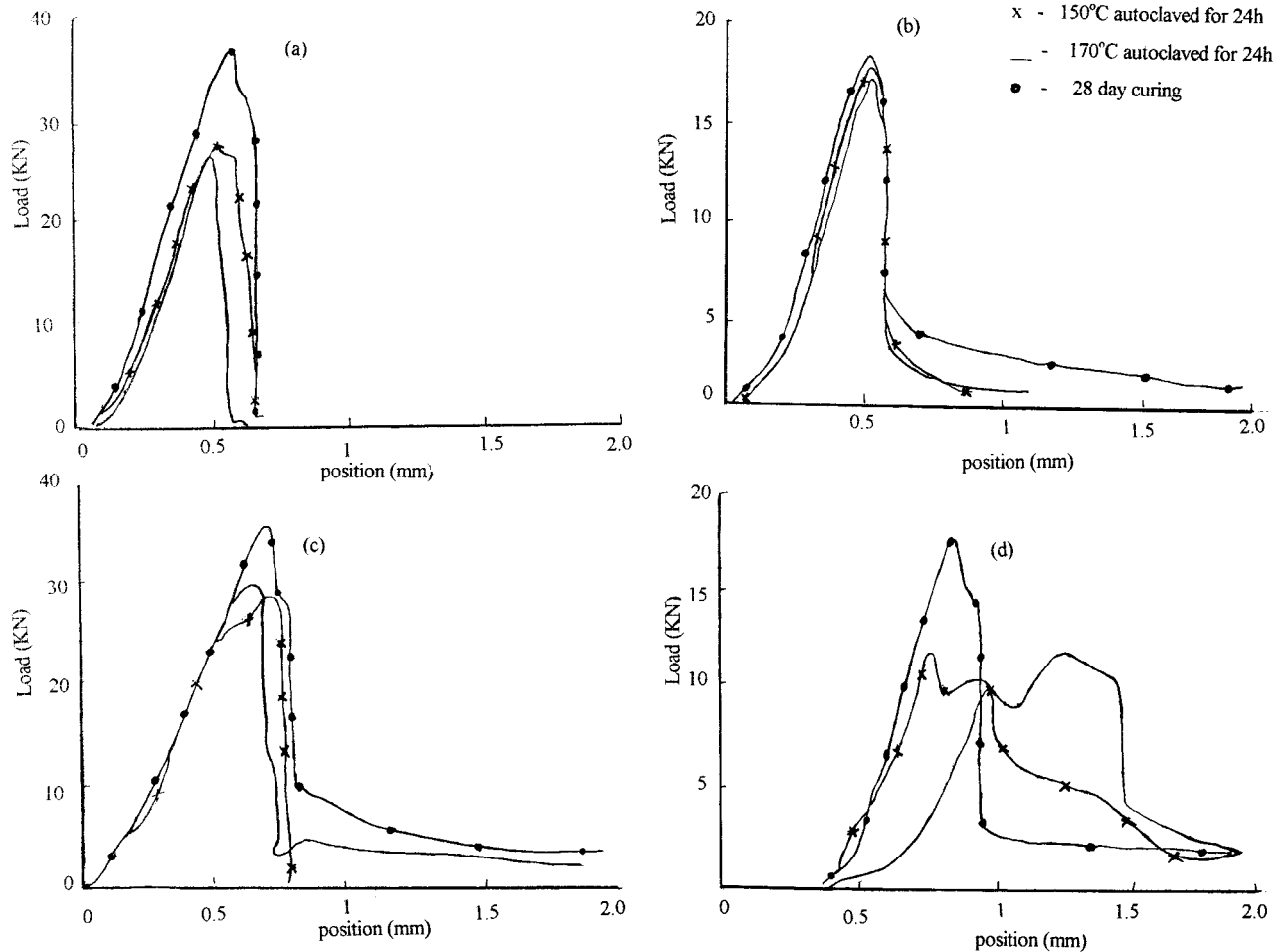


Figure 4 Average stress–strain graph of (a) cement, (b) untreated, rubber-filled cement paste, (c) cement + coupling agent, and (d) coupling-agent-treated rubber-filled cement paste.

