

SOLIDIFICATION/STABILIZATION OF PHENOLIC WASTE WITH CEMENTITIOUS AND POLYMERIC MATERIALS*

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Summary

Methods of handling organic wastes more safely and decreasing the degree of hazard of disposed organic wastes are becoming critical elements in any hazardous waste management planning. In this study the potential of a thermosetting polyester polymer to solidify/stabilize phenol, a primary constituent in many organic hazardous wastes and with a very low allowable level in drinking water, was investigated. The performance of rapid-setting high-strength polyester polymer in immobilizing 0.5 percent and 2 percent phenol has been studied in detail and compared to that of Type I portland cement. The effect of phenol concentrations on setting and microstructure of the polyester polymer and cement have been investigated. Phenol inhibits the setting of polyester polymer and cement and also produces large voids in the cement matrix. The phenol leachability and compressive and tensile properties were studied with curing time up to 30 days. Most of the polyester polymer solidified phenol specimens showed no measurable amount of phenol in the leachate after the extraction procedure test. The phenol recovery from cement matrix is very much dependent on curing time and initial phenol content. The compressive and tensile strengths of solidified waste reduces with increasing phenol content. The polyester polymer is very effective in rapidly solidifying/stabilizing phenol and the solidified waste has the potential to be used in construction applications.

Introduction

The production of millions of tons of hazardous wastes composed of organics in the form of sludges, slurries, and miscellaneous solids each year cannot be prevented, but must be controlled. In some cases, hazardous residues cannot be destroyed, reused, or converted to innocuous forms and, hence, require controlled storage or disposal. There is no universal waste treatment or immobilization process that will handle all variations of waste produced. However, a realistic goal is to minimize the risk related to management and ultimate disposal of hazardous wastes. The key preventative measures for minimizing the

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risk include waste control, reduction, reuse, stabilization, solidification, and encapsulation. In the U.S. solidification/stabilization (S/S) technology has been used at land disposal sites for attaining the no-free-liquid requirement of the Hazardous and Solid Waste Amendments of 1984 (in the Resource Conservation and Recovery Act, RCRA). Also, the National Oil and Hazardous Substances Contingency Plan (40 CFR 300) specifically includes waste stabilization as a method of remedying release of hazardous materials and controlling release of waste to the surface water. Notwithstanding some of its limitations, such as long curing time, relatively high porosity, and incompatibility with many organic wastes, portland cement is continuously being used as a primary ingredient in the solidification process. The primary concern of the current S/S technology, using cement and pozzolanic systems, is the interfering effects of organic contaminants which affect setting, chemical stability, and sometimes destroy the cement after setting. Due to the lack of understanding of treating organic wastes and anticipating problems from using the currently available treatment, regulators have used limitations on the amount of organics treatable with S/S technology, which range from 1 percent to 20 percent [1]. Hence the potential of modifying cement binders and other materials for solidification/stabilization of non-volatile organic hazardous wastes (liquids and semi-solids) must be investigated to meet the current demand in organic waste management. Polymers, which have been used successfully in nuclear waste disposal and in special industrial waste treatment, also have the potential for treating organic wastes. Polymers with their rapid-setting, high-strength, low permeability, and high corrosive resistance appear to have the potential for use with or without portland cement in hazardous waste management [1-6].

The two principal constituents of most commercial fixing agents are cementitious materials (portland cement, fly-ash, etc.) and sodium silicate. A limitation often cited is that the processes are incompatible with organics, but details of such incompatibility are generally not available [7]. A potential concern is that organics, even in small amounts, can alter the process sufficiently to substantially decrease the ability of fixing agents to immobilize the organics and heavy metals contaminated with organics. Indeed, it is well known that organics can alter the setting characteristics of portland cement. It is not clear whether, and at what concentrations, organic interfere with the relatively complex setting reactions resulting in a significantly altered cement matrix [1,7,8]. The question is of interest not just with respect to S/S technology, but also with regard to fundamental understanding of cementing reaction in the presence of organics. Polyhydroxy compounds are among the classes of organics which alter the setting characteristics of Type I portland cement. The effect of relatively small amounts (up to 0.5%) of triethanolamine (TEA) on the setting characteristics of portland cement has been studied mainly using differential thermal analysis, thermogravimetric analysis, and conduction calor-

imetry [8]. Between the amounts 0.17 to 0.5%, TEA greatly accelerates the initial set, but retards the final set and produces a weaker cement structure. The study suggests the possibility of a complex forming between the TEA and the hydrating components of portland cement. Sheffield et al. [9] have studied the effect of ethylene glycol, *p*-chlorophenol, and *p*-bromophenol on cement with a water/cement ratio of 0.4 and organic concentrations of 4, 10, and 20%. Of the three organics investigated, ethylene glycol not only had the most profound effect on setting and strength of cement but also was easily leachable from the cement matrix. Generally, all low-level inorganic waste materials can be solidified with cement and other pozzolanic (materials that set to solid mass when mixed with hydrated lime) systems and disposed of safely. Also air stripping can be used to remove over 90% of the volatile organics in the waste. But with high concentrations of non-volatile organics in the wastes, the potential of cement and other pozzolanic systems in S/S organic wastes is questionable. Organic sludges containing nitrocellulose could not be stabilized with cement [1], as are organic wastes containing hydroxyl or carboxylic acid functional groups, typical contaminants in biological wastes. Paint sludge, pesticides, and solvents are expected to delay or completely inhibit the reactions responsible for solidification of cement and other pozzolanic systems. Hence, it is appropriate to investigate the potential of other materials, especially polymer and polymer modified cement systems for S/S organic wastes.

