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Durability of Simulated Shredded Rubber Tire in Highly Alkaline Environments

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In applications where high strength is not of prime importance, automobile and truck tires can be recycled by shredding them and incorporating them in concrete. When the rubber is placed in the concrete, it should have minimal strength reduction and undergo minimal degradation due to the prolonged exposure to the concrete matrix. In this preliminary study, the stability of shredded rubber in concrete was simulated by exposing the shredded rubber to highly alkaline environments for up to 4 months. The degradation of rubber immersed in different chemicals was monitored by observing the changes in mass, swelling, tensile strength, and microstructure. The results show that the shredded rubber undergoes small change in a highly alkaline medium after 4 months, which suggests that the addition of rubber to concrete will not dramatically affect the durability of concrete. ADVANCED CEMENT BASED MATERIALS 1997, 6, 138–143. © *1997 Elsevier Science Ltd.*

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In the United States over 240 million rubber tires are discarded annually [1]. Recycling the tires as fuel for cement kilns, as feedstock for producing carbon black, as barriers for marine reefs, or in asphalt paving materials are alternatives to disposing the wastes in landfills [2–5]. However, these current recycling approaches are expensive and cannot handle the large stockpile of waste rubber [5,6]. Another method for recycling rubber tires is to mechanically shred the tires and incorporate the rubber particles into concrete for highway overlays and sidewalks [7]. Until now, most research on the use of rubber in concrete has been conducted using granular rubber [8–14]. Particle sizes of granular rubber used have ranged from 0.06 mm to 2 mm in diameter. A preliminary study showed that use of fibrous rubber [10.8 mm (length) × 1.8 mm (width)] in the mortar, compared with granular rubber, can improve some of the properties of the mortar [15,16]. When added to concrete products the rubber fibers provided some resistance to cracking. It was claimed that the addition of fibrous rubber to concrete improved shock wave absorption, reduced heat conductivity and noise level, and increased resistance to acid rain [17–19]. Organic and inorganic fibers (ranging from steel to asbestos to high-cost–high-modulus polyacrylonitrile fiber) have been used in mortar to enhance toughness and to provide resistance to plastic shrinkage cracking [20–22]. For example, polypropylene microfibers are used to reduce the plastic shrinkage cracking of concrete. The use of organic fibers is popular because of their chemical resistivity. The intent of this study is to determine the chemical susceptibility of rubber in a highly alkaline environment.

Stability of Rubber in Alkaline Environment

Rubber is a high molecular weight, amorphous polymeric material. Depending on the application, the formulation of rubber compounds may vary. A typical composition of a car tire is 58.6 wt% rubber, 29.2 wt% carbon black, 2.9 wt% zinc, 1.8 wt% stearic acid, 1.2% sulfur, 5.85% extending oil, and 0.4 wt% accelerators [23,24]. The amorphous regions of the rubber are likely to be susceptible to oxidation. Furthermore, rubber may undergo biochemical oxidation to produce sulfuric acid [25,26]. Attack by chemicals and microbes on rubber can lead to deterioration in the mechanical properties, reducing the working life of tire/rubber hoses to the extent of approximately 50% [27].

The rubber fiber used in concrete is exposed to a variety of alkali and alkaline chemicals. The fibrous rubber is prone to damage in the event of deterioration by alkaline chemicals. Any adverse effect on the fiber could ultimately influence the overall mechanical properties of rubber-filled concrete. Our goal is to study the degradation of rubber by exposing it to the alkaline environment in concrete.

