

Rubber Tire Particles in Cement Paste^{*}

CHOU L H¹, LEE M T², HUANG C C³, CHENG J D⁴, LU Y C²

(1. Department of Civil and Water Resource Engineering, National Chiayi University;

2. Department of Applied Chemistry, National Chiayi University;

3. Environmental Protection Bureau of Chiayi County;

4. Department of Soil and Water Conservation, National Chung Hsing University)

Abstract: The surface of powdered tire rubber was modified to enhance its adhesion to cement paste in this study. Sodium hydroxide solution, waste lubrication oil, and toluene etc. were used as adsorbed agents to modify the surface of the powder. Rubber particles were divided into three groups according to their particle sizes. Specimens with various amounts of rubber and different particle sizes were prepared to evaluate their physical properties. Microscopy was used to observe the structure of the specimens. Flexural, compressive and tensile strengths of the specimens were also measured in the experiments. Experimental results show that the saturated solution of sodium hydroxide is the most efficient agent among the three modification agents in enhancing the adhesion of rubber particle to cement paste. It is suggested that the adsorption of sodium hydroxide on the rubber surface will enhance the hydrophilic characteristics of surface. Lubrication oils with sulfur compounds, which carry free electron pairs, are expected to be useful in modifying the rubber surface to increase the interaction force between rubbers and cements. However, compositions and amounts of sulfur compounds within the lubrication oils were out of control in our experiments therefore no consistent results were gotten. As a surface modification agent in our experiments, toluene was less useful. The adsorption of toluene on the rubber surface will enhance its hydrophobic characteristics and will reduce the interaction force between rubbers and cements. It is believed that the interaction force between rubbers and cements dominates the mechanical properties of these specimens and the modification of rubber surface should be a main topic to be studied.

Key words: surface modification; waste management; cement paste; disjoining pressure

CLC number: TQ336.1 **Document code:** A **Article ID:** 0529-6579(2003)S1-0099-05

1 Introduction

The use of concrete has increased considerably recently. This inevitably led to quarrying of the preservation of natural resources. Consequently, there is a growing concern for environmental protection and a need to preserve natural resource by using recycled or waste materials.

The growing amount of waste rubber tires has resulted in an environmental problem. A large number of waste tires are discarded all over the world every year, and only a small proportion is either retreated or burned for energy recovery. Most of the waste rubbers are land filled or stockpiled. Since the waste rubber is not easily biodegradable even after a long period of land-fill, this is not only an environmental problem but also a waste of natural resources.

The use of granular rubber as an aggregate or additive to concrete has been studied for a long time^[1,3-6,8,10,13-21]. Previous research results showed the aggregating rubber could increase concrete's

flexibility, elasticity, and capacity to absorb energy. It is suggested that the rubberized concrete can be used, for example, in highway constructions as a shock absorber, or in sound barrier as sound absorber, or in building as earthquake shock-wave absorber, or in impact prevention structure such as Jersey barriers. It is believed that such concrete can also be used in the soil and water conservation construction materials.

Even amount of studies have been conducted, there are many inconsistent results which should be studied, for example, the influence rubber granules' size on the compressive strength of the concrete. Topcu^[18], Eldin and Senouci^[5] showed that the coarse grading of rubber granules lowered the compressive strength more than that of the finer grading. However, Alie et al^[1] indicated the opposite. To know the inconsistent results, some authors tried to modify the surface properties of the rubber particle to increase its adhesion to cement paste. The modified agents used in literature were sodium hydroxide solution^[17], water, carbon tetrachloride, and latex admixture^[6] etc.

* Received 10 December 2002; Accepted 18 April 2003

Corresponding author: mtlee@mail.ncyu.edu.tw (LEE M T)

In this study rubber surface modification with saturated sodium hydroxide, toluene and lubrication oil was conducted. The contact angles between the surface of modified rubbers and water were measured. Both advancing and receding contact angles were gotten. The influences of contact angles and hydrophilicity of the rubber on the rubberized concrete performance were discussed. A water film flux model is proposed to explain the influence of the properties of rubber on the hydration of cement.

2 Experiments

The first type of Portland cement was used. Rubber tires were mechanically ground to become small grains and used as an additive. Test specimens were prepared with water/cement equaling 0.5. The contact angle between rubber and water was measured to know the wettability of water on various rubber surfaces. CRUSS k121 was used in measuring contact angle. The surface of rubberized paste was observed with microscopy and recorded every 5 minutes. Experimental specimens were prepared with cubic molders. The compressive, flexural, and tensile strengths of the specimens were conducted followed ASTM standards (C109, C190, C348).

