The Preservation of Çankiri Limestone in Sulfur Dioxide Atmosphere by *In Situ* Polymerization of Ethyl Methacrylate

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ABSTRACT: Stone is one of the most important structural and monumental materials. The main aim of preservation of stone objects is to prevent their deterioration caused by external conditions and to increase their general resistance to changing environmental conditions. Many substances in various forms are being used for the consolidation of stones. One method is impregnation of the stone with a low molecular-weight monomer which is then polymerized within the stone. In this study, ethyl methacrylate was polymerized within Çankiri limestone by a sulfur dioxide–*tert*-butyl hydroperoxide redox initiator pair having a low decomposition activation energy. Mechanical stability of the original and polymer-loaded stones was measured. As the amount of the polymer in the limestone was increased, compressive strength also increased. The polymer-containing limestone was more resistant to abrasion by water and to the effects of acid rain. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 1761–1764, 1998

Key words: preservation; *in situ* polymerization; ethyl methacrylate; sulfur dioxide

INTRODUCTION

Stone is one of the most important structural and monumental materials. Being exhibited mainly outdoors, it suffers severely from the degradative action of frost damage, weathering movement of soluble salts, and attack by acidic gases in the atmosphere. Attack by atmospheric pollutants is the main cause of deterioration.[1,2] The main aim of preservation of stone objects is to prevent their deterioration caused by external conditions such as air pollution, water, wind, frost, and high temperature differences, and to increase their resistance to changing environmental conditions. For consolidation and protection of damaged stones, there are several methods. One of the these methods is based on the impregnation of stone by a

solution of synthetic polymers. A second method used for that purpose is to impregnate the stone with low molecular-weight monomers which are then polymerized within the stone. The main advantages of this method is the ease of diffusion of small molecules into the stone.[3,4] In practice, application of this method is prevented by the difficulties in selecting a suitable initiation system. For the polymerization of the monomers in the porous material of stone, it is important to use an initiating system which permits polymerization to occur at a lower temperature. For this to be possible, the initiating system must have a lower activation energy for its decay.[5] Generally, thermal decomposition of organic initiators used in polymer synthesis requires rather high temperatures. Initiation of a radical polymerization can be performed at low temperatures (near room temperature) by the use of redox initiation pairs. There are a number of redox initiator pairs that can be used for this purpose. In this study, it was determined that one of the main air pollutants— sulfur dioxide (SO_2)—could be used as a redox

polymerization initiator, the reducing agent being *tert*-butyl hydroperoxide (TBHP).[6] For this purpose, SO_2 was used as an initiator for the polymerization of ethyl methacrylate (EMA) previously impregnated into stone samples. The SO_2 used in this study was rather pure; however, once the kinetics of polymerization are clearly understood, the conditions for polymerization under ambient SO_2 can be established. The kinetics of polymerization and analysis of conversion of methyl methacrylate (MMA) with the SO_2-TBHP redox initiator system have been carried out in detail in our laboratory.[7] Limestones obtained from the Çankiri region of Turkey were used in this study. These are the types of limestone used for monuments in the capital, Ankara, which suffers heavily from air pollution.

EXPERIMENTAL

Ethyl methacrylate supplied by Janssen Chimica Corp. was stabilized with 15 ppm hydroquinone methyl ether. Before being used, it was passed three times through a column filled with alumina to remove the polymerization inhibitor. The SO_2 was freshly generated as the product of reaction between $NaHSO_3$ and H_2SO_4, dried over P_2O_5, and stored in steel cylinders.[8] The TBHP was obtained from Fluka Chemie AG.

Çankiri limestone samples were cut in fixed dimensions of $5 \times 3 \times 2$ cm³ and dried in a furnace at 40°C until constant weight was reached. They were kept in monomer containing fixed amounts of TBHP, and the time necessary for minimum monomer absorption was determined. The time determined was 150 min, and the stone samples absorbed 1.4 g monomer per 55 g stone in this period of time. The stones impregnated with monomer were transferred into a gas chamber through which SO_2 gas flowed at a constant flow rate, and the conversion curves were obtained. The temperature of the system was kept constant during the process. The experiments were performed at room temperature on three samples for each data point on the graphs. As the TBHP concentration was kept constant at $0.025M$ and the SO_2 flow rate was increased, the polymer yield was also increased due to the increase in SO_2 dissolved in the monomer.