Researchers at the Washington State University have successfully used polyester polymer in solidifying toxic chemical wastes, such as arsenic, cyanide, PCB, toxic metals, and pharmaceutical wastes [4-6]. If some of the inorganic constituents (NaCl, borate, sulfates, metallic hydrate) or the organic constituents (volatile compounds, insecticides, pesticides, and fungicides) in the waste are present in large amounts, the study shows that it may warrant either encapsulation or solidification and encapsulation. Lubowitz et al. [2,3] successfully used polybutadiene polymer binder for cementing the waste containing sodium metarsenate, and non-soluble arsenic trisulfide, and then encapsulated it by using 0.25-inch thick polyethylene jacket [3]. Cullinane and Jones [1] have clearly stated the need for fundamental research (mechanisms of immobilization and release of contaminants) to better understand the performance of organic polymers and other binders in the S/S of organic wastes.

The chemical reactivity of the waste generally controls the selection of the S/S options. Organic solvents, oils, grease, and other semi-solid and solid organics (at room temperature) are some of the potential wastes, and studies are needed to systematically evaluate and treat these wastes. Since the setting process of organic waste-binder matrix is time dependent and further complicated by the interfering effect of organics, setting and mechanical properties vary considerably over the first few days or months, depending on the binder system. Some organic wastes may require extensive pretreatment before they can be subjected to the S/S process. Many of the waste-binder compatibility

problems can be overcome by pretreatment steps to destroy or tie up some of the undesirable organic waste constituents. Also, pretreatment can reduce waste volume, improve processing techniques, and be more economical [10].

The results reported here are a part of a larger study to investigate alternative materials for S/S of hazardous wastes, such as organics and heavy metals, contaminated with organics prior to safe disposal or use in construction applications. Complete detoxification of organics and organic-metal wastes by chemical, biological, incineration, and other means are not always possible and hence it is appropriate to investigate alternative techniques, such as immobilization which dilute and/or isolate the hazardous waste. The study reported here is concerned with treating phenol and presents preliminary data on the setting, microstructure, leachability, and mechanical properties of polyester polymer with 0.5% and 2% phenol content. The performance of polyester polymer in S/S phenol was compared to that of cement with a water/cement ratio of 0.5.

Experimental program

Initially, the emphasis was on selecting a representative non-volatile organic pollutant and a rapid-setting polymer with good mechanical properties and corrosion resistance. The criteria used for selecting the nonvolatile organic pollutant for the preliminary study was its wide industrial use, toxicity, high boiling point, non-biodegradability, and the difficulty in solidifying with cement or other binding systems currently available. Phenol was one of the organics that clearly satisfied the waste selection criteria and is also listed as a EPA priority pollutant and a priority contaminant of petroleum products [11,12]. Phenolic compounds are widely used in many industries, including petroleum-refining, metal-making, fiberglass production, wood products, and synthetic-resin manufacture. McArdle et al. [12] have reported phenol concentrations between 3 to 17,000 $\mu\text{g}/\text{l}$ in the vicinity of some uncontrolled hazardous waste sites. Phenol and its derivatives are also used as inhibitors in polyamide and polyethylene polymers. Phenol has a melting point of 41°C , boiling point of 182°C , and a solubility of 9.3% in water at 25°C . Phenol is an extremely weak acid. The U.S. Public Health Service drinking-water standard limits phenol to 1 $\mu\text{g}/\text{l}$. Phenol is recognized as a general protoplasmic poison which is toxic in varying degrees to all living cells [13]. Although phenol is toxic, halogenated phenolic derivatives exhibit much higher toxicity and it is this subgroup which is extensively used as herbicides, fungicides, and preservative agents. Hence, treating phenolic wastes was considered a real challenge.

The selected polymer resin should be easily polymerized and cross linked near room temperature, solidify rapidly but in a controllable manner, and be highly corrosion resistant. Chemical attack studies at the University of Houston on cured polyester polymer have shown that gasoline, oil, and acetic acid

(all organic) had no measurable effect on the solidified polyester polymer. Also polyester polymer has been successfully used in nuclear waste disposal and in special industrial waste treatment [2–6]. Polyester polymer is extensively used in many other applications and there is a large data base on polyester polymer behavior available at the University of Houston [14] and hence polyester resin was selected. In the resin the unsaturated polyester (contains double bonded carbon atoms, $-C=C-$) was dissolved in styrene monomer. The resin had a viscosity between 4.0 and 5.0 Pa·s at room temperature and a specific gravity of 1.07.

Solidification/stabilization technology in the past has been developed primarily on a trial-and-error basis without firm scientific foundation. Hence in this study, every effort was made to overcome this shortcoming by monitoring the waste–binder system from the time of mixing to complete solidification. In order to achieve this goal, a systematic evaluation procedure was established and the test included: (a) continuous monitoring of reaction temperature for polyester polymer and setting time for cement; (b) EP (40 CFR Part 261, 1988) and TCLP¹ (40 CFR Part 260, 1988) leachate tests for solidified wastes at various curing times; (c) gas chromatography (GC) to quantify phenol leachate from EP and TCLP tests; (d) mechanical property (compression and tension) tests; and (e) morphological study using scanning electron microscope (SEM) to investigate the changes in the microstructure of the fixing agents due to the presence of phenol.

