Styrene-acrylonitrile co-polymer impregnated mortar

G. GÜNDÜZ, B. YETER, P. TUĞLU, I. AHMED Kimya Mühendisliği Bölümü, Orta Doğu Teknik Üniversitesi, Ankara, Turkey

The effect of radiation on the physical properties of styrene—acylonitrile co-polymer impregnated concrete was examined and compared with that of polymethyl methacrylate impregnated concrete. Monomer conversion, compressive and tensile strengths, molecular weight and water absorption were determined with changes in polymer loading. The impact strength and the acid resistance of styrene—acrylonitrile co-polymer impregnated specimens were also determined. Polymer loading was increased using vacuum and pressure impregnation techniques.

1. Introduction

The use of polymers in concrete was started only about two decades ago. Some of the polymerconcrete composites have excellent properties compared with ordinary concrete, such as improved compressive, tensile and impact strengths, a large reduction in water absorption and high resistance against acid attacks.

Among the three major types of composites, polymer impregnated concrete is known to be superior to the other types i.e. polymer cement concrete and polymer concrete [1, 2], as a result it was made the subject of the present study.

Several parameters have been examined in the past, and some of the possible uses of the composites were investigated [1-8]. In this research we mainly studied styrene—acrylonitrile co-polymer (SAC) which has not been studied before. It is known to be highly resistant to chemical corrosives. Actually there have been few research studies done on co-polymers. Some research studies done on co-polymers. Some research has also been carried out using polymethylmethacrylate (PMMA) for comparison. In the past PMMA was the must used polymer.

2. Methods and experiments

Test specimens were cylinders with dimensions, 5 cm in diameter and 10 cm in height. The aggregate was natural sand blended according to standards. A mortar mixture was prepared such that the cement/aggregate ratio was 1/3 and the water/ cement ratio was 0.6.

Specimens were cured at 95% relative humidity and 20° C for 28 days. They were then dried at 110° C for 1 day. The dried specimens were then immersed in liquid monomer until complete impregnation occurred which took about 5 h. In order to increase polymer loading, pressure and vacuum impregnation techniques were used. Pressure impregnation was carried out at 2, 5, 10 and 15 atm under a nitrogen atmosphere, while vacuum impregnation was done at 385 and 5 mm Hg. When the samples were completely covered with monomer, the vacuum was released. Monomer impregnated specimens were then polymerized by irradiation at different dose levels. The samples were kept in water during irradiation to eliminate monomer losses. The dose rate of the cobalt-60 irradiator (Atomic Energy of Canada Ltd., Gamma Cell 220) was 2.45 x $10^{17} \text{ eV g}^{-1} \text{ min}^{-1}$.

After irradiation, unreacted monomer was removed by drying. The conversion of monomer to polymer was determined by weighing the specimens.

Co-monomer is composed of 70% styrene and 30% acrylonitrile. This gives the greatest strength co-polymer [9]. To determine the molecular weight of the polymer or co-polymer obtained, the mortar specimens were crushed into small pieces and then extracted with toluene in a Soxhlet



Figure 1 Change of polymer loading with dose.

extractor. The molecular weight was determined by using a Cannon-Fenske viscometer with benzene (for PMMA) or butanone (for SAC) as solvent at 30° C. The equations given by Cohn-Ginsberg *et al.* [10] and Shimura [11] were utilized for PMMA and SAC respectively to calculate molecular weights.

Porosity analysis was carried out using a Rusaka Universal porosimeter which operates using the mercury impregnation technique.

The impact strength tests were carried out using a series of drop-tests performed with a rock toughness tester [12]. The tester is manufactured in accordance with Turkish Standards. TSE-699. A hard steel head is seated under the cast iron impact hammer which weighs 50 kg. The test procedure determines the toughness at failure under impact. The initial height of fall is calculated so as to give $0.02 \,\mathrm{kg} \,\mathrm{cm}^{-3}$ of the specimen. The initial height of fall is 4×10^{-4} m cm⁻³ of specimen. Therefore for any specimen of volume $V \text{ cm}^3$, the initial height is $h = 4 \times 10^{-4} V \text{m}$. In each test the height is increased by h until failure. The toughness is then determined by dividing the total impact work at failure by the volume of the specimen.

Each experimental point given on the figures was determined from an average of three tests.