The mechanical tests were performed by measuring the compressive strength of the original and polymer-loaded stones with a 100-ton hydraulic press (SBL Model CT-250 A).
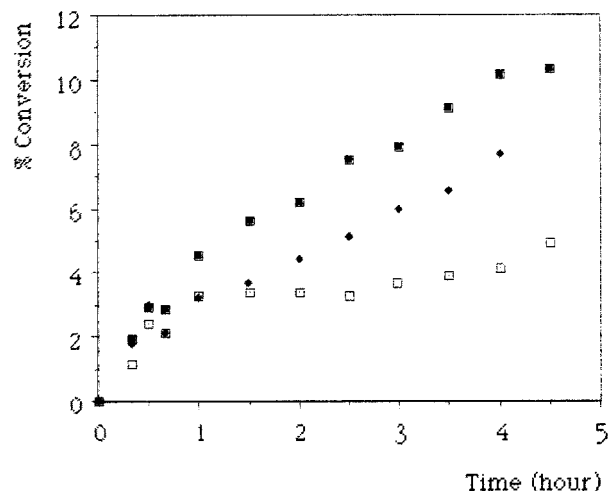

Figure 1 The conversion curves for Çankiri limestone at various flow rates of SO_2 (TBHP = Constant): (□) 3.8 mL/min; (◆) 4.6 mL/min; (■) 5.0 mL/min.

The abrasion test assesses the resistance of a stone sample to weakening and disintegration when subjected to cycles of mechanical degradation while wet. The stone samples were placed in a test drum, comprising a 2-mm standard mesh cylinder, which was totally submerged in water at room temperature. The drum was rotated at a speed of 20 rpm for a period of 10 min. (This is sometimes also called the "slake durability" test.) At the end of the test, the stone samples were dried to constant weight and, from the difference between this and their initial weights, percentage of weight loss was calculated. Abrasion tests in water were performed once for each sample by using an abrasion machine (SBL). Abrassion processes were performed by using acid solutions (H_2SO_4 and HNO_3) having a pH of 4.2, i.e., near the pH of rainwater in extremely polluted areas of Ankara. The acid solutions were sprayed onto the stone samples for 18 h. The solutions were renewed every 6 h. The ageing process was performed in a Thermotron Brand Model SM 16C conditioning room.

Preparation of samples and other relevant experimental details are given in part I of this study.[9]

RESULTS AND DISCUSSION

In this study the conversion curves were obtained by the gravimetric method. Figure 1 shows the conversion curves constructed for the polymeriza-

tion of impregnated EMA at room temperature for a fixed TBHP and varying SO_2 concentration.

In the consolidation of stone by *in situ* polymerization of vinyl monomers, the major drawbacks observed as aftereffects are crack formation and discoloration. When consolidation of some stones with polymers was studied, cracks were observed in carbonated stone samples preserved with MMA polymerized by γ-rays at 20–52°C.[10]

There are two alternative points of view accounting for the formation of these cracks in stone. The first states that the vaporization of unpolymerized monomer caused by the high temperature increase during polymization results in a pressure increase, and thus cracks are formed. According to the second point of view, these cracks are formed during polymerization when the volume shrinkage reaches nearly 20%. No cracking was observed in stone samples preserved with a polymerization system utilizing a benzoyl peroxide–*N,N′*-dimethyl aniline redox pair, but the original color of the stone was changed after such a treatment.[11]

Because no cracking and no discoloration were observed in this study, it is thought that both causes stated above were kept to a minimum and that the redox polymerization system used in this study presents the fewest problems encountered in similar work.
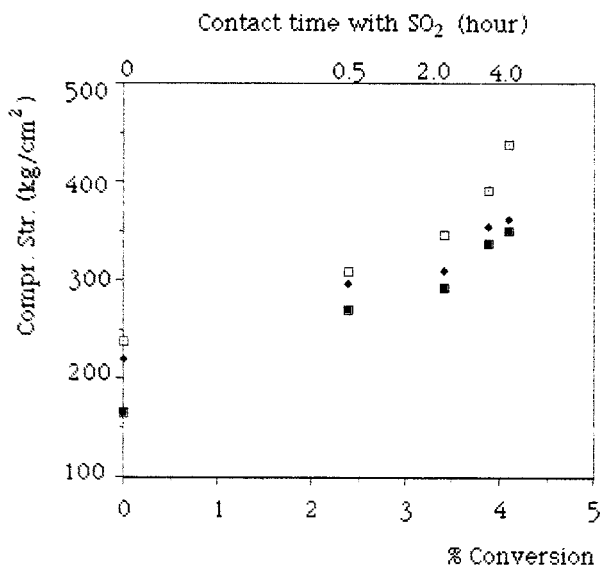
Table I   Results of the Abrasion Test in Water for Original and Consolidated Çankiri Limestone Samples After the Aging Tests

Stone	Aging Time (d)	Polymer (%)	Loss of Weight[a] (%)
ÇL	—	—	0.15
ÇL	—	10.4	0.04
ÇL + PEMA	—	10.1	0.04
ÇL + PEMA	—	7.0	0.09
ÇL	14	—	0.72
ÇL + PEMA	14	2.8	0.61
ÇL + PEMA	14	6.9	0.59
ÇL + PEMA	14	8.0	0.47
ÇL	28	—	0.75
ÇL + PEMA	28	2.8	0.67
ÇL + PEMA	28	7.9	0.62
ÇL + PEMA	28	8.4	0.56

[a] Percent of weight loss determined with respect to original weight of the stones.

