Journal of Polymer Research (2005) 12: 231–241
DOI: 10.1007/s10965-004-3206-7

Studies on Furan Polymer Concrete

Manickam Muthukumar and Doraisamy Mohan*
Department of Chemical Engineering, AC College of Technology, Anna University, Chennai 600 025, India
*(*Author for correspondence; Fax: +91-44-22352642; E-mail: dmohan@annauniv.edu; mohantarun@yahoo.com)*

Received 18 May 2004; accepted in revised form 9 September 2004

Key words: density, furan resin, polymer concrete, SEM, water absorption

Abstract

Good mechanical properties and excellent chemical resistance of polymer concretes make them cost effective material of construction for civil engineering applications. These properties of polymer concretes are dependant upon the type of polymeric binder and the filler materials used. In the present investigation, a series of polymer concretes based on furan resin have been prepared using an aggregate mix proportion having minimum void content. Density, water absorption and microstructure were studied for different combinations designed on the basis of mixture design concept of design of experiments. The effects of variables on the properties were discussed.

Introduction

The current standard building material, namely portland cement concrete prepared by binding aggregate with Portland cement, has a number of deficiencies which make it inappropriate for some applications. For instance, a suitable cure with portland cement takes approximately 28 days. In addition, chemical resistance to acid is lacking in Portland cement as is good tensile and flexural strength. Several attempts have been made to replace portland cement with different building material compositions to overcome the above described problems. Such substitute materials will compromise on one property such as strength for another property such as acid resistance or the like. These substitute materials have taken the form of both coatings and linings for portland cement as well as complete replacement materials [1].

Studies and tests have been performed on polymeric additives to concrete and polymeric materials used as substitutes for the typical hydraulic cement binder materials. For example, polymer cement concrete which is a mixture of conventional hydraulic cement concrete and high molecular weight polymers has been formed comprising generally thermoplastic or rubber polymers which are added as emulsions or dispersions to the hydraulic concrete mix. It has been found that the wear-resistance of polymer cement concretes is significantly better than Portland cement concrete and thus, polymer cement concretes have found use as floor and deck coverings in public buildings, industrial plants and bridges.

Extensive laboratory studies have been performed both on polymer-impregnated concrete and polymer concrete in which the hydraulic binder is totally substituted with a polymeric material [2]. Polymer concrete differs from typical Portland cement concrete, polymer cement concrete and polymer-impregnated concrete. Polymer concrete contains no cement or water. The development of physical and chemical properties of polymer concrete depends entirely on the chemical and slightly on the physical reaction between the polymeric binder, hardener and the aggregate system. Different types, properties and applications of polymer concrete have been extensively reported [3–7]. Since polymer concrete is a heterogeneous material, the properties of polymer concrete are highly variable. Contributions to the variability of the composite material include: heterogenity of the aggregate particles, polymer binder, etc. Application and performance of polymer concrete is dependent upon the specific polymer binder as well as the type of aggregate and its gradation [8]. The distribution of aggregates should be such as to allow for a minimum void volume for dry packed aggregates which will result in dense packing. Dense packing of aggregates in the polymer concrete matrix results in better properties. To achieve this, either the void content of the aggregate mix can be minimized [9] where the binder requirement for ensuring adequate bonding of all aggregate particles will be less or use loosely packed aggregate mix with higher binder content. Though the aggregate and micro filler form a major component of the total mass of the polymer concrete, there has not been much emphasis on the aggregate and micro filler mix proportion used in such systems. A review of literature shows that the aggregates used in polymer concretes are either fine particles [10] or the particle size distribution chosen are based on theoretical basis [11] suitable for portland cement concretes. The effect of aggregate mix proportion on the void content and a method of optimizing the mix proportion to have minimum void content has been reported [12].

Table 1. Types of furan resins and their properties

Sample No.	Resin description	FA (moles)	F (moles)	FAL (moles)	Viscosity cps at 25 °C	Specific gravity at 25 °C
1	A (Ra)	1	–	–	220	1.208
2	B (Rb)	1	0.25	–	253	1.213
3	C (Rc)	1	0.50	–	246	1.215
4	D (Rd)	1	0.75	–	287	1.219
5	E (Re)	1	–	0.5	216	1.205

Among the different binders, furan resins have excellent heat resistance, outstanding resistance against bases, strong acids, organic solvents, etc. Thus furan resins offer several advantages when properly cured over other synthetic resin based binder systems such as unsaturated polyester, epoxy, etc. Furan based laminating resins reinforced with glass fibers are used extensively as materials of construction in the chemical industry and also in other industries where corrosive conditions are encountered (e.g., power plants, steel mills, paper industry). The products are used in many different places, for instance, reaction vessels, floors, trenches, pits, catch basins, etc. [13].

The major raw material used in the synthesis of furan polymers are furfuryl alcohol and furfuraldehyde which are obtained from the agricultural wastes, making it a staple supply and relatively inexpensive compared to the other synthetic resins. Condensation products of furfuraldehyde and acetone in different mole ratios are more commonly used [14], even though other types of furan resins such as homopolymer of furfuryl alcohol or a copolymer of furfuryl alcohol and furfuraldehyde, etc. are also known to be good binders for chemical resistance application. In spite of this, the literature contains very few references in this regard [15, 16]. Thus furan resin has a good balanced property which makes it an ideal choice for polymer concrete applications.

The present investigation relates to an improved polymer concrete in which a series of low viscosity resin binder based on polymerized furfuryl alcohol, furfuryl alcohol – furfuraldehyde copolymer and furfuryl alcohol – formaldehyde copolymer are used, with a novel aggregate system optimized to have minimum void content. The polymer concretes prepared were characterized by measuring its density, water absorption and studying its microstructure using scanning electron microscope.

Materials and Methods

Technical grade furfuryl alcohol (FA) and furfuraldehyde (FAL) from Indo Rama Chemicals, Thailand was distilled under vacuum and used. Paraformaldehyde (F) in granular form with an assay of 96% formaldehyde is used as procured from Formal Y Derivadoss, Sweden. γ amino propyl triethoxy silane (Grade A1100) from Union Carbide Corporation, USA was used as received. Sulphamic acid (SA), p-toluene sulfonyl chloride (PTSC), o-phosphoric acid (OPA), benzene sulfonyl chloride (BSC), triethanolamine (all LR grades) were procured from Ranbaxy Chemicals, India and used as such.

Naturally occurring silica sand from mines of Tamilnadu Minerals (TAMIN), India was washed, dried and sieved into three different grades, having particle sizes 9.52–4.76 mm for grade I, 4.76–2.38 mm for grade II and 0.3–0.6 mm for grade V [12]. The silica sand chosen for the study was a high purity, high silica content, iron free and very low acid soluble type suitable for use in chemical resistance application and conforms to the chemical requirements of IS 650 [17]. Quartz powder #200 mesh, of particle size 75 microns was dried free of moisture in an electric oven by maintaining at 105 °C for 4 hours, cooled and used for the studies.

Furan polymers as detailed in Table 1 were prepared [18] by taking furfuryl alcohol (FA) in a three-neck round bottom flask fitted with a stirrer, condenser and thermometer. To this, second monomer (paraformaldehye (F) in the case of resins B, C and D and furfuraldehyde (FAL) in the case of resin E) and ortho phosphoric acid were added with stirring. The reaction mixture is maintained at 95 ± 5 °C. Viscosity is checked frequently and when it reached 250 ± 50 cps, the reaction mixture was cooled and neutralized with triethanolamine, stirred well and transferred into an airtight container. Suitable catalyst system for crosslinking the furan resin and adhesion promoter for improving the mechanical properties have been listed in Tables 2 and 3, respectively.