The performance of cement and polyester polymer in the presence of phenol was investigated by solidifying different percentages of pure phenol with the binders. Phenol concentrations of 0.5% and 2% were investigated in detail. Polyester polymer samples were formulated using 0.2 percent cobalt naphthanate as promotor and methyl ethyl ketone peroxide (MEKPO) as initiator. The initiator concentration was varied to obtain polyester polymer systems with varying solidifying times. A measured amount of phenol was directly added to the polymerizing polyester mix and cement paste with a 0.5 water/cement ratio. All the components were propositioned by weight to an accuracy of 0.001 grams. The phenol granules completely dissolved in the polyester resin. The change in temperature during the polymerization was continuously monitored using a J-type thermocouple connected to a recorder. The initial and final setting times for cement with and without phenol, were determined according to ASTM C191-74 using a Vicat needle. Cylindrical specimens were prepared in Teflon[®] molds for the leachate tests (EP) and mechanical property tests and were allowed to cure at room temperature. After removal from the molds cement samples were stored in air-tight bags in the humid room and polyester polymer specimens were cured at 60°C for 4 hours. Tests were done after curing times of 1, 3, 7, 14, and 28 days. The Structural Integrity portion

¹TCLP stands for Toxicity Characteristic Leaching Procedure.

of the EP test was performed on the polyester specimens because they were too strong to be broken into small particles for the TCLP test. In order to compare the results of EP test to TCLP test, studies were performed on cement with 2% phenol content. The leachate was analyzed for phenol using a GC (Perkin-Elmer Sigma 300 GC with Sigma 15 Data Station). Morphological studies were done on unextracted samples using a Scanning Electron Microscope (SEM). Mechanical tests were performed according to ASTM recommendations (ASTM C31, C39, C109, C496) and tests were done on a closed loop servohydraulic testing machine.

Test results and discussion

The effects of phenol concentrations on the setting, microstructure, degree of immobilization, and mechanical properties of polyester polymer and cement paste were investigated. If the solidified waste is to be used as a construction material its strength, toughness, and stress-strain relationships must be also better understood.

Setting time

An unsaturated polyester is formed by the reaction between polybasic acids (mix of saturated and unsaturated) and a polyhydric alcohol. This reaction also yields water. A typical structure of unsaturated linear polyester resin is formed by reacting ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$) with saturated dibasic suberic acid ($\text{HOOC}(\text{CH}_2)_6\text{COOH}$) and unsaturated fumaric acid ($\text{HOOCCH}=\text{CHCOOH}$). The unsaturated polyester resin used in this study was dissolved in styrene monomer. The chief factors in the extensive use of unsaturated polyester resins are: (a) ease of handling: polyesters in the uncured state are easily handled liquids and cure to solid material with no liquid or gases evolved; (b) rapid cure for a thermosetting resin; (c) ease of coloring: polyesters are light-colored liquids which can be readily pigmented to any desired color; and (d) good physical and mechanical properties with good corrosion resistance.

The polymerization of unsaturated polyester and styrene monomer is typically known as copolymerization since more than one type of monomer is involved in the polymerization process. The polymerization is initiated by the action of a free radical on the unsaturated portion of the polyester and styrene monomer. Free radicals can be formed by the decomposition of a relatively unstable compound called the initiator or catalyst. Methyl ethyl ketone peroxide (commonly used as initiator for room temperature cured systems) in the presence of a promotor (usually cobalt naphthanate) cleaves at the O-O bond to form a pair of free radicals that have unpaired electrons as shown in Fig. 1.

The newly formed free radical (R^\bullet) reacts with the monomer molecules and breaks the carbon double bond producing monomers with unpaired electrons

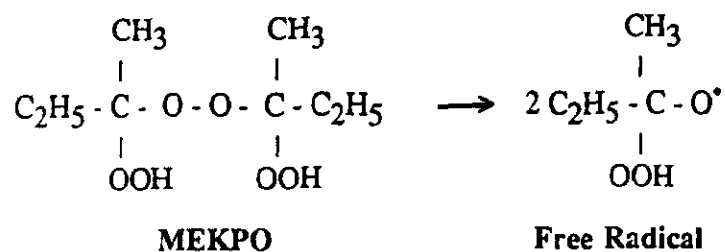


Fig. 1. Decomposition of methyl ethyl ketone peroxide (MEKPO).