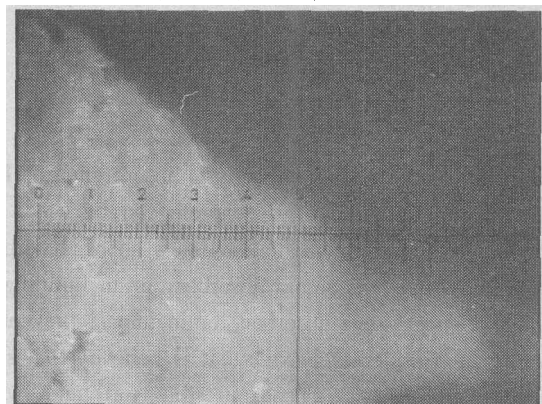


Fig.1 Rubber + cement (85 min)

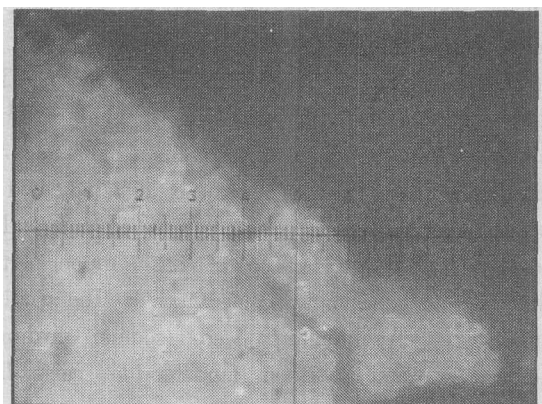


Fig.2 Rubber + cement (90 min)

3 Results and Discussions

The advancing contact angle of as-received rubber in water was 120 degrees and receding contact angle was 45 degrees. Rubber treated sodium hydroxide gives the advancing and receding contact angles 44 and 42 degrees individually. While rubber treated with lubrication oil has the advancing and receding contact angle angles to be 92 and 62 degrees individually. It is clear that sodium hydroxide reduces contact angles more significantly than that of lubrication oil. Toluene is less efficient in reducing contact angle than lubrication oil.

Fig.1 and Fig.2 show the surface structure of the cement paste at time 85 and 90 minutes.

Rubber particles used in this specimen were as received without any surface modification treatment. The pictures give the evidence that the paste cracks at the time about 85 ~ 90 minutes. However, the cracking is not in the interface of cement and rubber. The result is interesting and is worthwhile further study. It is believed that the cracking of the paste will affect the mechanical properties seriously. Fig.3 and Fig.4 depict the surface of rubberized cement paste with sodium hydroxide modified rubbers.

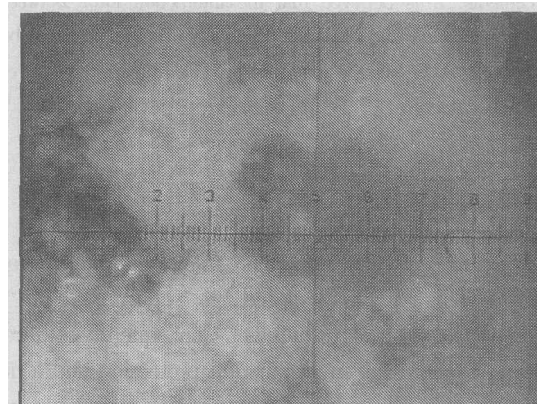


Fig.3 NaOH modified rubber + cement (5 min)

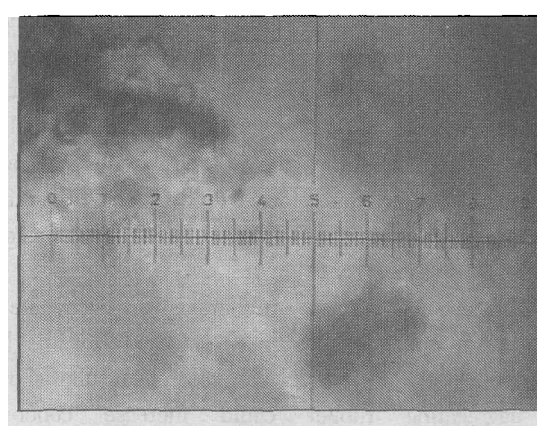
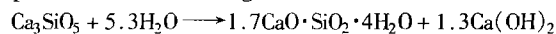


Fig.4 NaOH modified rubber + cement (90 min)