Preparation of Polymer Concrete

Polymer concrete mortar of different composition [19] as detailed in Table 4 was prepared by mixing required quantities of resin with additive, aggregate, microfiller and catalyst in a slow speed mechanical mixer fitted with a paddle stirrer. First aggregate, microfiller and catalysts were mixed in a powder mixer. Separately, additive was added to the resin, homogenized and to this, the premixed powder was added slowly while stirring at slow speed to ensure that no air bubbles are trapped in the prepared polymer concrete mortar. After complete mixing of the powder, the prepared polymer concrete mortar was used for casting specimens for studying density and water absorption adopting standard techniques [20, 21]. Specimen casting was carried out under vibration on a vibrating table, the vibrations being generated using high frequency electrical

Table 2. Gel time/working time for different catalyst systems

Catalyst	Phr	Gel time/working time (minutes)				
		Resin A	Resin B	Resin C	Resin D	Resin E
87% OPA	10	Gels after overnight	230	100	60	No gellation
BSC	7	145	80	55	40	120
60% PTSA	6	Local gellation				
PTSC	5	Soft and nail impression after overnight				
	10	Rubberish after overnight				
SA	2	Good overnight hardness, no nail impression				
	5	No working time				
PTSC/SA	5/2	Good overnight hardness, no nail impression, sounds metallic				

Table 3. Effect of silane adhesion promoter

Sl. No	Description	Composition (%)			
1	Resin A	10			
2	Aggregate				
	Grade I	31.68			
	Grade II	26.8			
	Grade V	21.52			
3	Microfiller	10			
4	Catalyst, percentage of resin	5 : 2			
5	Silane, percentage of resin	0	0.25	0.5	1
6		Compressive strength (MPa)⋆			
	1 day	17.9	23.5 (131)	27.8 (155)	30.7 (171)
	3 days	26.4	44.3 (168)	48.5 (184)	47.5 (180)
	7 days	35.6	60.8 (171)	65.5 (184)	67.3 (189)

⋆ Percentage of control in brackets.

Table 4. Mixture design combinations for polymer concretes

Sl. No	Resin (%)	Aggregate (%)	Microfiller (%)
1	7.5	77.5	15
2	9.375	83.125	7.5
3	11.25	78.75	10
4	13.125	74.375	12.5
5	15	70	15

vibrators. The aggregate percentage shown in Table 4 is a mixture of three grades, namely I, II and V in the ratio of 39.6 : 33.5 : 26.9 by weight of I: II: V. This ratio corresponds to the optimized aggregate mix proportion having least void content.

Results and Discussion

Furan resin was taken as the binder for the present investigation. Five different types of furan resins were synthesized using different mole ratios of furfuryl alcohol, furfuraldehyde and formaldehyde. Effect of different catalysts, silane coupling agent were studied and its dosage was fixed based on preliminary trials.

Using the optimized aggregate combination as one variable, silica powder (microfiller) and furan resin as the other two variables, instead of selecting combinations at random [19], using mixture design concept of design of experiments, different combinations were designed. Based on these combinations, for each of the five resin systems, polymer concretes were prepared and density, water absorption were studied. Further the microstructures were examined using scanning electron microscopy. The results of all the above aspects are discussed in the following section.

Studies on Different Catalyst System for Furan Resin

In order to convert the liquid furan resin into solid cross linked thermosets at room temperature, suitable catalyst were evaluated. Thus, p-toluene sulfonic acid (60% solution in water), o-phosphoric acid, benzene sulfonyl chloride among the liquid system and p-toluene sulfonyl chloride and sulfamic acid among the powder system were studied. Table 2 gives the results of gel time and working time, respectively, for liquid and powder catalyzed furan resins. Among the liquid catalysts, only benzene sulfonyl chloride was found to be efficient in fully curing the furan polymers; however it was having pungent odour and eye irritation. With p-toluene sulfonic acid immediate gellation was observed in all resin systems. In the case of o-phosphoric acid full cure was not realized.

Working time and overnight hardness of polymer concrete were used as a measure of evaluating powder catalyst for different furan resins at a binder content of 10%. P-toluene sulfonyl chloride was good in crosslinking the furan resin but was slow in its reactivity. Sulfamic acid catalyzed system showed good initial cure as observed by its quick setting time. Thus a combination of p-toluene sulfonyl chloride and sulfamic acid was selected to have a synergistic effect for polymer concrete studies using furan resin. This catalyst system for furan resin was found to be satisfactory based on preliminary investigation. However other catalyst system may also be used [16].

Studies on Effect of Adhesion Promoter

Silanes are considered as good adhesion promoter for systems involving organic and inorganic matrices. However these silanes are very costly and their dosage has to be optimum. Hence using resin A, the effectiveness of silanes in polymer concrete was studied at 0, 0.25, 0.5 and 1% based on resin. The input combination adopted and compressive strength measured at 1, 3 and 7 days of curing are given in Table 4. It can be observed that as the silane content increases, the strength increases. However after 0.5% the strength increase was very marginal. Based on the results obtained, 0.5% silane was found to have optimum property and thus was fixed for further studies on furan polymer concrete.

Studies on Furan Polymer Concrete

Polymer concretes of different composition as given in Table 4 were prepared and tested under identical conditions. Density of polymer concrete mortar of different composition was tested in the wet stage immediately after mixing. Water absorption was tested after seven days curing at 30 °C. The following section discusses the results observed from the above study.

Effect of Variables on Density

Density of different polymer concrete compositions was studied and given in Figure 1 which shows the effect of binder content on the density of different polymer concretes. At 7.5% resin content, the density was least for all binder systems. This can be explained on the basis that this combination has the least binder content combined with maximum microfiller content. Hence the consistency of the polymer concrete mix was very dry with poor compaction leading to voids thereby reducing the density.

Polymer concrete corresponding to 9.375% resin had maximum density in all systems showing that this combination has a better balance of resin content, aggregate and microfiller leading to dense packing. Since this composition had maximum aggregate content than any other combination and as the specific gravity of aggregate is more than

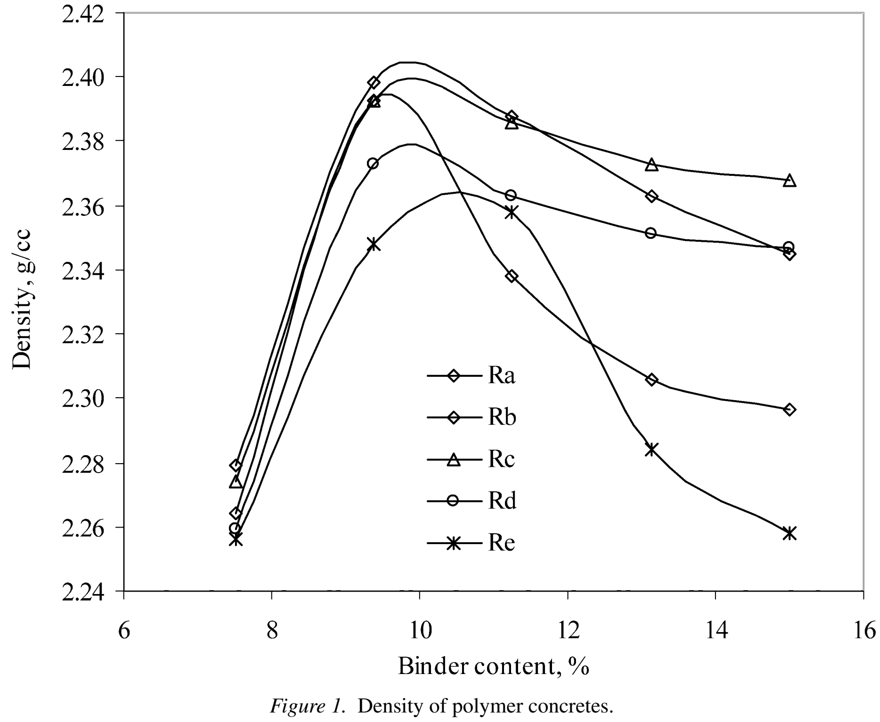

Figure 1. Density of polymer concretes.

