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DEVELOPMENT OF THERMALLY STABLE POLYMER CONCRETE

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Development of Thermally Stable Polymer Concrete

by

Taha Nasr El Din Megahed*, L. E. Kukacka, and J. J. Fontana

1. Introduction:

This work pertains to the development of a polymer concrete type that is thermally stable under working temperatures of 200° to 300°F. This material is highly durable and thermally stable with high flexural strength and ductility. Its consistency, while fresh, is suitable for both casting in place or precasting techniques.

Several optimization stages were applied ranging from mixing ratios and type of aggregate to resin formulation itself. An optimized range of mixing ratios is developed along with optimized mix ingredients, relating mechanical performance to elevated temperature at various degrees of workability.

2. Materials Used:

The aggregates used were made up by blending one of four course aggregates with sand. They were irregular gravel (G), a crushed limestone (L), and two crushed basalt stones B-1 and B-2. Silica powder was incorporated as a filler. The particle size distribution and gradings of the used aggregates are given in Table 1. Dispersed corrugated steel fibers with an aspect ratio of 20.0 and a length of 1-1/2 in. were used at 8% of the mix weight unless otherwise mentioned.

The resin system consisted of styrene (ST) and trimethylolpropane trimethacrylate (TMPTMA) monomers. Low and high-temperature-activated benzoyl peroxides were used as initiators, BFF-50 and DTBP. In addition, dimethyl aniline (DMA) was used as an accelerator and a silane coupling agent Al74 was also added. A thickening agent in the form of solid polystyrene (PST) was also incorporated. This resin system was principally based on earlier research findings made at the Brookhaven National Laboratory.(1)

3. Optimization of Mixing Ratio:

In this work, the weights of aggregate, filler, steel fiber and resin in the unit volume of fresh PC are identified as A, F, S and R, respectively. The ratios R/F and A/F are termed as the coefficient of mix richness (x) and coefficient of aggregate content (y), respectively. Using constant coarse and fine aggregate gradings, Table 1, the grading of all aggregate mixtures used were defined by the grading index I which is the coarse fine by weight.

For a fixed fiber content, a constant resin formulation and a specific type of aggregate, the mix variables can be reduced to x, y and I which uniquely define the mix. To evaluate the effect that x, y and I might have on the strength and the workability of the PC, 36 different mixes were investigated. These correspond to three values of I (0.4, 0.6 and 0.8), and three values of y (3.0, 4.0 and 5.0), each of which had four values of x ranging from 0.25 to 0.95.

Throughout these 36 mixes, one fixed resin formulation was used as shown in Table 2-a. The coarse aggregate used in all these mixes was irregular gravel (G). The full mixing ratios are given in Table 3. The steel fiber content was kept constant at 8%.

For each mix, eight 2.5 in.-diam x 5.0 in. cylinders and two 2 in. x 2 in. x 12 in. beams were cast, vibrated, cured at room temperature for 24 hr, then postcured at 300°F for four hr. Four cylinders from each mix were used in splitting tensile tests at room and elevated temperature. The beams were supplied with end pins for the measurement of coefficient of thermal expansion in accordance with ASTM standards.(2)

Cylinders to tested at elevated temperature were kept at 210°F for 24 hr prior to testing. After first taking reading at room temperature, the beams were subjected to each of the test temperatures for 24 hr before another reading was made.

3.1. Strength Results and Their Interpretation:

The average values of splitting strength at ambient and elevated temperature were plotted against (x), and the results are shown in Figure 1. Each of the family of curves represents a certain I -value, whereas within the same family three pairs of curves are produced representing three values of y . Each pair of curves represents the splitting strength- x relationship at room and elevated temperature.

The splitting strength was found to be inversely related to x within certain limits. As the value of x increases the strength decreases until a certain x -value is reached. Above this value, bleeding occurs and results in a reduction in the actual value of x and an increase in strength, particularly at low values of I or high values of y .

While handling these mixes, a visual inspection of workability showed that some of them did not have acceptable workability, i.e., too harsh or too sloppy. A qualitative definition of workability was established for use in this work, a low-workability (LW) mix and high workability (HW) mix. A LW defines a stiff-plastic mix suitable for casting shallow elements with or without light steel reinforcement and that need heavy mechanical vibrations. The mix could be used for slabs and shallow foundations. A HW defines an elastic mix suitable for casting plain narrow elements or heavily reinforced shallow ones that need moderate to slight vibration.