Fig.3 was the picture recorded at 5 minutes and Fig.4 was at 90 minutes. In Fig. 3 it was clear that some crystals produced. The crystals and some amorphous materials surround rubber particles. Huynh and Raghavan^[10] showed that the hydration of Portland cement occurred within a few minutes and the reactions can be simplified as the following:



Water diffuses into the inner of the cement particle through these crystals and amorphous materials and hydrating continuously. The diffusion rate affects the rate of the hydration reaction and eventually the physical and mechanical properties of the concrete. Initially, abundant water makes the hydration reaction occur quickly. However with the crystals surrounding outside the cement particle, the rate of diffusion of water is limited. The rate of hydration reaction changes from the reaction control to diffusion control. It is believed that continuous and quick supply of water into the cement particles is the most important point to be considered. Fig.4 shows no cracking occurs. The hydration products of cement adhere to rubber particles tightly. It is expected that concrete made of this type of rubber particles will have better mechanical performance than that of the as-received rubber particles.

Fig.5 shows the 28 days compressive strengths of four kinds of concrete with different surface-modified rubber particles. The compressive strength reduces about 25% for NaOH modified rubber in comparison with that of antithesis's results. As expected, specimen with sodium hydroxide modified rubber particles shows the best performance among the rubberized specimens. Fig.6 and Fig.7 give the flexural strength and the tensile strength in our experiments. They are similar to the results of the compressive strength. The flexural strength decreases about 22% and tensile strength decreases about 16% in comparison with that of antithesis's results.

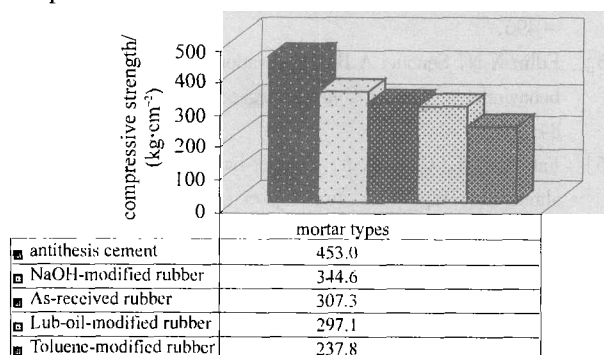


Fig.5 Compressive strength of experimental specimens

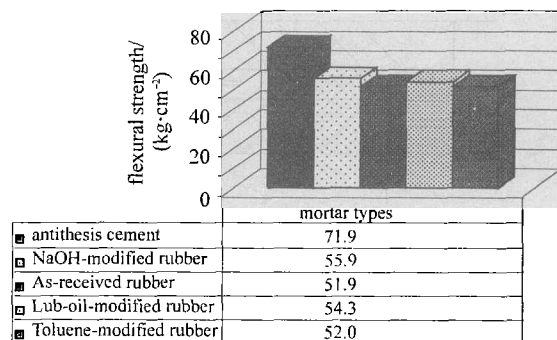


Fig.6 Flexural strength of experimental specimens

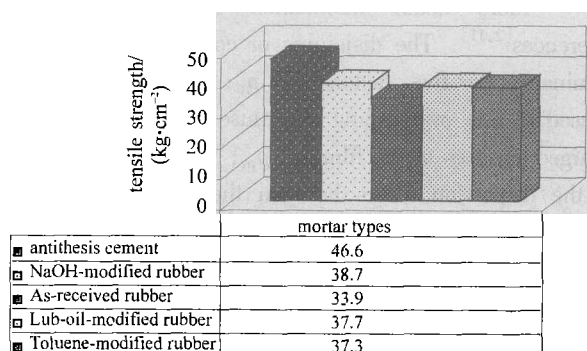


Fig.7 Tensile strength of experimental specimens

A water film fluid flow model (Fig.8) is proposed to explain the experimental results depicted above. It is supposed that there is a water film between the cement particle and the rubber surface. Small contact angle makes water wet the rubber surface easily. Water flows within the water film. Water diffuses into the cement particle through the porous amorphous medium. The direction of water flow depends on the pressure gradient within the water film. For a water film with a thickness less than 100 nm, the disjoining or conjoining pressure dominates it. The disjoining or the conjoining pressure is produced due to the overlapping of interfacial regions (as shown in Fig.9).