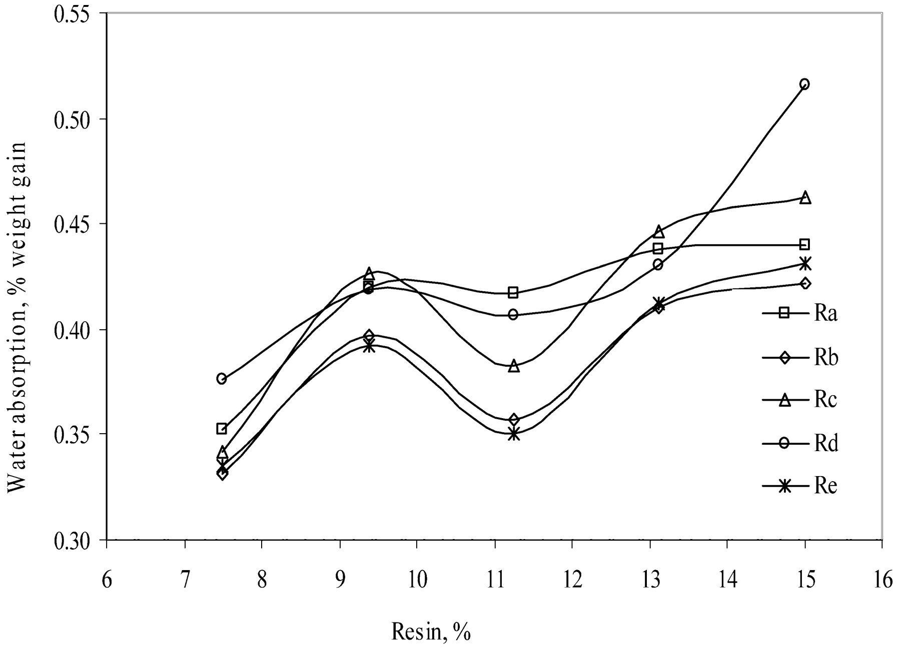

Figure 2. Water absorption of polymer concretes.

that of the resin, maximum density was observed. During crosslinking of these furan resins, water molecules are liberated which creates microvoids in the matrix in the hardened state. Since in the hardened state there is no possibility of the resin or microfiller filling those microvoids, the 9.375% binder containing composition showed higher water content eventhough it is denser than 7.5%. Above 9.375%, there was an excess resin over and above that required for filling the voids in between the aggregate particles and forms a thin layer covering the aggregate particles binding them together. This leads to resin segregation at the top surface, which increases with increasing resin content while casting, leading to lowering the density of the mix and it follows a similar trend further up to a resin content of 15%. The usage of aggregate mix containing minimum void has resulted in polymer concretes having higher density and good workability even at low binder content. Similar studies based on epoxy and unsaturated polyester resins have been reported for aggregates based on basalt, granite, etc. [22].

Effect of Variables on Water Absorption

Water absorption of polymer concretes was studied and reported in Figure 2 represented by weight gain as a function of resin content for different resin systems. It is observed that in all the resin systems water absorption was the lowest in polymer concrete having 7.5% resin content. As the resin content increases to 9.375% the water absorption increases, and then decreases for 11.125% and again increases thereafter for 13.125% and 15% binder content. This can be explained on the basis of lower microfiller content in the case of 9.375% and 13,125% combinations. As the microfiller content decreases, the extent of voids not being completely filled by the resin and microfiller increases. However, for the 15% binder content, the water absorption should decrease based on similar argument given above, whereas an increase in water absorption is observed. This may be due to the presence of micropores generated during curing of furan resin liberating water molecules [23] which is evident from the fact that the high formaldehyde resin, namely resin D, showed maximum water absorption.

Microstructure of Polymer Concrete

To understand the microstructure of polymer concrete, morphological studies were carried out. Scanning electron microscope (SEM, Model: Leica Stereoscan) operated at 20 KV and selenium detectors were used for the above study. Figures 3–7 show the surface of polymer concrete at a magnification of 300 times corresponding to polymer concretes made using resin C at 15, 13.125, 11.25, 9.375 and 7.5 % of binders, respectively.

The picture clearly shows the presence of voids in the polymer concrete mix. It can be seen from Figures 3 and 7, as the binder content increases the void size and number of voids decreases. Similarly among Figures 4, 5 and 6, as the resin content increases, microfiller content increases. However the increase in microfiller did not affect the flow as can be seen from the reduced void size and also from the void which becomes progressively uniform in shape. This confirms the improved flow of the higher binder containing polymer concrete mixes even at higher microfiller contents.

Figures 8–12 show the surface of polymer concrete at a magnification of 7000 times corresponding to polymer concretes made using resin C at 15, 13.125, 11.25, 9.375 and 7.5% of binders, respectively. It can be observed that as the resin content decreases from 15 to 7.5%, there is a progressive decrease in the micropores in the polymer chain generated during the curing reaction due to liberation of water molecules and a minor amount of formaldehyde. As the binder content increases in the composition, the micropores generated are higher than those corresponding to lower