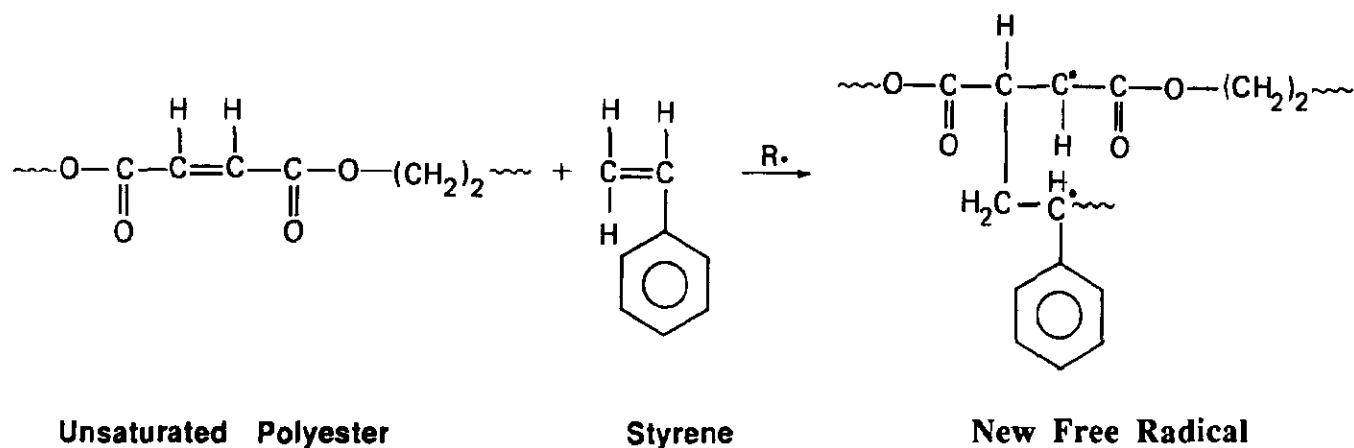


Fig. 2. Initiation of polymerization and monomer free radicals.

as shown in Fig. 2. The styrene monomer ($\text{CH}_2=\text{CHC}_6\text{H}_5$) is a polyfunctional compound and after reacting with the free radical it is capable of taking part in two separate addition reactions simultaneously to attach itself to the polyester chain to form a stable three dimensional network.

The new monomer free radicals seek out other monomer molecules and the sequence is repeated and results in a growing polymer network. As shown in Fig. 1 the rate of polymerization of polyester resin (represented by the time to peak exotherm) can be controlled by varying the concentration of the initiator. The polyester polymer solidifies almost immediately after the measured peak temperature. When the MEKPO concentration was changed from 0.3 to 2% for the polymerizing polyester-styrene copolymer, the time to peak exotherm reduced from 10 to 0.5 hours but the peak temperature increased from 23 to 170°C with a very sharp rise and fall.

With the addition of 0.5% phenol, more initiator is need for the polymerization to achieve the same time-to-peak exotherm as shown in Fig. 3. This observation is further reinforced with the 2% phenol system. This suggests that the effect of phenol should be first neutralized by the initiator before accelerating the polymerization process of the polyester-styrene system. Phenol inhibits the polymerization by directly reacting with the initiator free radical ($\text{R}\cdot$) and forming a non-radical compound (RH) by donating a hydrogen atom from the $-\text{OH}$ group and a phenoxy free radical ($\text{C}_6\text{H}_5\text{O}\cdot$). The phenoxy radicals can further react with any remaining polymer radicals and terminate the polymerization process [10]. For the leachability, morphology, and mechanical property study MEKPO concentrations of 1.8 and 10% were used to solidify

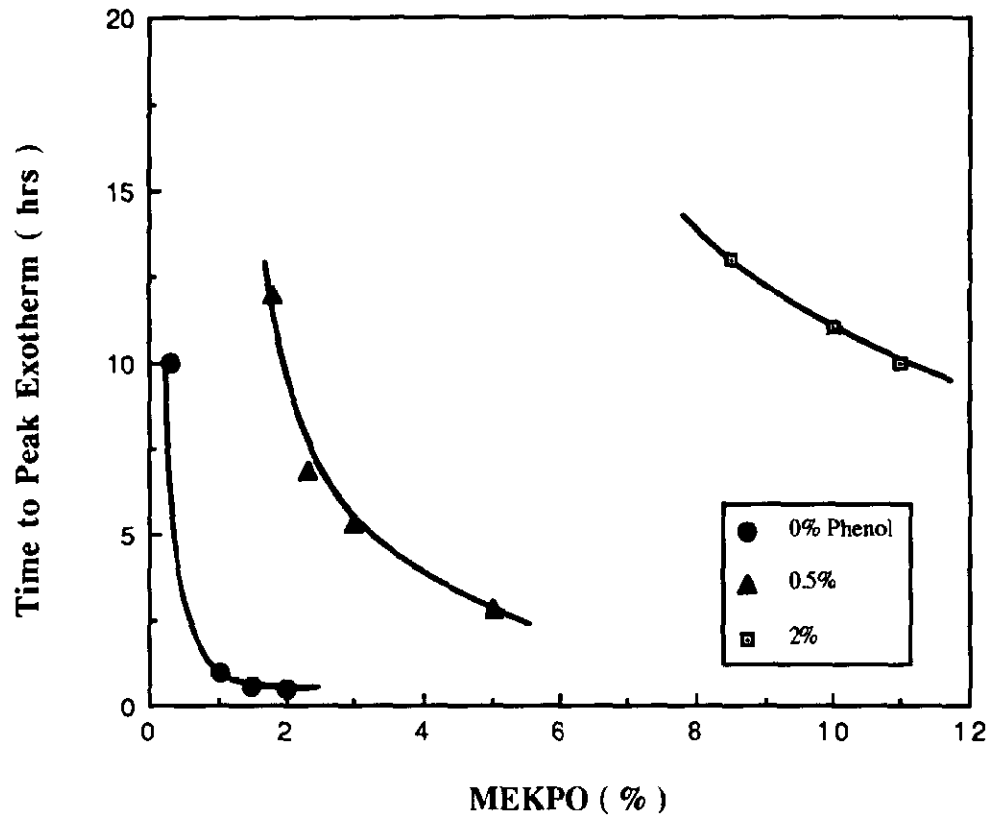


Fig. 3. Relationship between curing rate of polyester polymer and initiator concentration for various phenol concentrations.