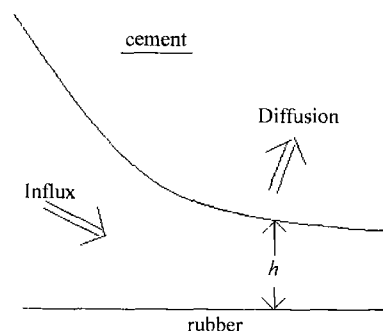


Fig.8 Water film flux model

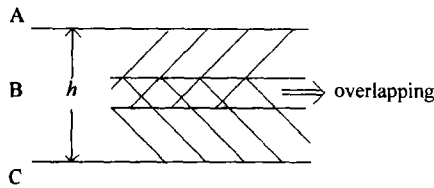


Fig.9 Illustration of disjoining pressure

$$P(h) = p_l - p_0$$

$p(h)$: pressure in thin liquid film

p_0 : pressure in bulk liquid

p_l : disjoining pressure

More detail information can be found in references^[2,11]. The disjoining or conjoining pressure is dominated by five factors: ① p_e : electrostatic effect caused by the overlapping of diffuse ionic layers at the charged surfaces of the film. ② p_m : molecular effect due to the dispersion forces between the substrate and the liquid film. ③ p_s : structural component due to the overlapping of the interfacial layers of the liquid with a structure modified in comparison with the bulk phase. ④ p_a : adsorption effect due to the overlapping of diffuse adsorption layers of neutral solute molecules. ⑤ p_c : steric effect due to a steric interaction between adsorption layers of surfactants or polymers. All the components of disjoining or conjoining pressure are function of film thickness. That says

$$p(h) = p_e(h) + p_m(h) + p_s(h) + p_a(h) + p_c(h) \quad (1)$$

p_e and p_m constitute the famous DLVO theory. Yang et al^[23] even discussed the interaction between cement particle with DLVO theory. p_c was experimentally proved to be important for concrete with chemical admixtures by Uchikawa et al^[22] and Neubauer et al^[15]. Derjaguin et al^[2] showed that the condition of stability of wetting films is

$$\frac{dp}{dh} < 0 \quad (2)$$

Where h is film thickness. Gauglitz and Radke^[8] showed the volumetric flow as a function of the total pressure driving force was:

$$\frac{Q\mu}{R\sigma} = \lambda \left(-\frac{dp(h)}{dh} \right) \quad (3)$$

Where Q : volumetric flow rate, μ : viscosity, σ : surface tension, λ : pore shape function, R : radius of pore. In equation (3), the liquid pressure is neglected in comparison with the disjoining or conjoining pressure.

The modification of rubber surface will change the surface charge and therefore electrostatic component of disjoining will change. Another components of the disjoining or conjoining pressure will also change with the adsorption of surfactants or neutral materials.

The change of the disjoining or conjoining pressure may induce the instability of the liquid and reduce water diffusion into the cement particles. Hydration reaction of cement may be inhibited in such condition and the performance of the concrete will decrease.

4 Conclusions

Surface modification of rubber particles is important to improve the physical and mechanical performance for rubberized concrete. Sodium hydroxide reduces the contact angle between rubber and water and enhances the electrostatic component of disjoining thus induces the film flow into the water film to supply the water needed for hydration reaction. Lubrication oil modified rubber will reduce the electrostatic component and may cause the disjoining pressure to change to the conjoining pressure. The conjoining pressure will change the wettability of water on the rubber surface thus makes the water film unstable. With the reduction the film flow rate, water diffusion into the cement particle will be inhibited. This makes the hydration reaction incomplete and reduces the performance of the concrete.

Acknowledges: Part of the financial support from Taiwan National Science Council with the project number NSC-91-2622-E-415-001-CC3 is acknowledged. Yuh-Tong Construction Corporation is also acknowledged for its financial support.

References:

- [1] Ali N A, Amos A D, Roberts M. Use of ground rubber tires in Portland Cement Concrete[J]. *Proc Int Conf Concrete*, 2000;379-390.
- [2] Derjaguin. *Surface Forces*[M]. New York: VCH Publisher's Inc, 1987.
- [3] Eldin N N, Senouci A B. Use of Scrap Tires in Road Construction[J]. *J Construction Engineering*, 1992, 118(3): 1217-1232.
- [4] Edlin N N, Senouci A B. Rubber-tire particles as concrete aggregate[J]. *J Material Civil Engineering*, 1993, 5(4): 478-496.
- [5] Edlin N N, Senouci A B. Observation on rubberized concrete behavior[J]. *Cement Concrete Aggregate*, 1993, 15(4): 74-84.
- [6] Fattuhi N I, Clark L A. Cement-based materials containing shredded scrap truck tire rubber [J]. *Construction and Building Materials*, 1996, 10(4): 229-236.
- [7] Gauglitz P A, Radke C J. The role of wettability in the breakup of liquid films inside constricted capillaries [J]. *AIChE Symposium*, 1986, 82(252): 50-63.
- [8] Hernandez-Olivares F, Barluenga G, Bollati M, et al. Static and dynamic behavior of recycled tire rubber-filled concrete [J]. *Cement and Concrete Research*, 2002, 32: 1587-1596.
- [9] Hunter R J. *Foundations of colloid science*[M]. New York: Oxford University Press, 1987: Vol. 1.