In the experiments, the effect of total radiation dose on per cent monomer conversion, polymer



Figure 2 Change of per cent conversion with dose.

loading, compressive and tensile strengths and on the molecular weight of polymer formed were determined. At maximum polymer loading, the impact strength, the resistance against acid effect and the reduction in water absorption were determined. The effect of polymer loading on the strengths were also determined for the cases of vacuum and pressure impregnation, polymerization being carried out at 7.5 Mrad of radiation:

3. Results and discussions

It is seen from Fig. 1 that, the optimum dose is about 1.3 to 2.0 Mrad for PMMA and 7.0 to 8.0 Mrad for SAC. The maximum polymer loading is about 6% for PMMA and 6.75% for SAC. The per cent conversions of monomers into polymers are shown in Fig. 2. At maximum conditions it is about 92% for methylmethacrylate (MMA) and 95.8% for styrene-acrylonitrile (SA). The reason that conversion does not reach 100% may be due to the loss of monomers by partially mixing with water and evaporation during irradiation. Actually MMA is known to interact with water in noticeable quantities [4].

SAC increases the compressive strength by about 4 times and PMMA by about 3.5 times, as is seen in Fig. 3. Two factors may account for the larger effect of SAC on the strength of the specimens. One is the higher compressive strength of pure SAC compared with pure PMMA [9, 13, 14] and the second is the 0.75% more polymer loading in the case of SAC. Polymer loading is probably much more critical to the increase in strength.



Figure 3 Change of compressive strength of the mortar with dose.



Maximum increases in splitting tensile strengths are about 4.1 times in PMMA and 6.1 times in SAC samples as is seen in Fig. 4. In both cases the tensile strength increases more than the compressive strength. This can be of real importance, because the low tensile strength is a limiting factor in the use of ordinary concrete. In cases where high tensile strength is the main objective, clearly SAC must be preferred to PMMA. But the higher radiation dosage needed for SAC is a disadvantage.

Further irradiation of the samples shows a decrease in both compressive and tensile strengths. However, it was found that the unimpregnated specimens showed no detectable changes in strength for the radiation doses used. In order to determine the changes in the organic phase, molecular weights were determined and plotted in Fig. 5. Degradation of polymers takes place after 1.3 Mrad for PMMA and after 6 Mrad for SAC. Degradation naturally takes place before these doses, but any degraded molecule acts like a radical and reacts with other molecules around it. Prolonged irradiation, past the complete polymerization limit results in a large degradation of polymer molecules and thus the compressive and the tensile strengths are lowered. The molecular weight of PMMA is in close agreement with other experimental findings [7].

The changes of compressive and tensile strengths with increased polymer loading by vacuum and pressure impregnation techniques are given in Fig. 6. It is seen that both pressure and vacuum impregnation give the same compressive strength since both types of experimental data produce almost the same curve. However pressure impregnation gives relatively larger tensile strength, as it is seen from Fig. 6 where the vacuum data are below the pressure data. In vacuum impregnation, polymer fibres can fill small pores since they are evacuated, while larger pores are preferably filled in pressure impregnation. This is also seen from Fig. 7. It can be concluded that compressive strength does not depend on the process technology, i.e. the technique of impregnation, but tensile strength does in the range of polymer loading studied. The distribution of polymer fibres in small and large pores is crucial in tensile strength.

The impact strength test also shows a great beneficial property of SAC impregnated mortar. As it is seen from Table I, the resistance to impact loading increases 7 to 15 times. This increase is a natural consequence of the increase in the plasticity of the mortar caused by the polymer formed in the pores.

Water absorption properties of PMMA and SAC mortar specimens can be seen from Tables II and III. Water absorption after 6 h is reduced by 92% in 1.29 Mrad PMMA, and 93.8% in 8 Mrad SAC samples. By the end of 6 weeks these values become 74% and 84.6% respectively. The lower water



Figure 5 Change of molecular weights of extracted polymers with dose.

Figure 4 Change of splitting tensile strength of the mortar with dose.



Figure 6 Change of strengths with polymer loading.

TABLE I Impact strength of control and SAC impregnated samples, (Radiation: 8 Mrad, Polymer loading: 6.75%)

Specimen	Number of blows to initiate- crack	Number of blows for failure	Total impact work [*] (kg m)	Toughness* (kg m m ⁻³)
Control	1	2	4-12	$2 \times 10^4 - 6 \times 10^4$
Impregnated	5	6	60-84	$30 \times 10^{4} - 42 \times 10^{4}$

*First value refers to crack initiation while the second one refers to failure.



Figure 7 Porosity distribution.