Based on these definitions, a workable range of x -values spanning from LW to HW was established for each of the 18 curves given on Figure 1. Within this range, the splitting strength is inversely related to x either at room or elevated temperature. The strength decreases by 15 to 20% as the I value is increased.

Values of x near the limits approaching LW and HW were extracted and the plotted data against their respective Y -values. These results are given in Figure 2-a. Each of these curves represents a given I and degree of workability. A direct relationship between x and y is evident, however, this dependency is more pronounced at high values of Y and I . Also Figure 2-a indicates

that using coarser aggregate permits higher values of y at the same x and workability, which implies a more economic mix. Furthermore, at high values of y , the workable range of x is wider which means a wider range of mixing ratios to choose from. Generally, an increase of 50% in x -value, at any y and I is sufficient to change the degree of workability from LW to HW.

Using the same approach, values of splitting strength corresponding to extreme workable values of x , were taken from Figure 1 and plotted in Figure 2-b against their respective values of y . Each of the derived 12 curves Figure 2-b represent a given workability and a certain I value at room or elevated temperature. All the curves indicate that the splitting strength is reduced at any y and I values when the mix workability is increased from LW to HW. This reduction ranged from 15% to 20%. At the same workability and y -value, splitting strength can be increased by about 10% by increasing I (using coarser aggregate). The most significant feature shown in Figure 2-b is that there is a favorable range of y -values from 3.5 to 4.5, at which highest splitting strength is reached irrespective of other mixing variables.

Similarly, values of R corresponding to workable values of x were calculated, and the results were plotted against x (see Figure 2-c). Again, each of the curves in this figure represent a specific I -value and a degree of workability. It is evident from these curves that there is a minimum resin content $R_{\min}$ corresponding to a specific x -value, x_{sp} . At this $R_{\min}$ and x_{sp} , y value is 4.0 irrespective of I or workability. Joining these points on X - R curves gives an almost straight line that identifies the X - R relation for highest splitting strength. Points of lower values on this line represent LW mixes, while higher values represent HW mixes. For more practical mix design, a range of optimized y -values ranging from 3.5 to 4.5 is used rather than a single value of $y = 4.0$. This yields an optimized mixing zone bound between lines 1 and 2 in Figure 2-c.

3.2 Measurements of Thermal Expansions and Their Interpretation:

The average values of thermal expansion, e_t , for mixes 1 through 18, were plotted against the test temperature $T(^{\circ}\text{F})$, and the results are shown in Figure 3. Note that groups denoted a, b and c represent mixes with $I = 0.4$

at $y = 3.0, 4.0$ and 5.0 , while groups d and e are for $I = 0.6$ at $y = 3.0$ and 4.0 . The different e_t - T relationships within each groups represent definite mixes corresponding to a given value of x .

Each of the given e_t - T curves, were plotted as a bilinear function with the two slopes giving coefficients of thermal expansion, to a proper scale, below and above the heat distortion temperature HDT. They are termed here as k_1 and k_2 , respectively.

The derived values of k_1 and k_2 are surprisingly small and as shown in Table 4, they varied from 4×10^{-6} to $5.2 \times 10^{-6}/F^\circ$ below the HDT, and 5.5×10^{-6} to $7.0 \times 10^{-6}/F^\circ$ above the HDT. The plotted e_t - T relationships indicate that increasing y helps reduce both k_1 and k_2 , particularly at low values of I (fine aggregate). However, for the same I and y , the coefficient of thermal expansion increased moderately with increases in x . Mixes with excessively high x -values showed a reduction in their expansion values probably due to bleeding and the consequent reduction in the actual x -value.