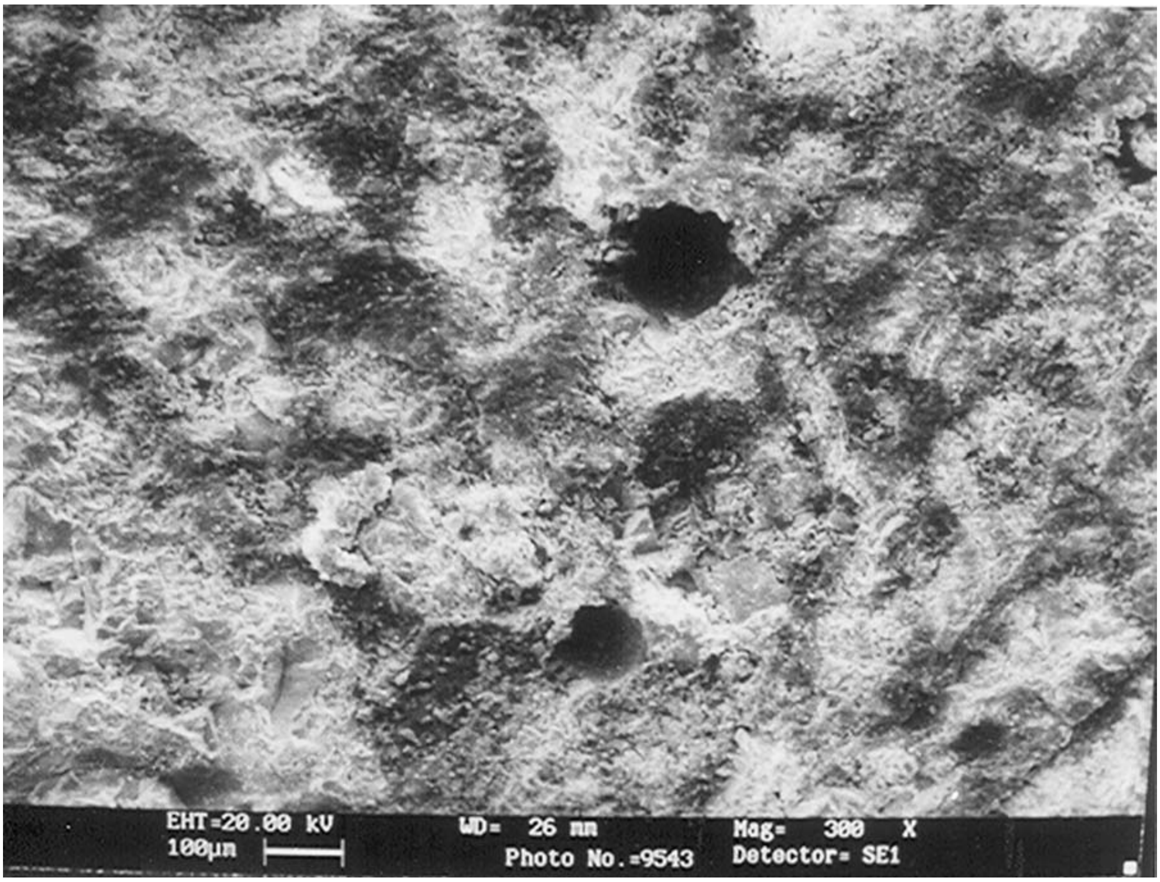

Figure 3. SEM picture of polymer concrete: 15% binder content, 300 times magnification.

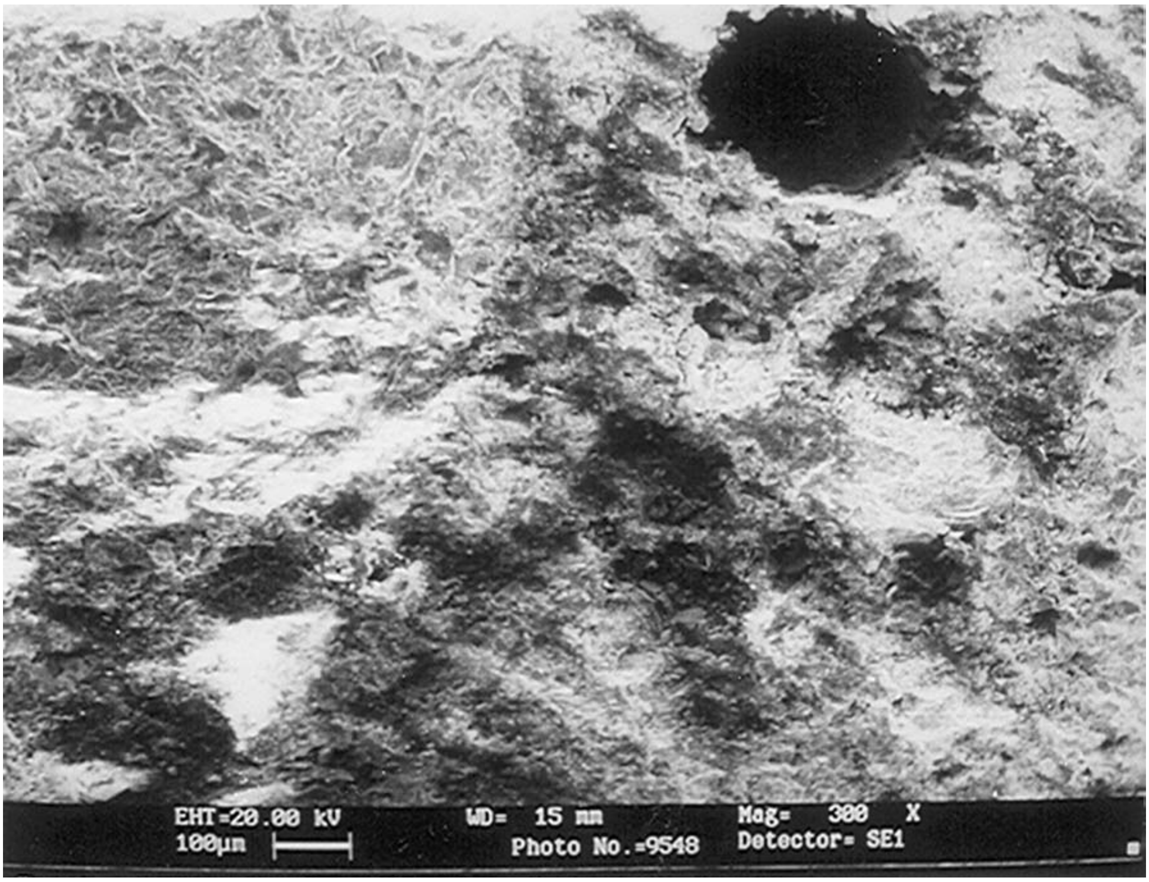

Figure 4. SEM picture of polymer concrete: 13.125% binder content, 300 times magnification.