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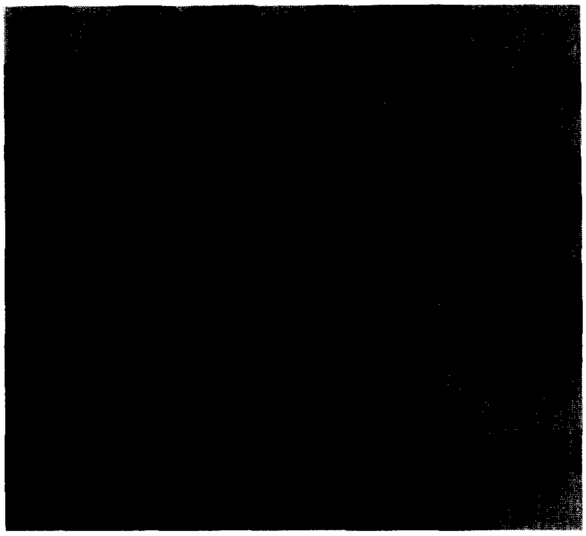

FIGURE 1. Picture of shredded rubber used in the study (scale divisions are in mm).

Hydration of Portland Cement

Portland cement on hydration (i.e., reaction with water) yields several products. The major hydration reactions of portland cement [typically 80% of portland cement is a mixture of dicalcium silicate (Ca_2SiO_4) and tricalcium silicate (Ca_3SiO_5)] can be represented as follows:

$$Ca_3SiO_5 + 5.3H_2O \rightarrow 1.7CaO.SiO_2.4H_2O + 1.3\,Ca(OH)_2 \quad (1)$$

$$Ca_2SiO_4 + 4.3H_2O \rightarrow 1.7CaO.SiO_2.4H_2O + 0.3\,Ca(OH)_2 \quad (2)$$

where $CaO.SiO_2.4H_2O$ approximates the composition of calcium silicate hydrate and $Ca(OH)_2$ represents calcium hydroxide [28–30]. The amount of calcium hydroxide formed is dependent on the ratio of di- and tricalcium silicates present in portland cement. The pH of calcium silicate hydrate suspension and calcium hydroxide is approximately 12.5. In addition, some alkali metal ions are usually present in the aqueous phase, in contact with hydrated portland cement, which will cause its pH to increase to above 12.5. By exposing the rubber fibers to highly alkaline environments for extended time periods, the stability of rubber fibers was investigated.

Experimental Procedure

Materials and Specimen Preparation

TABLE 1. pH change percentages of various chemicals upon exposure to rubber for different time periods

Chemicals	Final pH	Soaking Duration (days)
Water (pH = 7.00)	7.00 ± 0.00	1
	6.94 ± 0.33	3
	6.94 ± 0.01	7
	6.92 ± 0.03	14
	6.83 ± 0.08	21
	6.82 ± 0.03	28
NaOH (pH = 9.94)	8.60 ± 0.07	1
	8.54 ± 0.00	3
	8.32 ± 0.40	7
	7.47 ± 0.03	14
	7.01 ± 0.09	21
	6.82 ± 0.06	28
$Ca(OH)_2$ (pH = 13.09)	13.31 ± 0.02	1
	13.51 ± 0.06	3
	12.98 ± 0.02	7
	12.55 ± 0.01	14
	12.73 ± 0.04	21
	12.94 ± 0.03	28
Cement solution (pH = 13.64)	13.33 ± 0.03	28

Note: Three measurements made for each sample.

The process employed for shredding rubber tires often dictates the particle shape and particle size distribution [31]. Mechanically-ground tire rubber was used in this investigation. The dimensions of rubber particles were determined using an optical microscope. The fibrous rubber was received in bulk and separated into two size fractions by sieving using standard sieves (ASTM E11) [32]. Rubber fibers that passed through the 4.75 mm sieve (#6) and were retained by the 2.36 mm sieve (#8) were designated as FR 4.75. The size of fibrous rubber was approximately 10.8 mm long and approximately 1.8 mm in diameter. This rudimentary method of separation was deemed adequate for the study. Figure 1 shows the FR 4.75 rubber particle used for the study.