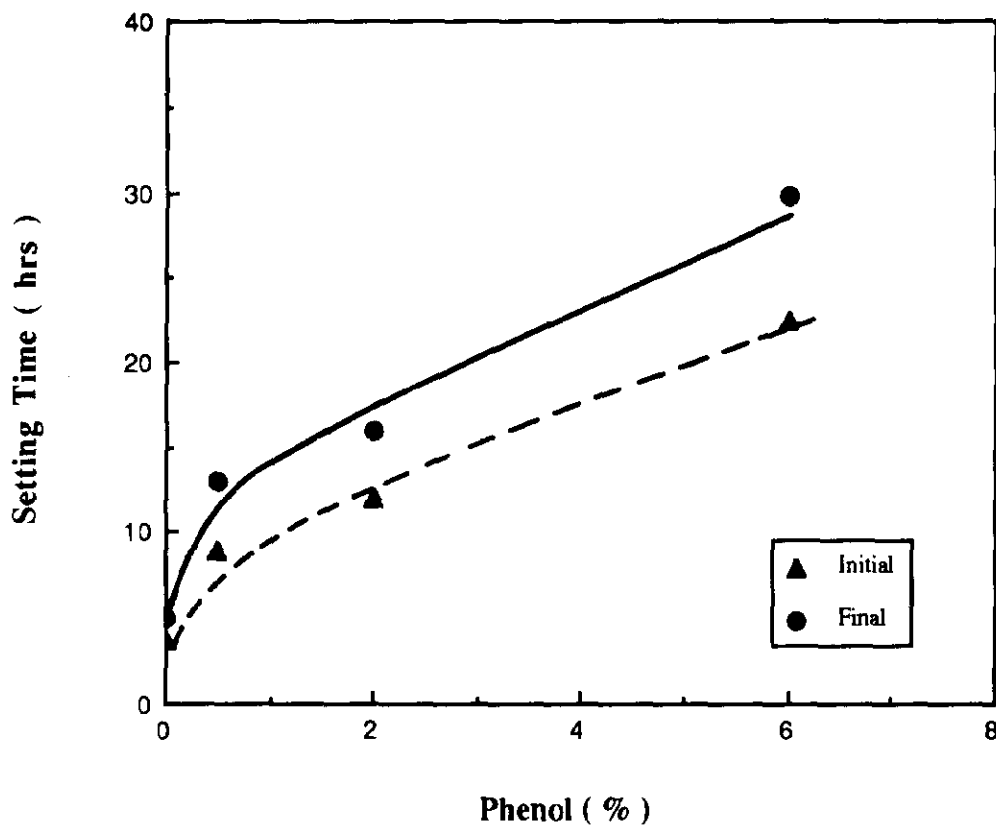


Fig. 4. Effect of phenol on the initial and final setting time of Type I Portland cement.

polyester polymer with 0.5 and 2% phenol. The control cement sample had an initial setting time of 3.8 hours and a final setting time of 5 hours. The change in setting time with phenol content is shown in Fig. 4. With the addition of 0.5 and 2% phenol, the initial setting times of cement were increased by 2.4 and 3.2 times, respectively. It took 4 hours more in each case for the final set, a 3.3

fold increase. It is of interest to note that Sheffield et al. have reported faster initial setting for cement with 4% *p*-chlorophenol and *p*-bromophenol with not too different final setting times [9].

Leachability

Figure 5 shows the EP results for the solidified phenol waste with the two binders under investigation. Polyester polymer with 0.5% phenol showed a