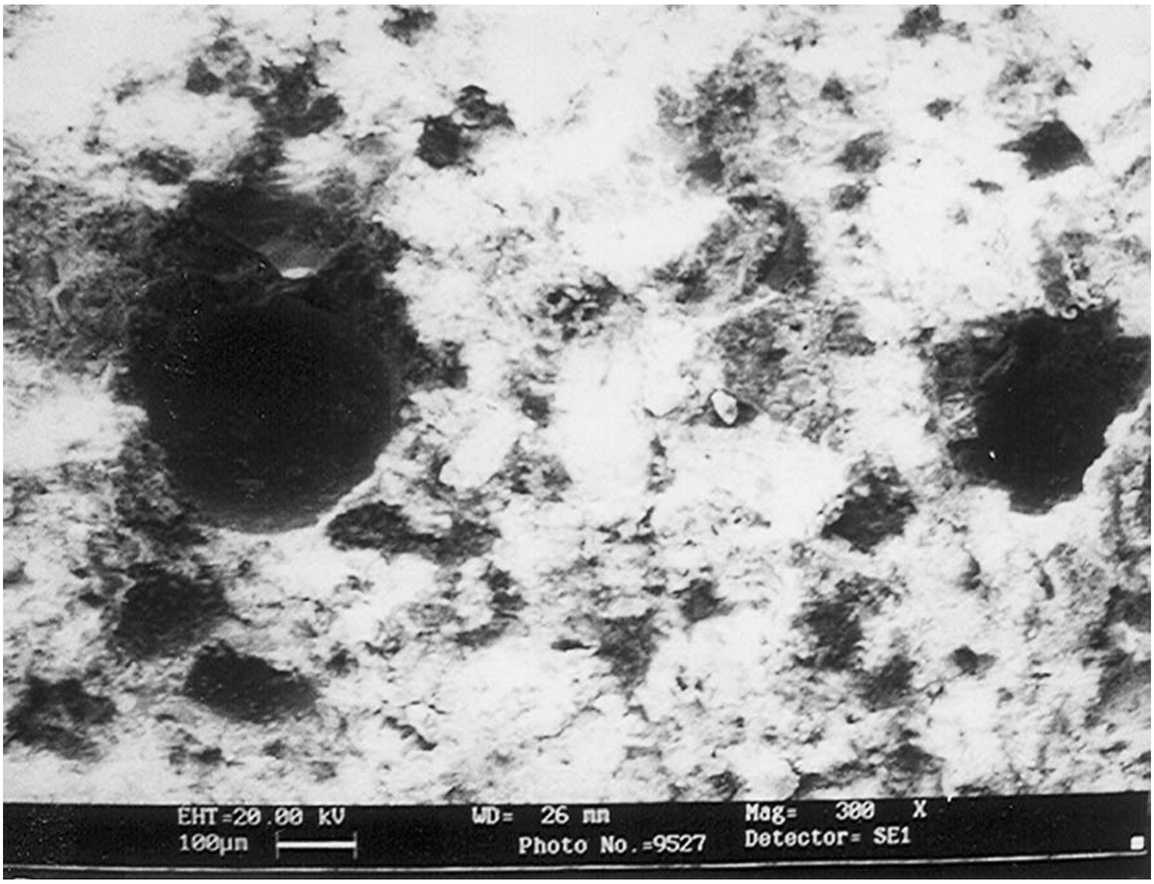

Figure 5. SEM picture of polymer concrete: 11.25% binder content, 300 times magnification.

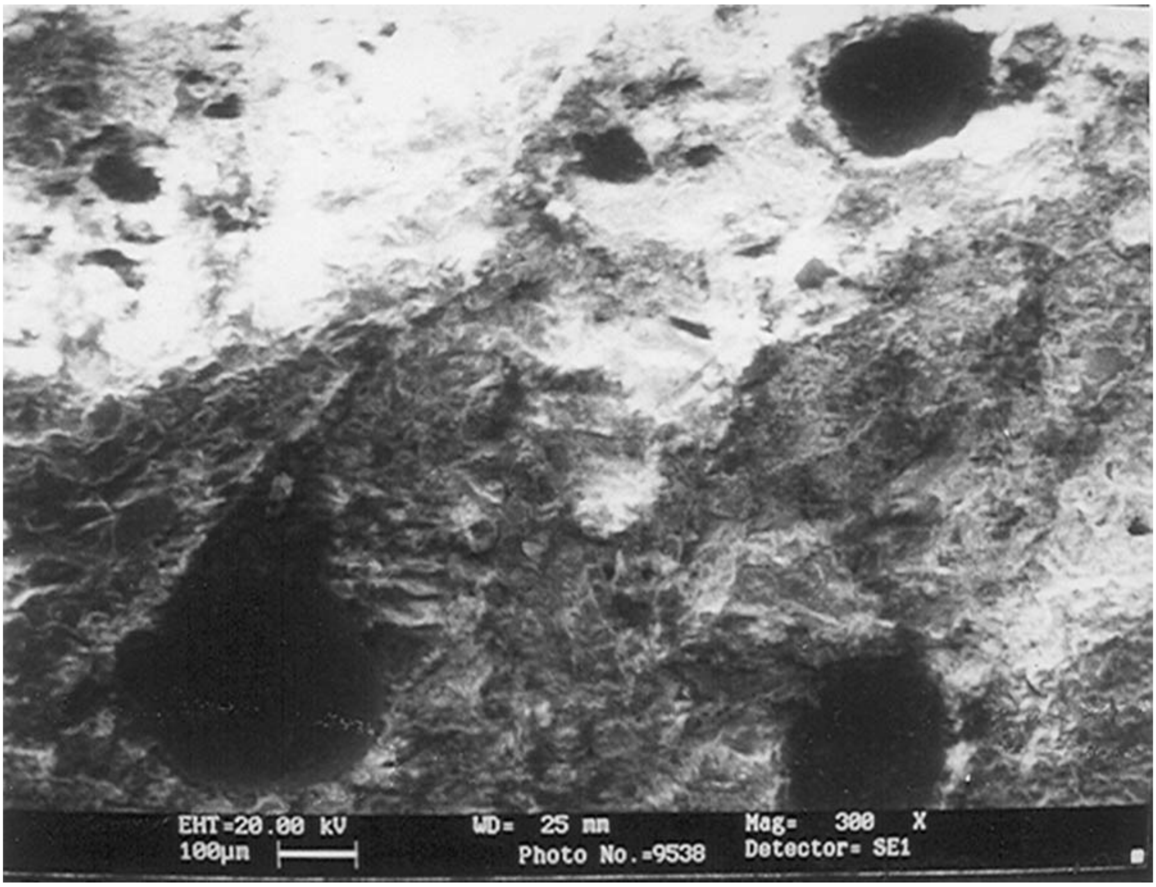

Figure 6. SEM picture of polymer concrete: 9.375% binder content, 300 times magnification.

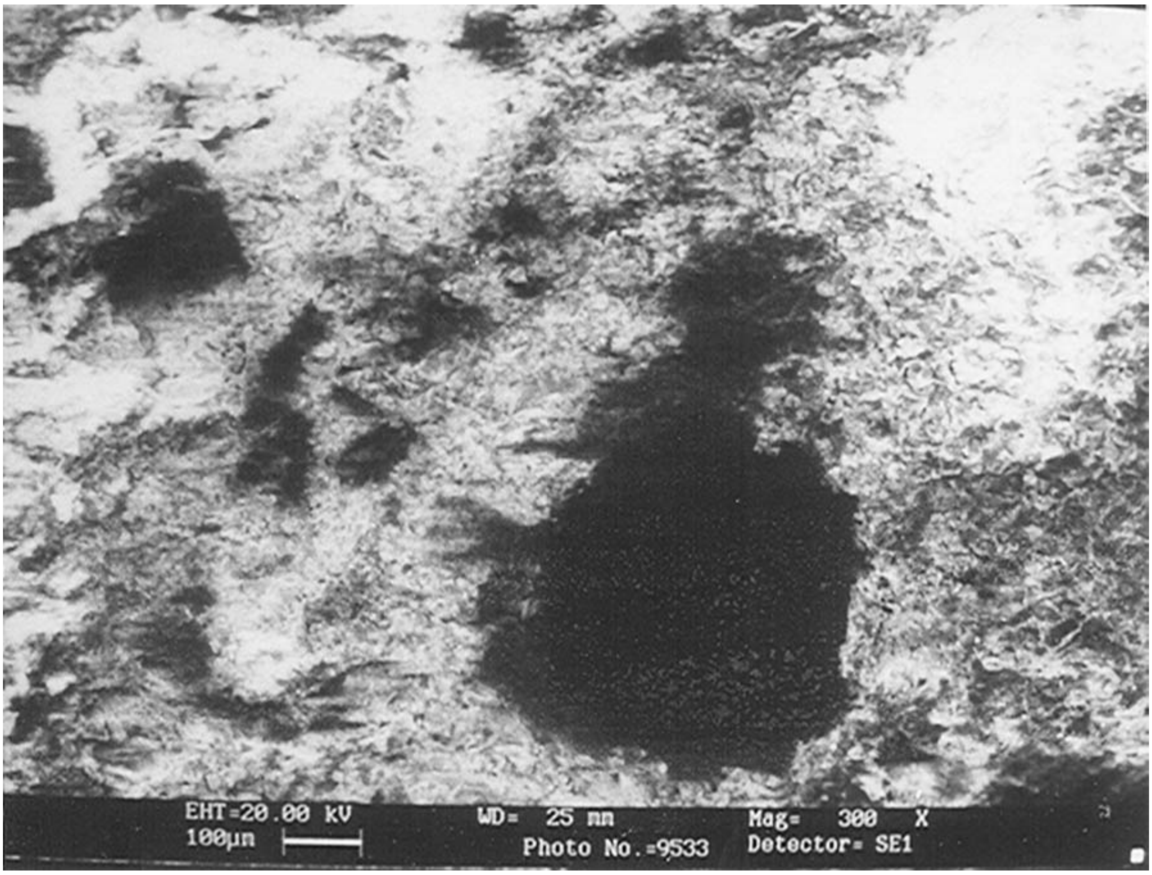

Figure 7. SEM picture of polymer concrete: 7.5% binder content, 300 times magnification.