DEGRADATION OF RUBBER FIBERS. Degradation experiments were conducted to simulate the aggressive environment surrounding rubber fibers in rubberized concrete by exposing rubber fibers to various chemicals with pHs between 10 and 13. The mass of FR 4.75 was determined prior to exposure to various chemical solutions. FR 4.75 rubber fiber was immersed in a sodium hydroxide (NaOH) solution of pH 10, $Ca(OH)_2$ solution of pH 12.5 or 12.6, and cement suspension of pH ≅13 at room temperature 23 ± 2°C for 3, 7, 14, 21, and 28 days and for 4 months. Cement suspension of pH ~13 was prepared according to Abdel-Azim's method [33] by mixing 206 g of type I portland cement and 100 ml of distilled water. At the end of treatment period, the pH of each solution was measured, and the solution was discarded. The treated fibers were retrieved and equilibrated with water. The process was repeated to recover

TABLE 2. pH of NaOH solution without rubber

Time (days)	pH
0	9.94 ± 0.00
1	7.82 ± 0.06
7	7.44 ± 0.18
14	7.18 ± 0.33
21	6.67 ± 0.26
28	6.56 ± 0.06

Note: Two measurements made for each solution.

alkaline-free rubber samples. The fibrous rubber was air dried to a constant weight. The reported mass results are averages of triplicate tests. The dried rubber fibers were saved for swelling measurement, strength determination, and microstructure analysis.

Test Method

SWELLING MEASUREMENT. Fibers of similar length and diameter were selected and their dimensions were recorded. The fibers were immersed in toluene, and at periodic time intervals, the fibers were removed and allowed to dry. The fiber dimensions were recorded. Active swelling time (which is the time that the rubber is immersed in toluene beyond which no changes in length of fiber were noticed) was determined for untreated rubber fibers. The treated fibers [fibers exposed to cement suspension, NaOH, or $Ca(OH)_2$] were immersed in toluene to record the active swelling time in toluene and the change in length.

STRENGTH DETERMINATION. Tensile tests were performed on all fibers, both untreated and exposed to different chemicals. At least 10 fibers were selected from each batch [as-received, exposed for 4 months in NaOH, 4 months in $Ca(OH)_2$, and 4 months in cement suspension] and tested. Care was taken to choose long fibers of uniform diameter. The fiber diameter was measured using a Digimatic low pressure calibre. The ends of the fiber were attached to mounting tabs. The tabs were clamped to the tensile grips so that the tested fiber is aligned perpendicular to the direction of grip. The test was performed on an Instron 5500 R (Model 1122; Canton, MA) machine with a rate of grip separation of 7 mm/min. Maximum stress and percent strain at peak of fibers, both untreated and exposed to chemicals, were recorded.

MICROSTRUCTURAL ANALYSIS. The surface characteristics of untreated and treated fibers were examined using Cambridge 360 scanning electron microscope (SEM; England) equipped with energy dispersive X-ray capability. The rubber fibers were mounted on aluminum stubs (2.5 cm in diameter) using tungsten/carbon paste and dried at 298°K. To avoid accumulation of electrical charge on the rubber surface, the specimens were coated with a thin layer of carbon.

Results and Discussion

Weight Loss Analysis and pH Determination

Table 1 summarizes the pH change of solution when rubber fibers are placed in alkaline medium for differ-

TABLE 3. Weight measurements of rubber fibers aged in different chemicals at room temperature

