Journal of the American Concrete Institute

ACI Journal

DECEMBER 1979/NO.12 PROCEEDINGS V.76

AMERICAN CONCRETE INSTITUTE

Dec. J1

No January issue

JOURNAL schedule changed

Responding to concerns from members that the high quality of the ACI JOURNAL was not reflected in the method used to present it this year, the Board of Direction has approved format and schedule changes for 1980.

At its meeting on Nov. 1, 1979, the Board approved a plan to publish the JOURNAL every other month in a larger size. The magazine-size JOURNAL (about 8 x 11 in.) will be typeset and contain in six issues the same papers that would have been published in twelve small issues.

The first issue with the changed look, January-February 1980, is scheduled to be mailed by early February to all members and subscribers. Subsequent issues will be mailed every other month after that.

Saving in binding and mailing costs realized from bimonthly publication, and saving from producing a larger magazine on high-speed equipment not available for the small size, will allow the JOURNAL to be typeset and still reduce total cost.

Remember--there will be no JOURNAL in January, but a double issue in February and in alternate months after that.

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Pertinent discussion of papers in the December 1979 ACI JOURNAL will be published in the October 1980 JOURNAL, along with authors' replies, if discussion is received by June 1, 1980. Discussion received after this date will be considered individually for publication or private response.

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Papers appearing in the ACI JOURNAL are reviewed according to the Institute's Publications Policy by individuals expert in the subject areas of the papers.

Disc. SP 58-19/From Polymers in Concrete, International Symposium, p. 329

Optimum Polymer Content in Concrete Modified by Liquid Epoxy Resins. Paper by Edward G. Nawy, Maurice M. Ukadike, and John A. Sauer

By R. A. BAREŠ[a]

The natural endeavor of the development of concrete technology is to improve some relatively unfavorable properties of this material, particularly its low tensile strength and the low resistance to external environment. Apart from a number of methods of improvement of the quality of portland cement concrete, which can be called conventional and consist particularly in the improvement of its workability while reducing the water-cement ratio (by an admixture of surface-active admixtures, plasticizers, etc.), improvement of the effectiveness of working to attain higher density, painstaking selection of components (to insure better distribution of internal structural stresses), etc., the development of macromolecular chemistry initiated the endeavor to improve the properties of cement concrete by its modification using plastics. The oldest and most widely used (although of still not entirely explained mechanism of behavior) are the modifications of the fresh concrete mix by thermoplastic polymers and latexes (PCC), and, in recent years, the impregnation of hardened concrete (PIC), mostly by thermosets. Apart from that, there originated and continuously expand the materials without portland cement in which the granular aggregate structure is bonded exclusively with plastics (PC), mostly thermosets.

From a number of criteria and requirements imposed on the properties of plastics admixtures to cement concrete, on the properties of cement and aggregate, and on the methods of working and curing, which have already been described many times, I should like to accentuate one extremely important factor: the compatibility of the admixture with cement paste. It is, for example, quite clear that no improvement can be attained by an admixture which is sensitive to alkali hydrolysis brought about by cement. It is equally clear that any admixture whose polymerization is inhibited or negatively influenced by water present in the cement paste or any other component of the system, is necessarily unsuitable.

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The summation of many experimental results (from bad to excellent) has really shown that a number of admixtures do not serve to build up a secondary structure or to improve the properties of cement paste, acting merely as a means enabling the reduction of the water-cement ratio and the improvement of workability. This tendency can be observed also from the changes of the slump of various mixes observed by the authors: the slump depends on the sum of both liquids in the system (epoxy resin plus water) and on the plasticizing effect of the resin (Fig. A) and does not exceed the limits customarily found for cement concretes. In this respect the authors' experiments can be considered rather as a traditional method of concrete quality improvement, although attained by new materials. Only very few admixtures have been proven to improve the microstresses (which are reflected in the resultant properties), e.g., by improving the homogeneity of the stress field at the phase interface resulting from an improvement of the bond of cement stone and aggregate; the cases of proved improvement of the cohesion properties of the cement paste itself are rare and the cases of origin of an entirely independent secondary continuous structure fostering the improvement of the resulting material are unique.* This applies to the admixtures of polymers as well as monomers, polymerizing during the hydration of cement.