In general, it is concluded that the resin system itself is the main contributor to the thermal stability and the measured values of k_1 and k_2 . This conclusion is based on the results which indicated that none of the mix variables had a significant influence on the recorded values. To verify this conclusion, a set of specimens were prepared to assess the effect of steel fiber content on thermal expansion. In this set, six different mixes that had identical values of x , y , and I as those of mix (6) were used. They differed only in steel fiber content which was varied from 0 to 10%. For each of these mixes, three beams were prepared for thermal measurements as before. Their e_t - T relationships are presented in Figure 4. The same pattern of bilinear functions was found and in general values of k_1 and k_2 are inversely related to S . As given in Table 5, values of k_1 and k_2 decreased from about 5×10^{-6} and $9 \times 10^{-6}/F^\circ$ at zero steel content to 3×10^{-6} and $5.5 \times 10^{-6}/F^\circ$ at $S = 10\%$. Both k_1 and k_2 values are plotted against S in Figure 5, and the results indicate that the fiber content has more effect on the k_2 -values. The k_1 value is only influenced at high values of S . Since the previously defined working

temperature of the PC under development is near the HDT, it can be concluded that only S values in the vicinity of 8% or more can help reduce k_1 . Once again, the values of k_1 and k_2 for specimens without fiber, indicate that the resin system has excellent thermal stability. Both k values are very much comparable to those of cement concrete and steel reinforcement.

4. Optimization of Coarse Aggregate Type:

Using resin formulation as given in Table 2, and the previously mentioned four types of coarse aggregates, G. L. B-1 and B2, four mixes were prepared using the mixing ratio of mix No. 30 of Table 3. The choice of the best type of coarse aggregate is based on its contribution to the mechanical properties and thermal stability.

For each type of aggregate, 18 2.5 in. x 5.0 in.-cylinders and three 2 in. x 2 in. x 10 in.-beams were cast and allowed to cure at ambient temperature for 24 hr. They were then post cured for four hrs at 300°F and cooled at room temperature. The cylinders were tested in splitting at room and elevated temperature (210°F), nine cylinders for each mix. The beams were tested in third-point-flexure at room temperature (75°F).

The average results from both tests are given in Table 6. The traced load-deflection diagrams for the four mixes are given in Figure 6 after being averaged out. The data indicate that the type of aggregate did not have any significant effect on the splitting strength either at room or elevated temperature. At the elevated temperature, the splitting strength is reduced about 15% on average.

On the other hand values for the modulus of rupture showed a clear dependency on the type of the aggregate used. As shown in Table 6, mix G gave considerably lower values than the other mixes which used crushed stones for a coarse aggregate. On average, a relative increase of 17.0% in modulus of rupture was obtained just by replacing the gravel with any of the three crushed stones used. Also, a comparison of the respective values of splitting strength and modulus of rupture shown in Table 6, indicates a relative increase in the

increase in the latter by about 5% for the G mix, and about 15 to 20% for the other mixes. However, the elastic flexural strengths for the four mixes measured at the first-crack, showed no differences. This suggests that any real contribution the crushed stones make to the flexural strength takes place only beyond elastic loads which implies an enhanced ultimate carrying capacity and consequently an improved factor of safety. This accounts for the comparable values of the flexural moduli of elasticity for the four types given in Table 6. As for ultimate deflections and the consequent flexural ductility, the derived values in Figure 6 show little, if any, effect of the type of aggregate. Previous work by Fontana⁽³⁾ suggested that flexural ductility is very much improved and controlled by the incorporation of dispersed steel fibers.

For further assessment of the effect of these types of aggregates on the thermal stability, and as strength deterioration of the four types were alike, comparison of thermal expansion was imperative. Three beams of 2-in. x 2-in. x 12-in. were prepared for each of the four mixes. These beams were cured only at room temperature, and then subjected to different testing temperatures without any post curing. In doing so, the effects of both aggregate type and curing temperature on the linear coefficient of thermal expansion, could be evaluated. The effect of aggregate type was evaluated by simply comparing the results of thermal measurements for the four mixes, while the effect of curing was assessed by comparing values of k_1 and k_2 for the G-mix to a similar mix that was post-cured [mix (5) in Table 4].

The averaged bilinear functions of e_t -T for the four mixes are plotted in Figure 7, and their derived values of k_1 and k_2 are given in Table 7. These results indicate that the type of aggregate has an appreciable effect on thermal expansion. Mix B-2 displayed the lowest k_1 value while the G-mix had the highest value. Hence, angular and rough crushed stones appear to have a restraining influence on thermal expansion.