Chemicals	Initial Weight (g)	Final Weight (g)	Percent Weight Change	Soaking Duration (days)
Water (pH = 7.00)	10.04 ± 0.03	10.04 ± 0.03	0.00	1
	10.25 ± 0.17	10.25 ± 0.16	0.00	3
	10.09 ± 0.06	10.09 ± 0.06	0.00	7
	9.90 ± 0.09	9.87 ± 0.07	−0.30	14
	9.04 ± 0.46	9.05 ± 0.46	0.11	21
	9.81 ± 0.08	9.81 ± 0.09	0.00	28
NaOH (pH = 9.94)	9.31 ± 0.11	9.29 ± 0.12	−0.21	1
	9.64 ± 0.15	9.64 ± 0.13	0.00	3
	9.19 ± 0.04	9.17 ± 0.08	−0.22	7
	9.72 ± 0.03	9.70 ± 0.03	−0.21	14
	9.79 ± 0.09	9.75 ± 0.10	−0.41	21
	9.78 ± 0.02	9.74 ± 0.00	−0.51	28
	9.29 ± 0.05	8.91 ± 0.05	−4.09	120
$Ca(OH)_2$ (pH = 13.09)	9.31 ± 0.07	9.31 ± 0.07	0.00	1
	9.12 ± 0.14	9.14 ± 0.17	0.22	3
	9.28 ± 0.05	9.29 ± 0.06	0.11	7
	9.28 ± 0.06	9.28 ± 0.06	0.00	14
	9.61 ± 0.33	9.57 ± 0.35	−0.42	21
	9.56 ± 0.21	9.67 ± 0.21	1.15	28
	9.63 ± 0.03	8.72 ± 0.03	−9.45	120
Cement solution (pH = 13.64)	9.22 ± 0.12	8.96 ± 0.13	−2.82	28
	9.29 ± 0.09	8.42 ± 0.07	−9.36	120

Note: Three measurements made for each sample.

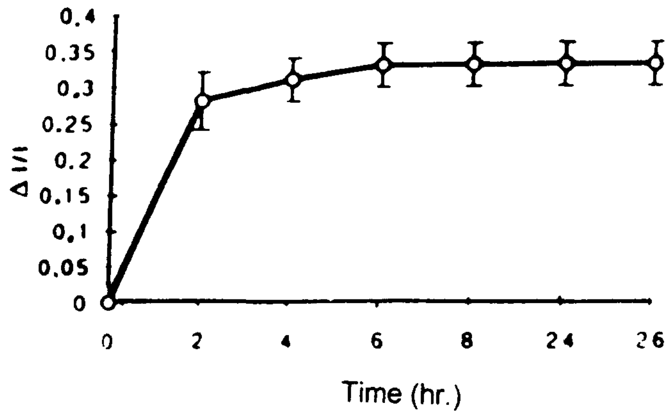

FIGURE 2. Percent change in length of rubber fiber to duration of rubber fiber swelling in toluene.

ent lengths of time. Rubber fibers immersed in distilled water served as the control (Table 2). The control experiment showed only a minor pH change over a 28-day period. Nelsen et al. [4] also found that leaching of rubber tires produced trace amount of metals in water and no major change in the pH of the solution. Of the three alkaline solutions [NaOH, $Ca(OH)_2$, cement suspension] studied, the pH of NaOH solution with rubber dropped considerably and its pH became neutral after 28 days. Similarly, the pH of NaOH solution without rubber (Table 1) also dropped, suggesting that the NaOH may have reacted with carbon dioxide in the water and atmosphere to lower the pH of the solution.

Table 3 summarizes the results of mass loss analysis of rubber fibers when the fibers were placed in various chemical solutions for a predetermined time period at room temperature. As expected, the control test (rubber fiber in distilled water) showed no significant mass loss from the fibers. Initially only a marginal mass change was noticed for rubber immersed in the NaOH and $Ca(OH)_2$ solutions. This might be explained by the absorption of chemicals by carbon black present in the rubber. However, with time, the mass change was increased for rubber in cement suspension and $Ca(OH)_2$ solution than in NaOH solution. Mass loss and pH change suggest that the rubber fibers may undergo small changes in highly alkaline medium. To determine the changes in microstructural properties and macroproperties of rubber, the swelling and tensile strengths of rubber were measured.

Swelling Measurement

To quantify the extent of degradation of rubber fibers, swelling experiments in toluene were conducted. Figure 2 shows a plot of $\Delta l/l$ and the duration of immersion of rubber fiber in toluene. The active swelling time was found to be close to 6 hours. Table 4 shows the swelling data versus time for averages of 7 to 10 rubber fibers. Presented in the table are the results of rubber fibers exposed to water, NaOH, and $Ca(OH)_2$ medium for 1, 3, 7, 21, and 28 days and 4 months. To determine whether there were significant differences in the swelling data due to the type of alkaline medium, a t-test was used; it predicts the statistical difference between fibers exposed to alkaline medium for various lengths of time and fibers not exposed to chemicals. Confidence levels below 95% were considered not statistically significant. The reported confidence level for the data of all the fibers is approximately 50%, except for 120 day fibers in NaOH and cement suspension. The reported data are averages of triplicate samples. Thus, it can be inferred that the samples, when immersed in alkaline media, undergo little change.