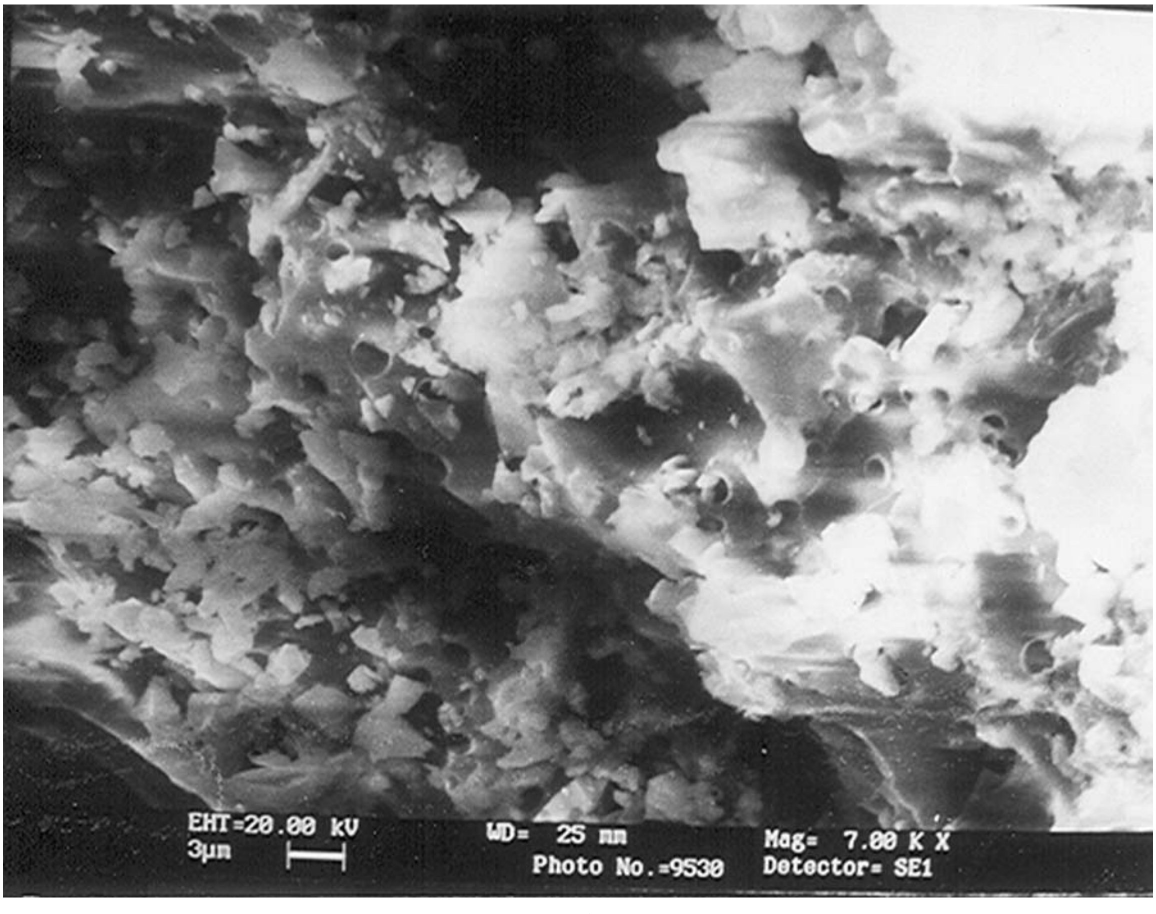

Figure 8. SEM picture of polymer concrete: 15% binder content, 7000 times magnification.

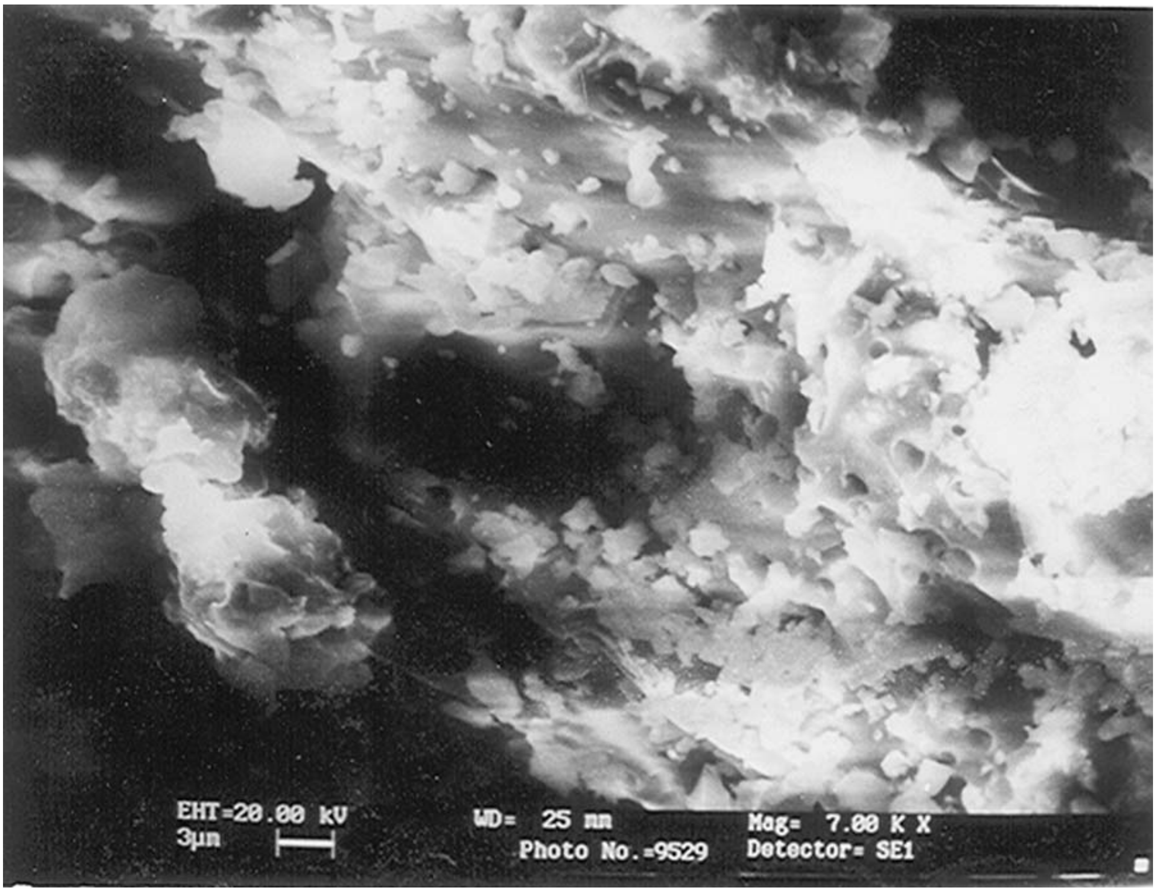

Figure 9. SEM picture of polymer concrete: 13.125% binder content, 7000 times magnification.