It is worth mentioning that a comparison of the values of k_1 and k_2 for mix G which was not post cured (see Table 7), to those from a similar mix that was post cured (mix 5 in Table 4) shows that curing at elevated temperature has an insignificant effect on thermal expansion, and it is the resin system itself that is maintaining these low values of thermal expansion.

5. Optimization of Resin Formulation as Related to Manufacturing Techniques:

PC generally suffers excessive setting shrinkage strains and for successful use of such PC in construction, these strain must be minimized. This is in addition to the high thermal sensitivity of PC that constitutes a serious limitation in certain applications. In an attempt to minimize shrinkage strains, the effects of the addition of a thickening agent and a high temperature-operable peroxide were examined as related to different curing conditions.

5.1. Control of Setting Shrinkage Strains:

One mixing ratio, mix No. 9 in Table 3, was used to cast four mixes differing only in resin formulation. In this formulation, the polystyrene (PST) ratios by weight of resin were zero, 2.8%, 3.4% and 4.2%. The four resin formulations are listed as b, c, d, and e in Table 2. Immediately after filling the mold box of the shrinkage measurement device with the fresh mix, automatic recordings of the setting strains and the exotherm were made. The results for the four mixes are shown in Figure 8-a, b, c, d. The shrinkage measuring device was designed by the DuPont Company and was built and calibrated at Brookhaven National Laboratory.

All mixes showed early expansion strains, then started to shrink at the time the peak exotherm was reached. At 2.8% PST, the final net strain was about 0.0002-shrinkage, while at 3.4% PST, the final strain was expansion of about 0.00015. Higher PST ratios gave higher final expansion strains, which at 4.2% reached 0.0004. On the other hand, it is clear that the mix without PST, Figure 2-d, had excessive shrinkage strain to the extent that measurements had to be terminated after about one hr at which time the recorded shrinkage strain was 0.003. By simple extrapolation, a PST-ratio of about 3.15% of resin

weight should give a stabilized mix with zero final setting strains. Another effect of the addition of PST is that it reduces the exotherm of the fresh PC mix slightly and shortens the time required to reach the peak exotherm. This simply implies that the resin reactivity is reduced by the addition of PST.

5.2 Effect of optimized PST ratio on the mechanical performance of PC:

The previous findings showed that without the addition of PST, extremely high shrinkage strains take place after the mix is hardened. On being restrained, these strains cause internal tensile cracks or matrix flaws that might seriously affect the mechanical performance.

Using mix No. 30 of Table 3, and B-2 type aggregate four mixes 1, 2, 3 and 4, were prepared using four different resin formulations as given in Table 8. Eight cylinders for each mix were cured at 210°F (99°C) for four hr immediately after casting, then cooled to room temperature. Four of the cylinders were tested in splitting at room temperature, the rest at 210°F (99°C). The recorded splitting strength values of the mix given in Table 9 which did not have DTBP nor PST, were used as reference values. The addition of DTBP gave a slight increase of about 5% (Mix No. 3), while the addition of PST gave a relevant increase of about 25% (Mix No. 2). Mix No. 1 which had both DTBP and PST gave an increase of 30%.

These data which are summarized in Table 9, show clearly the significant contribution of PST to the splitting strength and they indicate that the thickening agent contributes more than just reducing shrinkage strains. On the other hand, the high-temperature peroxide did not help to improve the strength either at room or elevated temperatures.

5.3 Effect of curing conditions:

To this point in our study, all specimens had been cured at room temperature and then post-cured at 210°F (99°C) for four hr. This postcuring condition was based on some exploratory measurements carried out at the outset of this work. However, with the addition of PST and DTPB, a wider range of curing conditions had to be explored in order to determine the most suitable conditions for the highest possible mechanical performance.

5.2.A Curing condition for precasting:

For precasting, usually the main goal is to set the most favorable curing conditions that will yield the highest ratio of performance/energy consumption rates. Based on the previous optimization studies, a mix was chosen at $X = 0.5$, $Y = 4.0$, and $I = 0.8$, using B-2 aggregate and the optimized resin formulation 1 given in Table 8. Thirty-two 2.5-in. diam x 5-in. long cylinders were cast and cured at room temperature for as short a time as was necessary for demoulding. They were then divided into four groups numbered 1 through 4. Groups 2, 3 and 4 were double cured for four hr at 210°F, 300°F, and 350°F (99°, --°, --°C), while Group 1 was kept at room temperature. Each of these groups were then divided into two subgroups for testing in splitting and compression at ambient temperature.