The authors, together with others (A, B, C) express a very optimistic view of the admixture of epoxy resin to cement paste, accentuating the improvement of the strength in comparison with control samples. However, the problem can be considered also from the opposite point of view. If we take the properties of neat PC (i.e., without the presence of cement paste) as initial state (100 percent), we can see that any presence of water is unwelcome and means a reduction of strength; moreover, the admixture of cement beyond the limit permissible in the system for microfiller, has also a negative effect. Naturally, the unfavorable effect of water can be limited, to a certain extent, by a suitable selection of the hardener or the method of processing; the unfavorable effect of the water in the system is also somewhat suppressed by the fact that the induced water is partly consumed for the hydration of the microfiller, viz., cement.

On the other hand, it can be observed that also an admixture of epoxy resin to cement concrete has a rather negative effect on the hydration of cement and the formation of dense cement stone structure (which can be best observed in the mixes with good workability, with a higher water-cement ratio). In the mixes with a low

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*At the conference on "Polymers in Concrete," London, 1975, W. O. Nutt expressed his many years of experience with polymer admixtures by the following incisive words; "I have come to the conclusion, after some 32 years of playing with polymer emulsions, that really the polymer composition is irrelevant. Really, exactly what the chemistry of the polymer is has nothing to do with the result you get. You can add old boots, providing they are strong enough!"

water-cement ratio, a small improvement of strength can be due primarily to the improvement of their density as a result of better workability: epoxy resin affects the mix as a lubricant, a (very expensive) plasticizer. Apart from this effect in the initial phase of cement setting the resin binds the individual hydration centers, thus making an impression of a certain increase of strength as compared with control samples.

If the system contains that much epoxy resin that it can form a continuous structure, it takes the load-bearing function on itself; such system can be assessed as a PC impaired by the presence of cement paste (and particularly of the water in it). The system with the same quantity of epoxy resin (with regard to the filler) in the absence of water will always afford a higher strength than in the mixture with cement paste, if the mix is perfectly processed (D) (Fig. B). Only if no continuous epoxy structure forms (because of the shortage of epoxy resin in the mix) does the cement structure take over the load-bearing function of the system; this cement structure may be impaired by the presence of the particles of the epoxy polymer or oligomer.

It is obvious from these considerations that it is equally possible to take an opposite view from that taken by the authors and consider the admixture of epoxy resin in cement concrete as unsuitable for the mutual incompatibility of both binders. For the assessment in this respect some conclusions ascertained by the authors are not surprising; for instance, a certain reduction of strength for p/c = 0.8 in comparison with p/c = 0.6 is a phenomenon observed a long time ago, and due to more unfavorable internal primary stresses of the system in the first and the second structural zone as compared with the third zone (D); some phenomena are caused or accentuated by an excessive quantity of microfiller (cement) in the granular system; a small change of the porosity of such systems; the pores of the systems with cement structure not filled with epoxy resin (low p/c); etc.

In my opinion, there is only one way to make epoxy resin cooperate actively with cement paste and achieve some discernible contribution. It is the way selected by the authors which lies in the method of working of the mix: the mixing of dried filler with resin (to envelop the filler particles with a thin resin film) and only afterwards to mix these particles with cement paste. It is actually a multiple microapplication of connecting fresh cement paste with hardened concrete (or aggregate) (E), which can improve particularly the tensile strength as a result of an increase of the bond energy between the filler and cement paste. Such material, however, can be hardly considered as "concrete modified by liquid epoxy resin" in the exact meaning of this term.