Strength Determination

Figure 3 shows the ultimate strength and ultimate strain of untreated and treated rubber fibers. Tensile strength of fibers have been known to vary within a batch. The strength of the fiber is governed by the number and size of the flaws in the specimen. Therefore, a minimum of ten fibers were tested and reliable strength and strain data were judged to have been obtained. The rubber fibers retained their strength even after prolonged exposure to highly alkaline medium. The rubber fibers did not undergo degradation, sug-

TABLE 4. Swelling measurements of fibers immersed in different chemicals

Type of Rubber Fibers Exposed to Chemical Solution	Time (days)	Change in Length (mm)	Confidence Intervals*
Water	0	7.0 ± 0.9	
	1	7.3 ± 1.0	<50%
	3	7.1 ± 0.7	>99%
	7	7.8 ± 0.7	>80%
	21	8.0 ± 0.5	<50%
	28	7.1 ± 1.1	<50%
NaOH	1	7.3 ± 1.1	<50%
	3	6.6 ± 0.9	>50%
	7	7.1 ± 0.7	<50%
	21	6.7 ± 0.6	>50%
	28	6.8 ± 0.4	>50%
	120	6.3 ± 0.6	<95%
$Ca(OH)_2$	1	7.7 ± 1.0	>80%
	3	7.7 ± 1.0	<50%
	7	7.3 ± 0.7	>50%
	21	7.1 ± 0.7	<50%
	28	7.1 ± 0.9	<50%
	120	6.8 ± 0.9	<50%
Cement solution	28	7.1 ± 1.1	<50%
	120	6.2 ± 0.9	<95%

*Statistically significant difference between samples exposed to alkaline medium and samples exposed to chemical medium.

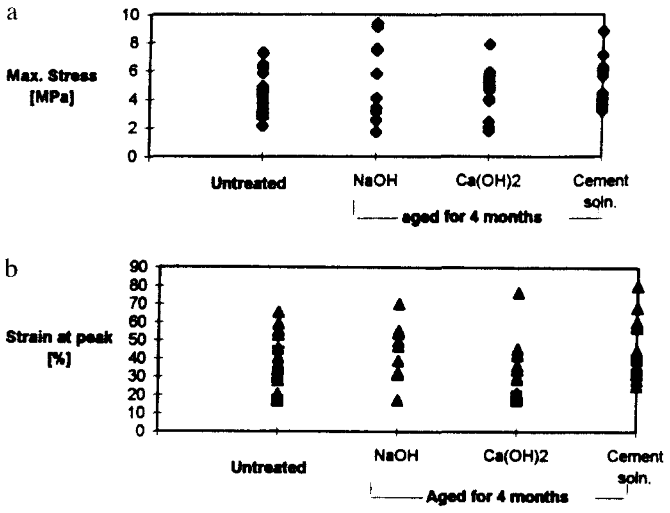

FIGURE 3. Tensile strength of chemically aged and untreated fibrous rubber for (a) maximum stress and (b) strain at peak.

gesting that fibers placed in mortar will not lose their strength over 4 months.

Microstructural Analysis

SEM was used to study the microstructural features of rubber before and after exposure to cement suspension for 4 months. Figures 4a and 4b are SEM observations of the shredded untreated and treated fibrous rubbers at 50×. The micrographs of both types of rubber fibers had similar morphological features. A buildup of $Ca(OH)_2$ was noticed on the surface of treated rubber fiber. However, the gross texture of the treated fiber remained intact. The observations are in agreement with the small reduction in mass of rubber fibers, small comparative pH change of the test solution, and retention of strength of the fiber upon exposure to various chemicals for 4 months. However, since the study was limited to 4 months of alkaline exposure, the observations should be viewed with caution.