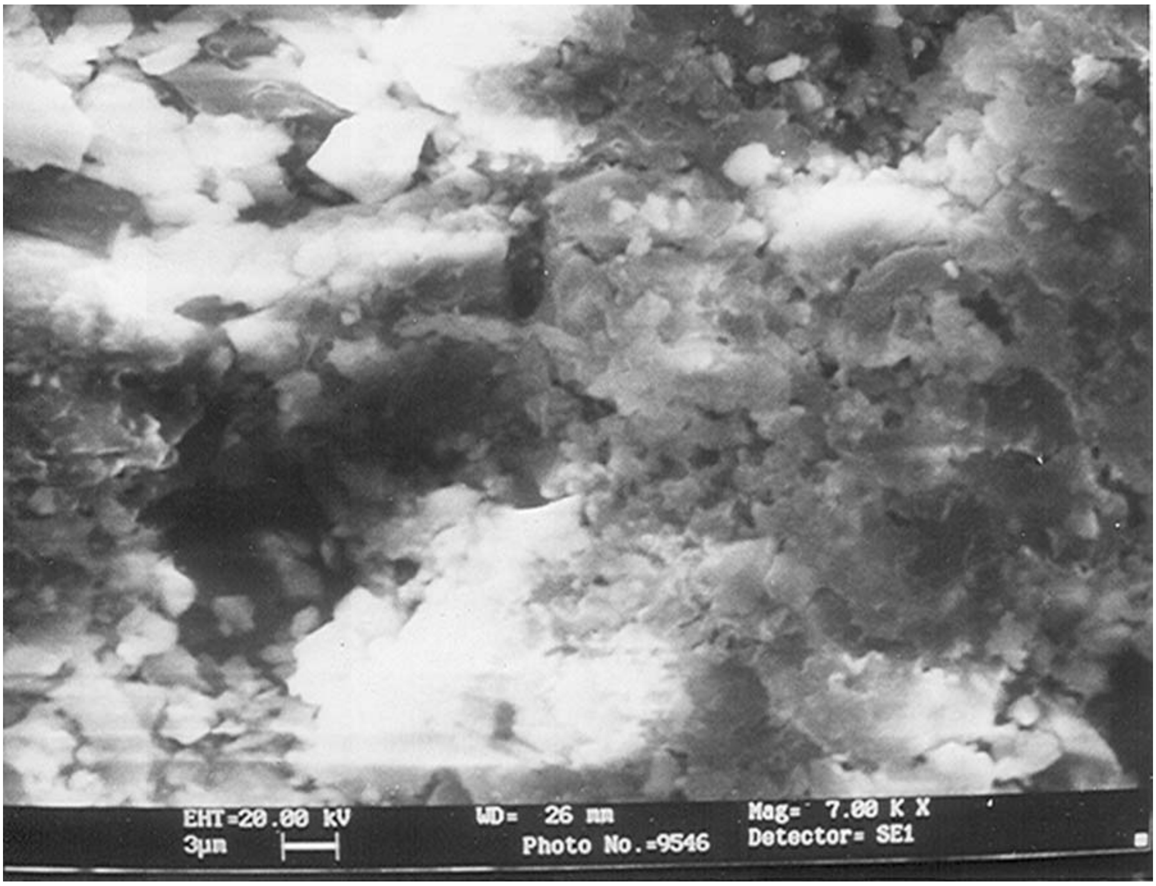

Figure 10. SEM picture of polymer concrete: 11.25% binder content, 7000 times magnification.

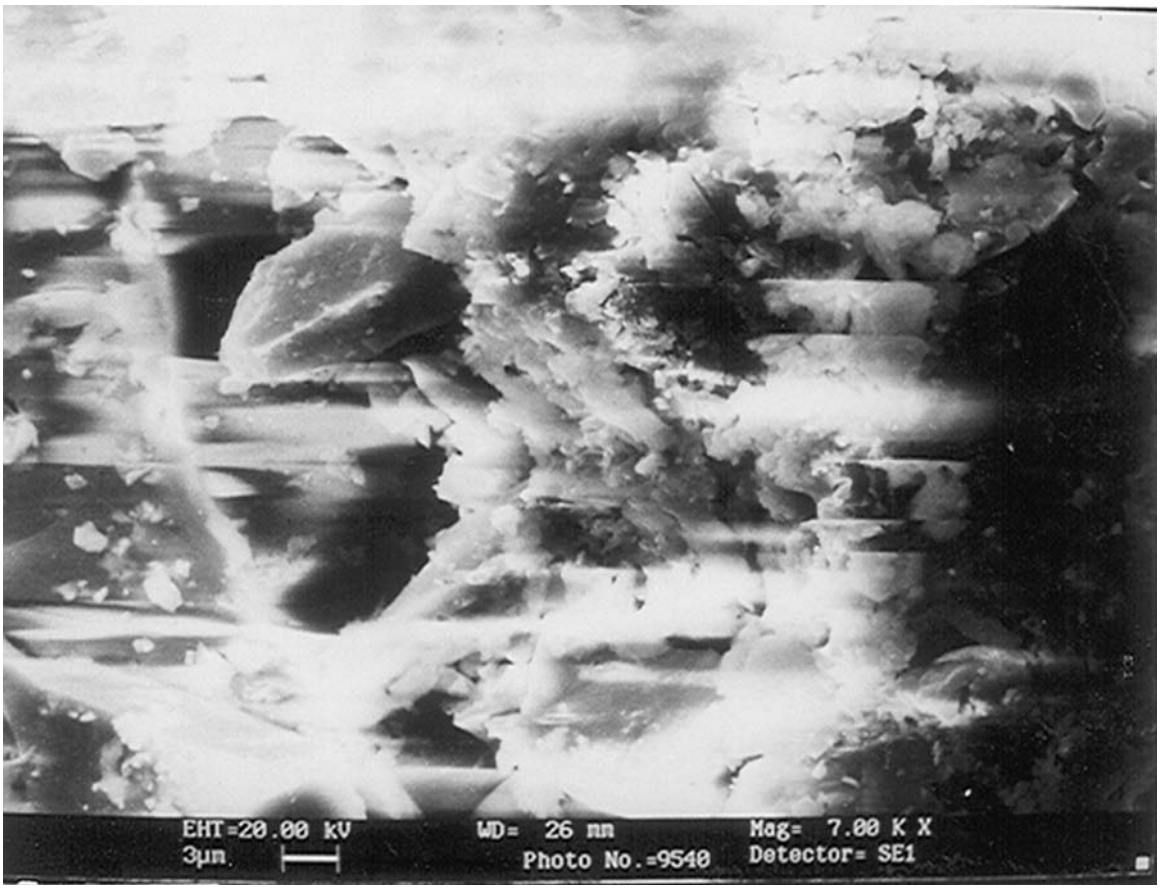

Figure 11. SEM picture of polymer concrete: 9.375% binder content, 7000 times magnification.