The determination of the mechanical properties of stones subjected to various periods of ageing cycles is one of the most important criteria in the evaluation of the properties of a consolidant material. Figure 2 shows the compressive strength of unaged limestones and limestones aged for 14 and 28 days. The compressive strength of original (untreated) Çankiri limestone was determined to be 238 kg/cm^2. As seen from Figure 2, an increase in compressive strength of EMA + TBHP-impregnated Çankiri limestone occurred upon contact with SO_2. As the contact time increased, polymer yield increased, which directly improves the mechanical strength of the stones. At the end of 4 h of contact time, the compressive strength of the original stone samples increased to 438 kg/cm^2 as compared with 238 kg/cm^2 for the original stones before contact. The compressive strength was 220 kg/cm^2 for the 14-day-aging untreated Çankiri limestone, reduced to 165 kg/cm^2 after a 28-day aging period. The compressive strength of limestone increased to twice its original value after 28 days aging. The compressive strength increased with increasing polymer content for the polymer-loaded samples after ageing.

It is very well known that one of the major causes of stone deterioration is abrasion caused by water and acid rain. To observe the abrasive effect of water, the original and consolidated stones were subjected to abrasion tests in water. The experiments were carried out in two steps, before and after aging tests. As explained in part

Figure 2   Change in compressive strength of original and polymer-loaded Çankiri limestone with percent of conversion and aging time (flow rate of SO_2 = 3.8 mL/min): (□) original limestone; (◆) limestones aged for 14 d; (■) limestones aged for 28 d.

Table II Results of the Abrasion Test in Acid Solution for Original and Polymer-Containing Stone Samples

Stone	Acid	Polymer (%)	Loss of Weight (%)
ÇL + PEMA	H_2SO_4	—	0.13
ÇL + PEMA	H_2SO_4	3.8	0.11
ÇL + PEMA	H_2SO_4	7.8	0.08
ÇL + PEMA	H_2SO_4	8.8	0.06
ÇL + PEMA	HNO_3	—	0.10
ÇL + PEMA	HNO_3	4.4	0.08
ÇL + PEMA	HNO_3	8.0	0.06
ÇL + PEMA	HNO_3	8.6	0.06

I of this study,[9] the samples were weighed before and after abrasion tests. The results are shown in Table I. As seen from Table I, the percentage weight loss for the polymer-containing stones was less than the original samples and the deteriorated mass was reduced with increasing polymer content of the stones. Due to the low polymer content, the consolidation caused no sealing of open pores in the stone. Most probably, poly(ethyl methacrylate) (PEMA) films with water-repellent properties deposited at the inner surfaces of the stones protect them against abrasion.

Sulphur dioxide and nitrogen oxides are the principle precursors of acid deposition. Several works have proved that acid rain caused by atmospheric pollution harms historic monuments, and sulfuric acid formed by SO_2 causes erosion and cracking on the surface of stones containing calcium carbonate, such as marble, limestone, etc., forming soluble calcium sulfate.[12,13]

The original and consolidated stones were treated with sulfuric acid and nitric acid solutions and percentage weight loss was recorded (Table II). As seen from Table II, the sulfuric acid and nitric acid solutions caused almost similar abrasion in the original stones. Cheng and colleagues reported that the loss of marble in sulfuric acid solution was almost three times that lost in nitric acid solution.[14] In acid solution tests, the deteriorated mass was decreased with increasing polymer content. This is most probably due to the resistance of PEMA to degradation in acidic media and the protection of substrate stone surfaces by the polymeric film.

CONCLUSIONS

Mechanical and wet abrasion tests were applied to Çankiri limestones consolidated via PEMA obtained by one air pollutant (namely, SO_2) induced by *in situ* polymerization of its monomer. Sulfur dioxide has been used in pure form as an initiator for the polymerization of EMA impregnated into Çankiri limestone. This does not imply that this technique is intended to make use of ambient SO_2 as an initiator; this is actually possible but would require longer contact times, considering the relatively low level of SO_2 in the urban atmosphere. Once the kinetics of polymerization of methacrylates by this initiator pair are well understood, even ambient levels of SO_2 can be utilized to initiate polymerization.

The compressive strength and abrasion properties of stone samples were found to be highly improved upon treatment with this consolidant material.

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