The results are given in Table 10, and they show that curing at elevated temperature increases the strength compared to that of samples cured at room temperature. This increase was about 35%, and was almost the same for the different elevated curing temperatures. It seems that a curing temperature of about 200°F (--°C), when combined with the exotherm, is sufficient for the dual-peroxide polymerization system.

After selecting a curing time of 4 hr and a curing temperature of 210°F (99°C), as the best curing condition, two additional groups of specimens were made from the same mix but without DTBP. These groups are identified as No. 5 and 6 in Table 10. Group 5 was cured at room temperature, while Group 6 was post-cured as before. Both groups were tested in splitting at room temperature and, as shown in Table 10, their results are very similar to those of Groups 1 and 2. This once again indicates the slight, if any, improvement in strength at room temperature by incorporating DTPB in the resin.

As said earlier, the addition of DTBP had no clear cut effect on strength deterioration at elevated temperatures. To verify this effect, three groups, nine cylinders each, were cast using Mix No. 30 of Table 3. Groups 1 and 2 continued resin formulation a given in Table 8, while Group 3 had that of formulation. The three groups were cured at 210°F (99°C) for 4 hr, then tested at room, 210°F (99°C) and 300°F (150°C). Groups 1 and 3 were tested in splitting while Group 2 was tested in compression.

The results from these three groups are given in Table 11. Splitting and compressive strength deterioration reached about 24% and 20%, respectively, for Groups 1 and 2 that had a dual-peroxide. Almost the same percentage of deterioration was found with Group 3. Similarly, at higher temperatures, 300°F (150°C), the deterioration in splitting strength of Group 1 and 3 was about 30%. This similarity in strength reduction confirmed the little contribution DTBP might have either in strength development or deterioration. It has to be noted that the reduction in strength at 210°F (99°C) recorded with these mixes is relatively high when compared to previous reductions of about 15-20% recorded with early mixes made without PST or DTBP. This implies that the additional increase in splitting strength at ambient temperature due to the incorporation of PST and/or DTBP, is almost lost completely at elevated temperatures.

To identify the most beneficial curing time as related to curing temperature, different curing times were tried at 210°F (99°C) and 300°F (150°C). For double curing at 210°F (99°C), six curing times were chosen: 1, 2, 4, 6, 8 and 24 hr. At 300°F (150°C) the curing times were 4 and 8 hrs. For each of these curing conditions, 8 cylinders were cast using mix No. 30 of Table 3 and resin formulation 1 of Table 8. A control set of 8 cylinders that were cured at room temperature was also prepared from the same mix. All of these cylinders were tested in splitting at room temperature and 210°F (99°C).

The test results, table 12, indicate that neither curing time nor curing temperature had any significant effect on the strength recorded at room temperature. A curing time of one hr at 210°F (99°C) gave almost the same strength at room temperature as any other curing time and temperature. The only difference was in strength deterioration, where higher values of curing times or temperatures gave slightly less strength deterioration at elevated temperature. Also, it was noted that specimens cured at room temperature, increased in strength after being stored at 210°F (99°C) for almost 20 hr. The elevated temperature clearly enhanced the polymerization process and the strength was relatively improved.

5.3.B Curing conditions for casting in place:

The suggested working temperature for which the present PC was developed is about 200°F. Thus, the following tests were carried out to simulate this working temperature and to determine the rate of strength development.

Twenty-four cylinders of 2.5-in. diam x 5.0-in. long were cast using mix No. 30 of Table 3, B-2 type aggregate and resin formulation 1 of Table 8. These specimens were stored at 210°F (99°C) from immediately after casting until testing at the same temperature in splitting and compression at different ages; 8 hr., 48 hr. and 7 days (8 cylinders each). For evaluating the effect of the addition of DTPB, the same mix but without DTBP was used for casting eight cylinders. They were similarly cured at 210°F for 8 hr. and 48 hr. and tested in splitting at these ages and at the same temperature.