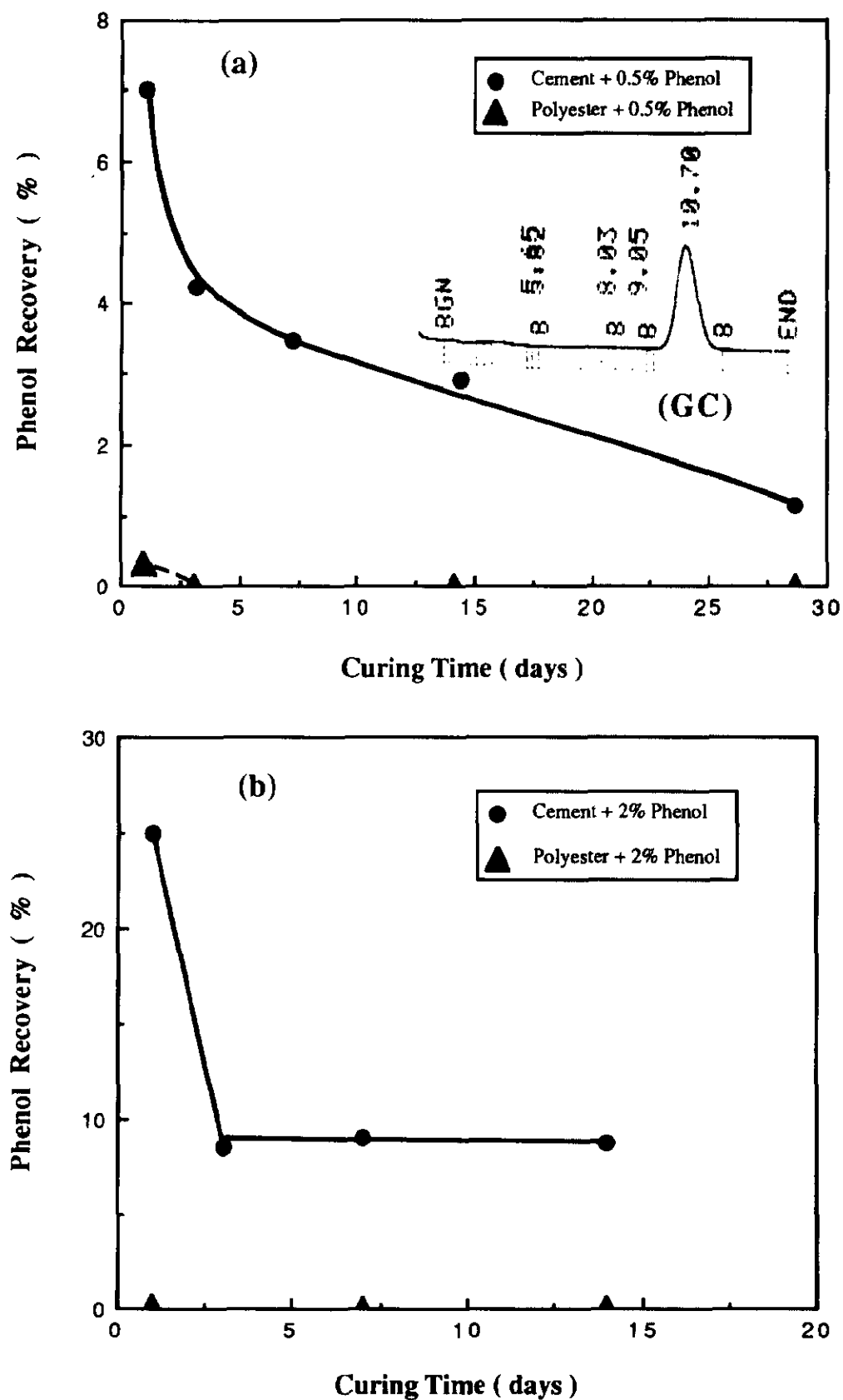


Fig. 5. Percent recovery of phenol from EP Test (Structural Integrity). (a) 0.5% Phenol and (b) 2% phenol.

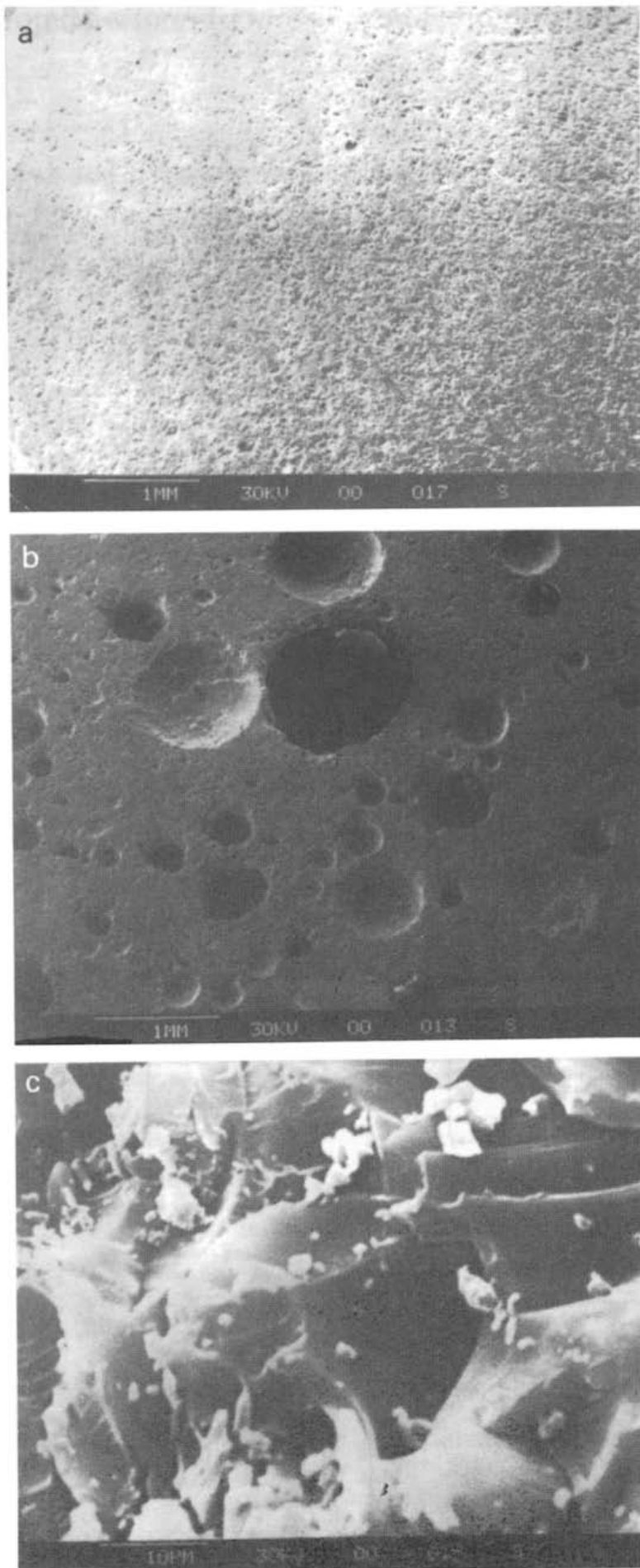


Fig. 6. SEM micrographs: (a) cement only, (b) cement with 2% phenol, and (c) polyester polymer with and without 2% phenol.