Conclusions

We investigated the stability of rubber fibers incorporated in concrete. Tests were done with fibers in alkaline solutions of pH 10 or 12 for predetermined time intervals. The following conclusions can be drawn from this study:

1. Rubber fibers undergo small changes under highly alkaline medium. The small reduction in mass of rubber fibers was in agreement with the small pH change of test solution.
2. The tensile strength data indicate the retention of strength by the fibers after immersing in chemical solution for 4 months.
3. The micrographs of as-received and aged fibers suggest that the texture of the fiber was not changed due to exposure to cement suspension for 4 months.

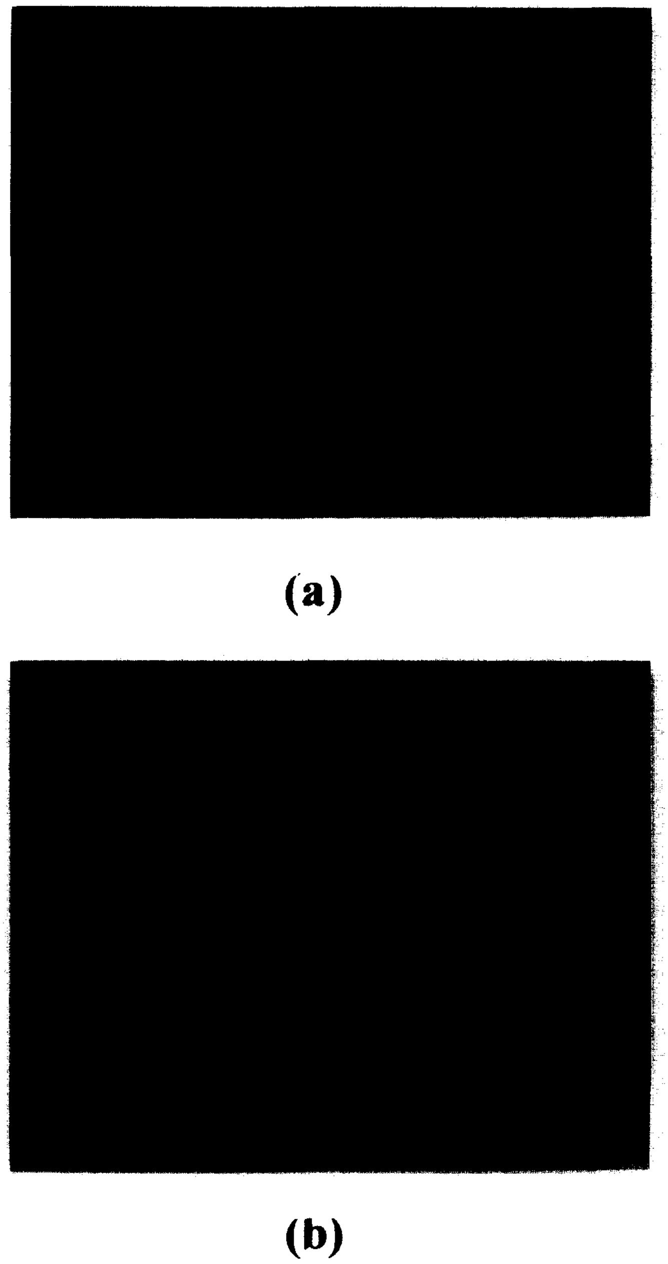

FIGURE 4. SEM of (a) as-received rubber fiber and (b) rubber fiber exposed to cement suspension for 4 months (50×).

If rubber filled concrete can be used for an application, a number of tests to study the durability should be conducted. Depending on the application, some of the tests that can be performed are resistance to sulfate attack and freeze-thaw effect. The findings are preliminary but they do provide a benchmark for long term chemical stability study.

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