Results from the 40 cylinders are given in Table 13. Both splitting and compressive strengths had very little dependency on time duration at 210°F (99°C). While the compressive strength values were almost constant for the three testing times, those of splitting strengths showed some improvement, rather than deterioration, at longer times. Similar behavior was found with zero-DTBP mixes. In both cases, an increase of about 10% in splitting strength occurred as the exposure time was increased from 8 to 48 hr. After 48 hr. the rate of splitting strength development was almost zero and no variation took place. On the other hand, slight deterioration took place in the compressive strength as the exposure was time increased. This implies that splitting strength benefits more from exposure time than compressive strength.

The above results are contradictory to the 25% deterioration in splitting strength at 210°F found in previous tests on precasting, in which specimens were double cured, allowed to cool, then exposed to elevated temperatures for almost 20 hr before testing. This suggests that as long as the curing temperature is maintained continuously, the strength development will continue until the polymerization reaction is completed.

This deterioration took place when specimens were allowed to cool and then exposed to elevated temperatures which in such a case would loosen the polymerized crosslinked matrix rather than help further polymerization.

However, it should be noticed that the absolute values of splitting strength recorded in this set of specimens, Table 13, are considerably lower than those of Table 12 which were recorded at room temperature. This suggests that while continuous curing at elevated temperature is more effective for elements under elevated working temperature, double curing for almost one hour at 210°F (99°C) is more effective for elements under normal ambient working temperatures.

5.4 Effect of fiber type and content:

So far, all the previous mixes used 8% of corrugated steel fiber 1 1/2-in. long and with an aspect ratio of 20. As stated previously, this value of 8% was reached in other work⁽³⁾ to meet ductility requirements for PC structures subjected to dynamic loads.

In the present work, this 8% concentration gave reasonable values for the coefficients of thermal expansion as well. However, to evaluate the effect of fiber type itself, another 1.0-in. long hooked steel fiber with an aspect ratio of 60.0 was examined. Using this steel fiber and mix No. 30 of Table 3, with B-2 aggregate type and resin formulation 1 of Table 8, two mixes were prepared at two different steel fiber contents, 4% and 8%. For each mix, twelve 2.5-in. diam x 5.0-in. long cylinders were cast. They were immediately cured at 210°F for 4 hr, then allowed to cool. Splitting tests were conducted at room, 210°F (99°C) and 300°F (150°C). As shown in Table 14, with 8% fiber, the splitting strengths were found to be only slightly higher than those of samples containing the corrugated steel fiber mixes. This slight increase in splitting strength cannot be justified economically since the hooked-type fibers cost twice as much as the corrugated type.

At a 4% concentration of the hooked type, same cost as 8% of the corrugated type, the splitting strength was almost 25% less, at any testing temperature, than the respective value at 8%. This is shown in Table 14. Comparison of values of the splitting strength of samples containing 8% of the corrugated type with those containing 4% of the hooked type shows a decrease of about 15% caused by the latter. This confirmed the viable use of the corrugated steel fiber and precluded any potential benefit by the use of the hooked steel type.

6. Conclusions:

For the chosen resin system and the mixing ingredients investigated in this work, the following conclusions were reached. They are applicable to to all PC mixes lying within the workable mixing ranges discussed previously.

1. For a given aggregate grading, the highest strength mix is one that has the lowest possible mix richness (X), i.e., the lowest resin: filler ratio. This ratio is directly related to the aggregate content at a given workability. However, using a coarser aggregate grading allows for an increase in aggregate content at the same mix richness X without impairing workability; this means a more economic mix.

2. The workable mixing range is wider at higher aggregate contents at any grading. A relative increase in mix richness X of about 50% is required to change a low workability mix to a high workability mix, at any aggregate content and grading.

3. The strength is increased by increasing the grading index (using coarser aggregate) at the same aggregate content and degree of workability; this increase can reach 10%.

4. At the same aggregate content and grading, the strength is decreased by 15-20% if workability is changed from low to high by increasing X.

5. Irrespective of aggregate grading or degree of workability, the highest strength is reached at a favorable aggregate content $Y = 3.5$ to $Y = 4.5$.