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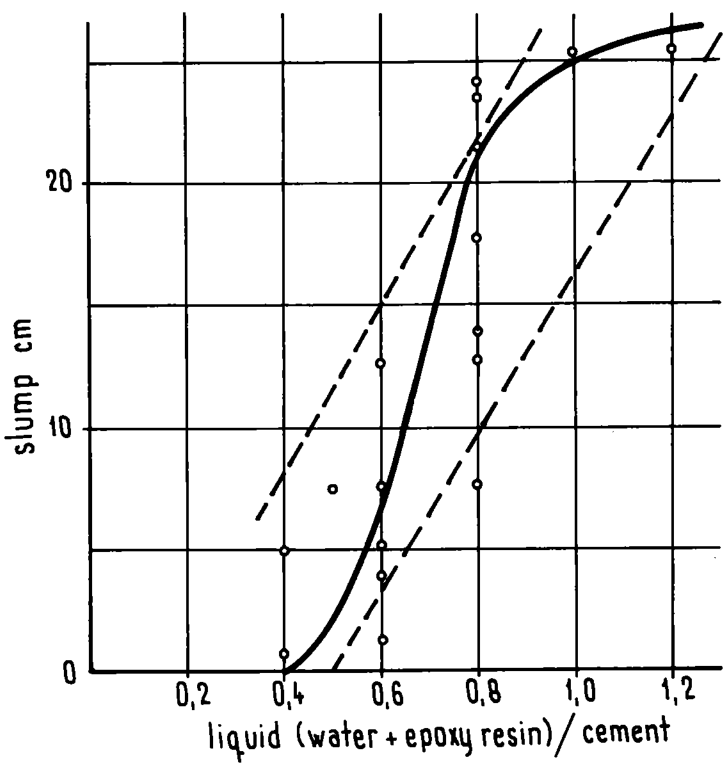

Fig. A--Slump plotted against the quantity of liquids (according to the authors' test)

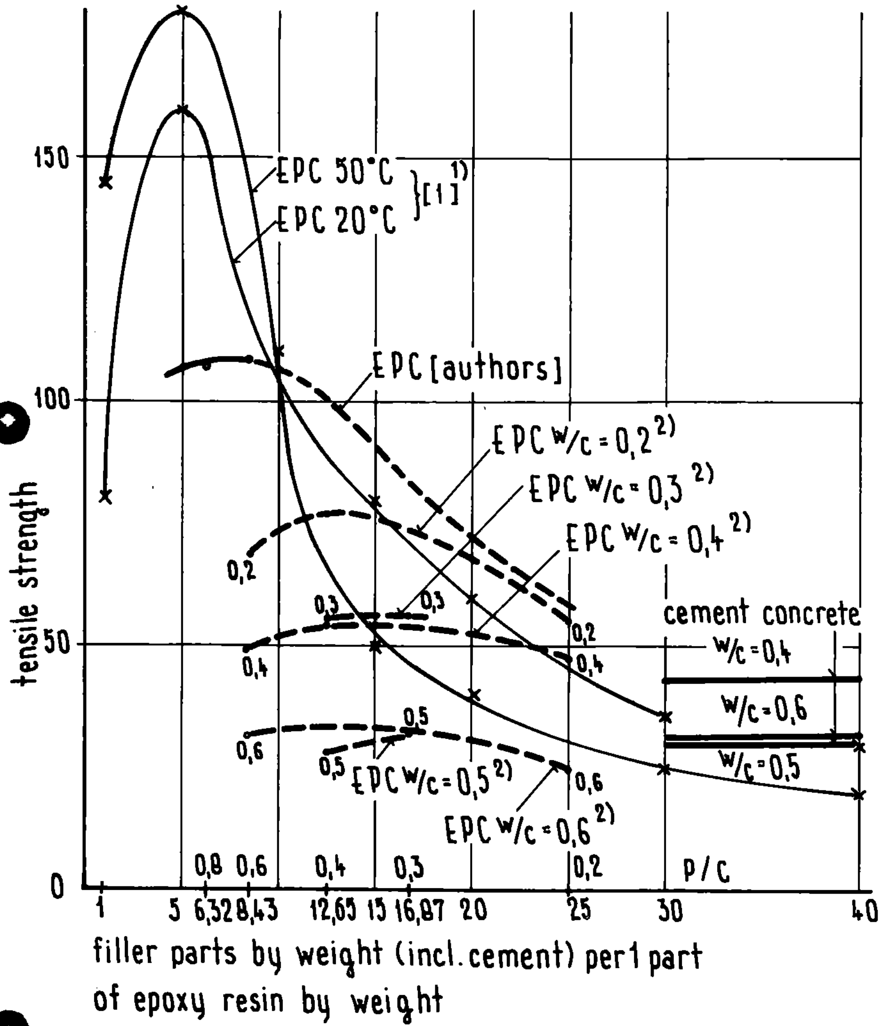

Fig. B--Tensile strength plotted against the epoxy resin-filler ratio (according to the authors' tests and Reference D). (1) flexural tensile strength (without microfiller (Reference D). (2) tensile splitting strength (microfiller = cement) (authors)

AUTHORS' CLOSURE

The authors are grateful to Mr. Bareš for his lengthy expose on polymer-modified concrete. A great deal has been written about the various types of polymer materials that can be developed and it is generally known that apart from its use in the impregnation of cast concrete, polymers may be used as a binder to make polymer concretes or as modifiers to make polymer-modified concretes. Where the polymer is the binder, cement may or may not be used as a filler.