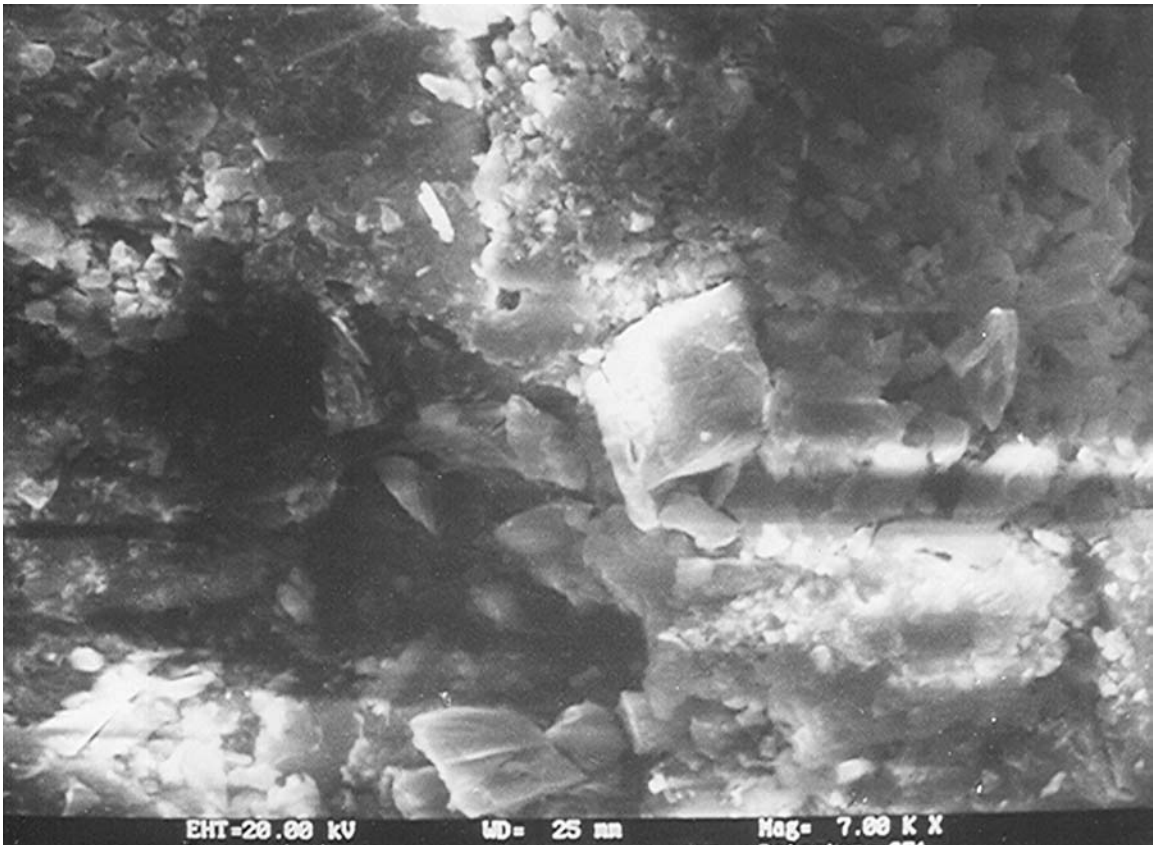

Figure 12. SEM picture of polymer concrete: 7.5% binder content, 7000 times magnification.

concentration of binder leading to higher water absorption. However, for higher binder containing compositions, the corresponding resin and microfiller content are also high. This leads to minimization of interparticle void compared to other compositions as observed in SEM. Similar findings based on epoxy resin have been reported [24].

Summary and Conclusion

Polymer concretes were made using a series of furan resins and an aggregate mix proportion having minimum void content. Density, water absorption and microstructure using scanning electron microscope were studied for all the compositions. The low void content in the aggregate mix proportion has resulted in polymer concretes having higher density. The low viscosity of the furan resin has resulted in polymer concretes of low binder content leading to formulations which are cost effective. Further, the furan polymer concrete evaluated can be used for a wide variety of applications in heavy industrial environments where strength and chemical resistance are important, due to its superior chemical and temperature resistance combined with its low cost and ease of availability, in place of conventional binders like epoxy, polyesters, etc.

References

1. S. Popovics, *Concrete Making Materials*, Hemisphere Publishing Corporation, McGraw-Hill, Washington, 1979.
2. R. Kreis, *Int. Polym. Sci. Tech.*, **18**, 69 (1991).
3. ACI Committee 548, *Guide for the Use of Polymers in Concrete*, ACI 548.1R, American Concrete Institute, Detroit, 1997, p. 1.
4. ACI Committee 548, *Guide for Polymer Concrete Overlays*, ACI 548.5R, American Concrete Institute, Detroit, 1998, p. 1.
5. ACI Committee 548, *Polymer Concrete – Structural Applications*, state-of-the-art report, ACI 548.6R, American Concrete Institute, Detroit, 1996, p. 1.
6. D. W. Fowler, *Cement Concrete Comp.*, **21**, 449 (1999).
7. L. C. Muszynski, in *Encyclopedia of Polymer Science and Engineering*, Wiley, New York, 1988, Chapter 12, p. 462.
8. V. V. L. K. Rao and S. Krishnamoorthy, *ACI Struct. J.*, **95**, 153 (1998).
9. V. V. L. K. Rao, *Cement Concrete Agg.*, **15**, 97 (1993).
10. Y. S. Soh, Y. K. Jo and H. S. Park, *Polymers in Concrete*, E&FN SPON, London, 1997, p. 67.
11. W. B. Fuller and E. T. Sanford, *Trans. ASCE*, **59**, 67 (1907).
12. M. Muthukumar, D. Mohan and M. Rajendran, *Cement Concrete Comp.*, **25**, 751 (2003).
13. A. Gandini, in *Encyclopedia of Polymer Science and Technology*, 1988, Chapter 7, p. 454.
14. G. K. Solovjov, V. P. Tramvovetsky and D. Kruger, *ACI Mater. J.*, **91**, 158 (1994).
15. A. Gandini and M. N. Belgacem, *Prog. Polym. Sci.*, **22**, 1203 (1997).
16. G. K. Solovjov, V. P. Tramvovetsky and D. Kruger, *ACI Mater. J.*, **91**, 158 (1994).
17. IS 650, *Specification for Standard Sand for Testing of Cement*, Bureau of Indian Standards, New Delhi, 1987.
18. M. Choura, N. M. Belgacem and A. Gandini, *Macromolecules*, **29**, 3839 (1996).
19. M. Muthukumar, Ph.D. Thesis, Anna University, Chennai, India, December 2002.
20. ASTM C905, *Standard Test Methods for Apparent Density of Chemical Resistant Mortars, Grouts, Monolithic Surfacings and Polymer Concretes*, American Society for Testing and Materials, PA, 1996.
21. ASTM C413, *Standard Test Method for Absorption of Chemical Resistant Mortars, Grouts, Monolithic Surfacings*, American Society for Testing and Materials, PA, 1996.
22. J. R. Clifton, L. Czarnecki, A. Garbacz and P. Lukowski, *Optimization of Polymer Concrete Composites: Final Report*, National Institute of Standards and Technology, Gaithesburg, MD 20899, 1999.
23. R. Gonzalez, J. M. Figueroa and H. Gonzalez, *Eur. Polym. J.*, **38**, 287 (2002).
24. L. Czarnecki, P. Lukowski and R. Nejman, *Cement Concrete Comp.*, **18**(6), 417 (1996).