6. There exists a definite minimum resin content (R_{min}) corresponding to a specific mix richness (X_{sp}) at which the highest strength is reached for given aggregate grading and degree of workability. The relationship between R_{min} and X_{sp} is a linear function with its small values representing low workability mixes and its high values representing high workability mixes. The lowest point of this linear function is $X_{sp} = 0.39$ and $R_{min} = 6.7$ for $I = 0.8$ and low workability, while the highest point is $X_{sp} = 0.65$ and $R_{min} = 10\%$ for $I = 0.4$ and high workability.

7. Strength deterioration of the developed PC-mixes without PST at 210°F (99°C) is in the order of 20%. This value is slightly higher for coarser aggregate mixes. The addition of dual peroxide has little effect on strength deterioration as well as curing condition. However, samples cured at high temperatures (300°F , 150°C) for long times seem to suffer less deterioration. The strength deterioration is directly related to the degree of applied temperature. Specimens exposed to 300°F (150°C) suffered as high as 30% deterioration.

8. The values for the coefficients of thermal expansions are comparable to those of steel and cement concrete. Mix variables other than resin formulation have moderate effect on thermal expansion. Increasing mix richness or decreasing aggregate content slightly increase this expansion. Dispersed steel fiber considerably affects the thermal expansion and can result in a decrease of about 40% at fiber contents of about 8 to 10%. Generally, the measured coefficients of thermal expansion have two distinct values, below and above heat distortion temperature, of about $5 \times 10^{-6}/^{\circ}\text{F}$ and $7 \times 10^{-6}/^{\circ}\text{F}$.

9. Crushed stone aggregates improve more effectively the modulus of rupture of the mix. An increase of 17.0% was reached when crushed basalt was substituted for gravel. The modulus of rupture is higher than splitting strength by about 15% for crushed stones-mixes. This increase is only about 5% when gravel is used as coarse aggregate.

10. Crushed stones when used in the mix help reduce the expansion moderately. However, they have little effect on flexural moduli of elasticity or elastic flexural strength.

11. Mix setting shrinkage is inversely proportional to the percentage of the thickening agent. With 3.15% polystyrene in the resin, excessive setting shrinkage strains of a value of 0.003 are reduced to zero.

12. Generally, post curing at elevated temperature helps increase strength by as much as 35%. This is true whether dual-peroxide was used or not. The relative increase in strength by the addition of PST is counteracted by a high strength deterioration at elevated temperature in the order of 25%.

14. Continuous exposure to elevated temperatures starting while the mix is still fresh, helps enhance the polymerization process and results in no relative strength deterioration after as long as 7 days at 210°F (99°C). On the other hand, subjecting specimens, that are postcured and allowed to cool, to elevated temperature leads to appreciable strength reduction. Hence, casting in place at continuous elevated temperatures would not constitute any limitations as far as strength deterioration is concerned. For precasting, however, and for controlling both strength development and its deterioration, cast elements should be subjected to 200°F (93°C) immediately after casting for at least one hour.

15. Corrugated steel fibres have better performance/cost efficiency than the hooked fibers despite the latter has an aspect ratio three times as much that of the former.

Table 1. Gradings of the fine and coarse aggregates used.

Blended sand

U.S. sieve size:	No. 8 (2.38 mm),	No. 16 (1.19 mm),	No. 20 (0.83 mm),
Percent Passing:	100	84	69
U.S. sieve size:	No. 30 (0.539 mm),	No. 40 (0.417 mm),	No. 50 (0.205 mm),
Percent Passing:	49	34	16
U.S. sieve size:	No. 100 (0.147 mm)		
Percent Passing:	20		

Irregular Gravel (7):

U.S. sieve size:	1-1/2 in.	1/2 in.	3/8 in.	No. 4 (4.7 mm)	No. 8 (2.36 mm)
Percent Passing:	100	97	50	6	0.0

Crushed Basalt (B-1 and B-2)

U.S. sieve size:	1-1/2 in.	1/2 in.	3/8 in.	No. 4 (4.7 mm)	No. 8 (2.36 mm)
Percent Passing:	100	99	63	1.0	0.0

Fine Silica Flour (F)

U.S. sieve size:	No. 120 (0.12 mm)	No. 140 (0.105 mm)	No. 200 (0.074 mm)
Percent Passing:	100	96	90
U.S. sieve size:	No. 270 (0.053 mm)	No. 325 (0.044 mm)	
Percent Passing:	82	73	

Table 2. Various resin formulations used in mixing ratio optimization.