For the purposes of our investigation, one may think of polymer cement concrete and ordinary concrete as existing on opposite ends of a spectrum. Between them is a material having a range of properties depending on the relative contents of cement, water, and polymer.

Investigations have shown that it is possible to continuously change ("modify") the properties of concrete from that of ordinary concrete to that of polymer concrete. Thus the term polymer-modified concrete.

It is, of course, quite valid to view the spectrum from the opposite end, as Mr. Bareš has done, and look on the subject as one of modifying polymer concrete by the addition of cement and water; a study that is also relevant from the point of view of reduction of setting time and cost, and improvement in workability.

If one were merely concerned with obtaining the maximum strength (disregarding the problem of cost, mixing, and placing), a suitable blend of sand and stone aggregates could be mixed with the polymer to get a "neat" strong polymer concrete if cement is added. The authors are aware of the numerous research efforts in this direction.

The objective of this investigation, however, was to examine the materials that exist between polymer cement concrete and cement concrete. Specifically the questions that were posed are: (1) which polymer material is most suited to cement concrete modification?; (2) how does the content of polymer or water affect the properties of the polymer-modified concrete?; and (3) what are the reasons for the observed phenomenon?.

Polymer-cement-water mixes containing little water and a p/c ratio of over 0.6, which fall into the category of polymer cement concrete, have very short setting times and a tendency to adhere to all surfaces, making them difficult to work with. The mixes with over 1.0 total liquid-cement ratio have excessive slump.

The authors considered the practical significance of these results too obvious to warrant any further elaboration. To obtain a polymer material that can be used extensively in construction with conventional tools, a certain amount of water is necessary. In addition, polymer and water contents must be kept within certain limits.

Several experiments by the authors and many others have shown that for any improvement in mortar or concrete to be obtained by the addition of a polymer, the polymer must be compatible with cement components as well as the products of cement hydration. It is therefore disturbing to the authors to read Mr. Bareš's quote "... really polymer composition is irrelevant." It is quite clear at this time that only a fraction of the existing polymer materials satisfy the criterion of compatibility with cement paste. We believe that the polymer system used in this study is one of them.

Mr. Bareš pointed out that the presence of "free" water in polymer concrete is unwelcome. The same is true of ordinary portland cement concrete. The extra water generally used in these mixtures is necessary to obtain adequate workability. The ideal situation or the optimum strength condition is obtained when there is no free water in the system and sufficient workability still exists.

The authors' data as well as Mr. Bareš's show that PMC's or "neat" polymer concrete's (PC) strength increases with increasing polymer content (decreasing filler parts by weight per 1 part of epoxy resin by weight, Mr. Bareš's Fig. B) to a maximum, then begins to decline with further addition of polymer. So without getting into the chemistry of the polymer or cement reactions, it can be stated that excessive polymer is detrimental to both PMC and "neat" PC. Obviously the decrease in density as a result of increased liquid (polymer) content more than offsets any increases in bonding forces due to the additional polymer. This explains the decrease in strength observed when the polymer is added to concrete or polymer concrete that already has a high liquid content (e.g., w/c, of 0.6 or p/c = 0.6). The decrease is not due to the polymers inhibition of cement hydration.

If the polymer interfered with cement hydration, a decrease in strength on its addition to the mix of w/c = 0.4 and p/c = 0 should also occur. This is not the case. There is, instead, an increase.

The authors and Mr. Bareš are in agreement that polymer in the mixture aids strength gain by permitting a reduction in the water content. However, the authors feel that additional strength is gained from the stress-relieving action of polymer fibers where they bridge microcracks in the PMC mass. The latter distinguishes the polymer from the other additives (plasticizers, etc.) and accounts for higher strength gains and other property improvements recorded by its use.