very small amount of phenol recovery on the third day but there was no measurable phenol in the leachate thereafter. Cement showed 7% recovery after 3 days and about 1% after 28 days of curing. Figure 5(b) shows the results for the 2% phenol systems where the phenol recovery is substantially increased for the cement and no measurable amount of phenol was recovered from the polymer systems. The phenol recovery from the cement solidified waste is very much dependent on curing time. From limited TCLP tests on 2% phenol-cement samples after 1, 3, 7, and 14 days of curing the phenol recovery was 57.1, 89.2, 100, and 100%, respectively. This may suggest that the phenol is *not* chemically bound to the cement.

Morphology

In Figs. 6(a) and 6(b) SEM micrographs of the cement matrix with and without phenol are compared. Morphological studies have shown that even low concentrations of phenol (0.5%) can cause a number of large pores in the cement matrix with blister-type appearance similar to that shown in Fig. 6(b) for cement with 2% phenol. The presence of large voids will substantially increase the porosity of cement and make it susceptible to increased leaching. No change in the morphology of the polyester polymer was observed, even at 2% phenol concentration (Fig. 6(c), same for polyester with and without phenol), which also supports the EP test results where no phenol was leached from the polyester polymer.

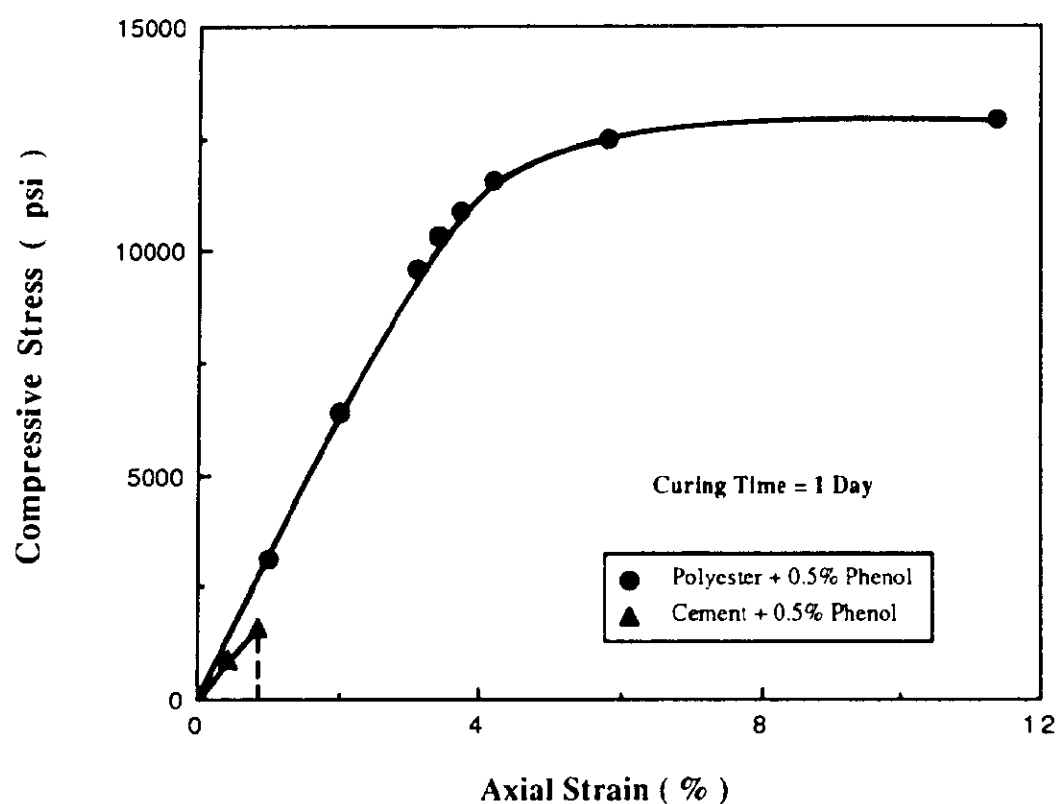


Fig. 7. Compressive stress-strain relationship for polyester polymer and cement with 0.5% phenol after a day of curing.