- [10] Huynh H, Raghavan D. Durability of simulated shredded rubber tire in highly alkaline environments[J]. *Advanced Cement Based Materials*, 1997, 6: 138 – 143.
- [11] Israelachvili J N. *Intermolecular and surfaces* [M]. London: Academic Press, 1985.
- [12] Kalachandra S, Shah D O. Interfacial properties of thin liquid films in relation to boundary and hydrodynamic lubrication in the eye[J]. *AIChE Symposium*, 1986, 82 (252): 64 – 71.
- [13] Lee B I, Burnett L, Miller T, et al. Tire rubber/cement matrix compositions[J]. *J Mater Science Letter*, 1993, 12 (13): 967 – 968.
- [14] Li Z, Li F, Li J S L. Properties of concrete incorporating rubber tire particles[J]. *Mag Concrete Research*, 1998, 50 (4): 297 – 304.
- [15] Neubauer C M, Yang M, Jennings H M. Inter-particle potential and sedimentation behavior of cement suspensions: effect of admixtures[J]. *Advanced Cement Based Materials*, 1998, 8: 17 – 27.
- [16] Raghavan D, Huynh H, Ferraris C F. Workability, mechanical properties and chemical stability of a recycled tire rubber-filled cementitious composite [J]. *J Mater Science*, 1998, 33: 1745 – 1752.
- [17] Segre N, Joekes I. Use of tire rubber particles as addition to cement paste[J]. *Cement and Concrete Research*, 2000, 30: 1421 – 1425.
- [18] Topcu L B. The properties of rubberized concrete [J]. *Cement Concrete Res*, 1995, 25(2): 304 – 310.
- [19] Topcu I B. Assessment of the brittleness index of rubberized concretes[J]. *Cement and Concrete Research*, 1997, 27(2): 177 – 183.
- [20] Topcu I B, Avcular N. Collision behaviors of rubberized concrete [J]. *Cement and Concrete Research*, 1997, 27 (12): 1893 – 1898.
- [21] Toutanji H A. The use of rubber tire particle in concrete to replace the mineral aggregates [J]. *Cement Concrete Composites*, 1996, 18: 135 – 139.
- [22] Uchikawa H, Hanehara S, Sawaki D. The role of steric repulsive force in the dispersion of cement particles in fresh paste prepared with organic admixture [J]. *Cement and Concrete Research*, 1997, 27(1): 37 – 50.
- [23] Yang M, Neubauer C M, Jennings H M. Inter-particle potential and sedimentation behavior of cement suspensions [J]. *Advanced Cement Based Materials*, 1997, 5: 1 – 7.

废轮胎橡胶粒在水泥浆体内之接口问题

周良勋¹, 李茂田², 黄朝琴³, 郑皆达⁴, 吕佑均²

(1. 台湾嘉义大学土木与水资源工程系;

2. 台湾嘉义大学应用化学系;

3. 嘉义县环境保护局;

4. 台湾中兴大学水土保持系)

摘 要: 探讨粉碎后之废轮胎橡胶颗粒表面改质方法, 以强化其与水泥浆间作用力的问题。使用之改质剂有氢氧化钠溶液、含硫量较高之润滑油与甲苯。粉碎之橡胶颗粒依其粒径大小分为三群。试体除做抗压、抗拉与抗剪等强度测试以了解物理及机械性质外, 并以金相显微镜实时观测水化过程中橡胶与水泥结合情况。实验结果发现, 以氢氧化钠处理过之橡胶颗粒与水泥泥之结合最好, 此乃因强化其表面亲水性, 有利于与水泥作用。反之以甲苯处理之橡胶结果最差, 因其表面之亲水性较小。以润滑油处理之橡胶所得试体之性质较不稳定, 此与含硫量与处理过程有关。文中并提出以显微镜做线上实时观测试体表面水化变化以做为试体制作改进之参考依据。此方法可降低试体制作之庞大人力与材料费用。

关键词: 表面改质; 废弃物处理; 水泥浆体; 离分压

中图分类号: TQ336.1 **文献标识码:** A