ter-to-cement ratio of 0.35 by mass, except that rubber replaced a portion of cement. Figure 4(b) shows the average stress–strain graph for the rubber-filled cement paste. As expected, there is a decrease in the compressive strength of the cement paste upon the addition of rubber. We notice a minor change in the average fracture stress value and a mode of fracture with changes in the preparation condition (autoclaved at 150°C for 24 h or at 170°C for 24 h). Brittle fracture behavior was noticed for all the autoclaved specimens. There is a minimal adhesion between the rubber and the cement paste. This is consistent with our peel strength data for the untreated rubber cement specimen.

By adding the GMPTS coupling agent to specimens with the rubber cement mixture and autoclaving, we noticed changes in the fracture behavior of the specimens. Figure 4 shows the

average stress–strain curve for composite specimens with the coupling agent. When the coupling-agent-treated rubber cementitious composite specimen was aged for 28 days, we found no substantial improvement in the fracture stress and strain of the composite; and the behavior was similar to the 28-day-cured rubber cement mixture with no coupling agent. When the specimen was autoclaved, the composite was able to withstand a fraction of the ultimate load for long periods of time (observed as a tail in the stress–strain curve). Both the 150 and 170°C autoclaved specimen show a considerable amount of tailing in the stress–strain curve. The observation of a large tail in the autoclaved rubber cement composite with the bonding agent is the evidence of greater ductility. The ductility in the autoclaved specimens suggests that the rubber adhered to the cement paste.

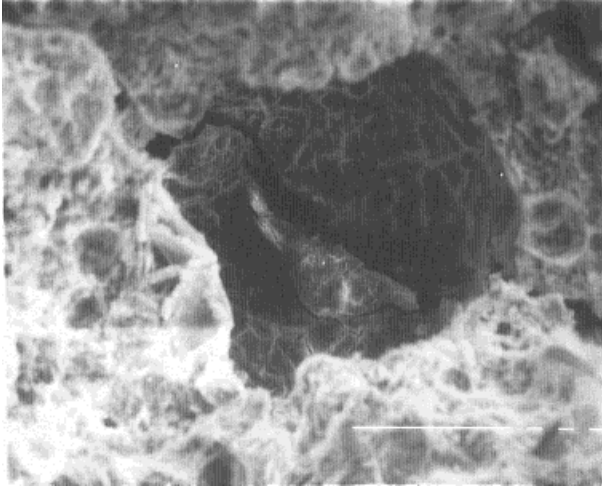


Figure 5 SEM micrograph of the fracture surface of a cement paste containing rubber and a silane coupling agent (215X).

The findings are consistent with the peel strength data. Figure 5 is a micrograph of the fracture surface of the rubber-bonded cement composite. The micrograph shows torn rubber particles in the cement matrix. Unlike the untreated rubber particle, in which we noticed a particulate pull out, we observe tearing of the rubber particulate in a treated rubber cement composite, suggesting the role of coupling agent in strengthening the interface.

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions were drawn from the current study:

1. The compressive and flexural strength of mortar decreased with the increasing contents of rubber. At 20 mass % of rubber, the average fracture stress of the 28-day-cured specimen is roughly 50% that of the 28-day-cured cement paste control. When untreated rubber is added to the cement paste, the pull-out of the rubber particles from the cement paste was noticed. This was taken as evidence of weak interfacial bonding between the rubber and the cement.
2. When the rubber and cement were cured with a bifunctional coupling agent at an elevated temperature, an improvement in the interfacial strength between the rubber and cement was noticed. In the range of the mass of the coupling agent studied, the

adhesion between the rubber and cement increased with the mass of coupling agent.

3. Autoclaving of the coupling-agent-treated rubber-filled cement composite changed the shape of the stress-strain curve to suggest increased ductility.

It is recommended that further tests be conducted to provide more information on the effects of the type of coupling agents on the adhesion and the fracture behavior of the rubber-filled cement paste. The study should be expanded to mortar and concrete specimens to verify the benefits of adding coupling-agent-treated rubber in improving the adhesion with cementitious systems.

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