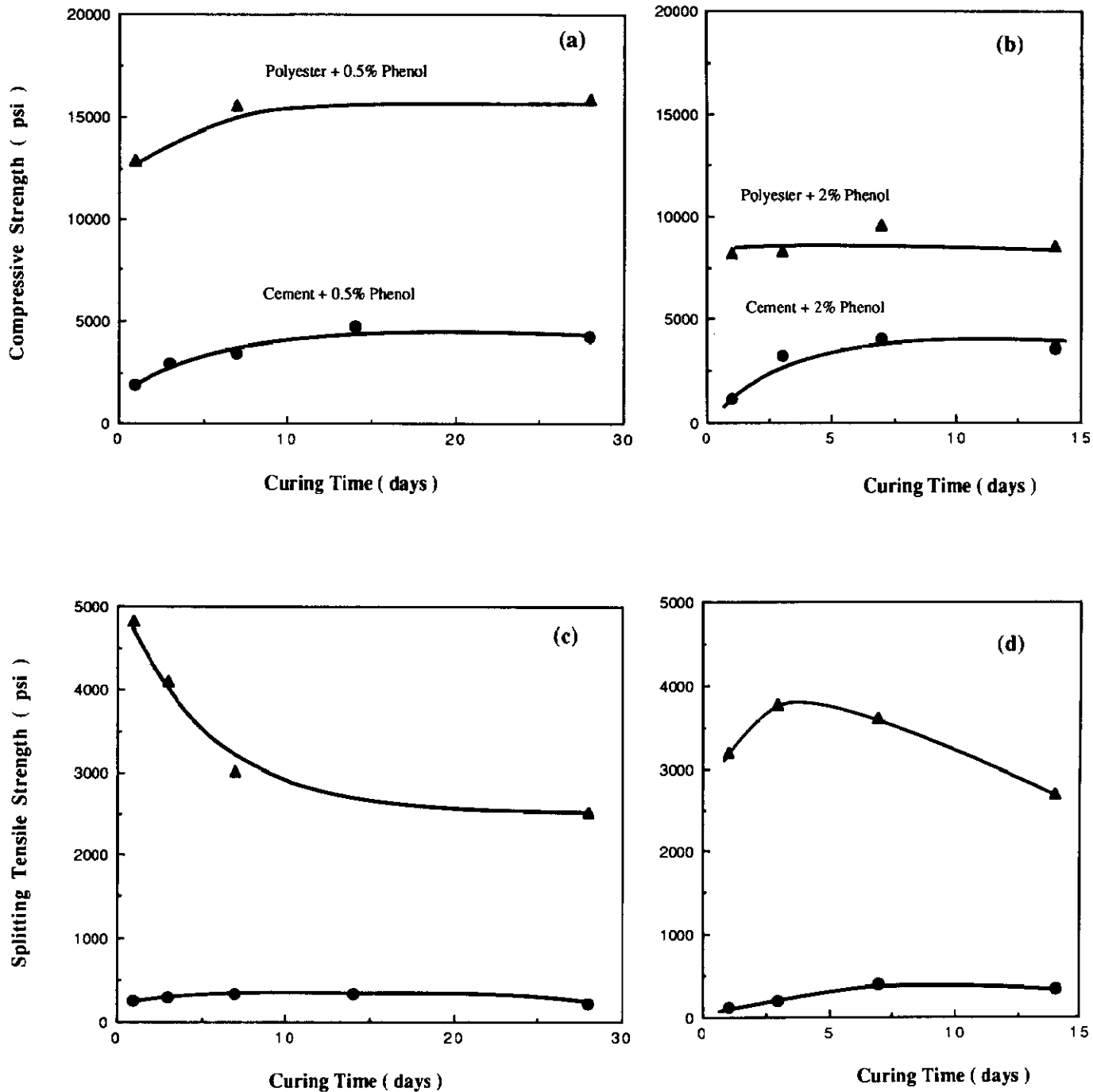


Fig. 8. Variation of compressive and splitting tensile strength of polyester polymer and cement solidified phenol waste with curing time.

Mechanical properties

The compressive stress–strain relationship for polyester polymer and cement with 0.5% phenol after a day of curing is shown in Fig. 7. Compared to the cement, polyester polymer specimens are stronger, tougher (area under the stress–strain curve), and also yield before failure, which are some of the desirable properties for a construction material. The variation of compressive strength and splitting tensile strength for polyester polymer and cement with 0.5 and 2% phenol is shown in Fig. 8. The compressive strength of polyester polymer either increases slightly or remain almost constant after 3 days of curing but decreases by about 30% with an increase in phenol content. The splitting tensile strength of polyester polymer shows a decreasing trend with curing time and higher phenol content. The compressive and tensile strength

of cement with phenol increases with curing but decreases with higher phenol content. On an average the polyester polymer had a 3 to 5 times higher compressive strength and a more than 8 times higher tensile strength than cement of the same phenol content.

Conclusions

In this study the potential of polyester polymer in stabilizing/solidifying phenol was investigated and the results are very encouraging. The performance of polyester polymer was compared to that of cement with a water/cement ratio of 0.5. Phenol inhibits the setting of cement and polyester polymer. In the case of polyester polymer, higher concentrations of initiator were used to neutralize the effect of phenol and to initiate the polymerization process. Under most testing conditions polyester polymer systems showed no measurable amount of phenol recovery. Phenol recovery from the cement was dependent upon the curing time and the initial phenol content. Limited TCLP tests show almost total phenol recovery from cement. Phenol also produces large voids in the cement microstructure. Increasing the phenol concentration from 0.5 to 2% reduces the compressive strength and splitting tensile strength of polyester polymer and cement. The polyester polymer solidified phenol waste has substantially higher compressive and tensile strength than cement solidified waste.

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