TABLE II Water absorption of PMMA impregnated specimens with varying radiation doses

Total dose	Water absorption (wt %)				
(Mrad)	6 h	1 day	3 days	2 weeks	6 weeks
Control	8.15	8.43	8.60	8.88	9.32
1.17	0.91	1.13	1.41	2.11	3.26
1.29	0.79	1.11	1.42	1.98	3.09
2.37	0.74	1.17	1.38	1.81	2.49
3.43	0.84	1.22	1.44	1.82	2.41

absorption by SAC samples can be explained by the larger polymer loading of about 0.75%. At larger doses water absorption increases.

The acid resistance of SAC samples was tested at 15% H₂SO₄ solution which is the most reactive solution. As can be seen from Table IV, unimpregnated samples lose 4.5% of their weight while impregnated samples lose only 1.2% by the end of 1 day. So impregnated samples are 3.75 times more resistant to acid. At the end of 12 days, the resistance ratio is 4.56 based on rough surface area measurements. The increase in the ratio can be explained by the loss of some monomers into the water phase from zones close to the surface during irradiation.

Acknowledgements

Dr T. Ertürk, Metallurgy Department, is gratefully acknowledged for his continuous interest and discussion of results. Thanks are also due to Mrs F. Ecevit for typing the manuscript and to Mr A. Akgünes for the figures. Thanks are also extended to the Chemistry Department for the use of the cobalt-60 irradiator, and to the Materials of Construction Laboratory of the Civil Engineering Department for the use of the strength test devices. Members of the Mining Engineering Department are acknowledged for their help in carrying

TABLE III Water absorption of SAC impregnated specimens with varying radiation doses

Total dose	Water absorption (wt %)				
(Mrad)	6 h	1 day	3 days	2 weeks	6 weeks
Control	8.19	8.45	8.63	9.26	9.99
8.00	0.50	0.59	0.76	0.91	1.53
8.50	0.70	0.76	0.97	1.40	2.20
9.50	0.74	0.80	1.06	1.54	2.49

TABLE IV Resistance of control and SAC impregnated samples to acid attack (Radiation: 8 Mrad; Polymer loading: 6.75%)

Time	Weight loss (%)		
(days)	Control	Impregnated	
1	4.5	1.2	
3	12.7	2.8	
6	25.3	4.3	
12	44.9	8.7	

out porosity experiments, and the members of PETKIM, Turkey for supplying styrene.

References

- "Polymers in Concrete", American Concrete Institute, Publication SP-40, 1973.
- 2. D. J. O'NEIL, Int. J. Polymer Mater. 6 (1977) 73.
- V. I. SOLOMOTOV, "Polymer Cement Concretes and Polymer Concretes", United States Atomic Energy Commission, Division of Technical Information, Translation Series, AEC-tr-7147, 1967.
- 4. J. GEBAVER and R. W. COUGHLIN, Cem. Conc. Res. 1 (1971) 187.
- K. SINGER, A. VINTHER and Z. FÖRDOS, in "Proceedings of the 3rd Tihany Symposium on Radiation Chemistry", May, 1971, Tihany, Hungary, edited by J. Dobo and P. Hedvig (Akademiai Kiado, Budapest, 1972).
- 6. "Transportation Research Board, Polymer Concrete", National Research Council, USA, No. 542, 1975.
- 7. C. RAMOS and A. NUFIOZ-ESCALONA, Cem. Conc. Res. 6 (1976) 273.
- OHGISHI, H. ONO, K. ARAKI and Y. KASAHARA, in "Mechanical Behaviour of Materials, Proceedings of the 3rd International Conference", Vol. 3 (Pergamon Press, London, 1979).
- H. F. MARK, N. G. GAYLORD and M. N. BIKALES, "Encyclopedia of Polymer Science and Technology", Vol. 1 (Interscience Pub., New York, 1964) p. 425.
- 10. E. COHN-GINSBERG, T. G. FOX and H. F. MASON, Polymer 3 (1962) 97.
- 11. Y. SHIMURA, J. Polymer Sci. A-2 4 (1966) 423.
- K. KOZAKÇI, M.Sc. Thesis, "A study on Impact Strength of Concrete and Related Test Methods", 1974, Orta Doğu Teknik Üniversitesi, Ankara.
- A. X. SCHMIDT and C. A. MARLIES, "Principles of High Polymer Theory and Practice" (McGraw Hill Book Co. Inc., New York, 1948).
- R. E. KIRK and D. F. OTHMER, "Encyclopedia of Chemical Technology", Vol. 19 (Interscience Pub., New York, 1969) p.85.

Received 8 February and accepted 30 June 1980.