Formulation	5ST%	TMPTMA%	DMA%	Al74%	BFF-50%	PST%	DTBP%
a	56.4	37.6	1.0	1.0	4.0	--	--
b	56.1	37.4	1.0	1.0	4.0	--	0.5
c	54.4	36.3	1.0	1.0	4.0	2.8	0.5
d	54.0	36.0	1.0	1.0	4.0	3.4	0.5
e	53.6	35.7	1.0	1.0	4.0	4.2	0.5

ST, styrene

TMPTMA, trimethylolpropane trimethacrylate

DMA, dimethyl aniline

Al 74, silane

BFF, 50% active benzoylperoxide

PST, polystyrene

DTBP, ditert butylperoxides

Table 3. The various 36 mixing ratios investigated.

I	X	y = 3.0				X	y = 4.0				X	y = 5.0			
		R	S	F	A		R	S	F	A		R	S	F	A
0.4	0.55	7.4	8.0	21.1	63.4	0.5	8.3	8.0	16.7	66.9	0.65	9.0	8.0	13.8	69.2
	0.45	9.3	8.0	20.7	62.0	0.6	9.8	8.0	16.4	65.7	0.75	10.2	8.0	13.6	68.2
	0.55	11.1	8.0	20.2	60.7	0.7	11.3	8.0	16.1	64.6	0.85	11.4	8.0	13.4	67.2
	0.65	12.9	8.0	19.8	59.4	0.8	12.7	8.0	15.9	63.4	0.95	12.6	8.0	13.2	66.2
0.6	0.3	6.4	8.0	21.4	64.2	0.4	6.8	8.0	17.0	68.2	0.5	7.1	8.0	14.2	70.8
	0.4	8.4	8.0	20.9	62.7	0.5	8.4	8.0	16.7	66.9	0.6	8.4	8.0	14.0	69.7
	0.5	10.2	8.0	20.4	61.3	0.6	9.6	8.0	16.4	65.7	0.7	9.6	8.0	13.7	68.7
	0.6	12.0	8.0	20.0	60.0	0.7	11.3	8.0	16.1	65.6	0.8	10.8	8.0	13.5	67.7
0.8	0.25	5.4	8.0	21.6	64.9	0.35	6.0	8.0	17.2	68.8	0.45	6.4	8.0	14.3	71.3
	0.35	7.4	8.0	21.2	63.5	0.45	7.6	8.0	16.9	67.5	0.55	7.7	8.0	14.0	70.7
	0.45	9.3	8.0	20.7	62.0	0.55	9.1	8.0	16.6	66.3	0.65	9.0	8.0	13.8	69.2
	0.55	11.1	8.0	20.2	60.7	0.65	10.6	8.0	16.3	65.1	0.75	10.2	8.0	13.6	68.2

Table 4. Derived values* of coefficients of thermal expansion for the first 18 mixes.

Mix No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
k ₁	4.9	5.1	5.2	4.7	4.2	4.6	4.4	4.8	4.2	4.3	4.6	4.0	4.2	4.4	4.1	4.7	4.5	4.3
k ₂	0.3	6.9	7.0	6.7	5.9	6.8	6.5	6.2	6.7	5.5	6.7	5.5	6.2	6.7	6.5	6.8	6.3	6.8

*Given values are in $10^{-6}/F^{\circ}$.

Table 5. Derived values* of coefficients of thermal expansion for different S% mixes.

steel fiber content %	0.0	2.0	4.0	6.0	8.0	10.0
k ₁	4.9	4.8	4.7	4.2	3.9	3.1
k ₂	8.9	8.3	7.6	6.8	6.0	5.6

Table 6. Effect of aggregate type on some of the mechanical properties of PC.

aggregate type	G	L	B-1	B-2
splitting strength at ambient temperature, psi	2140.0	2190.0	2170.0	2290.0
splitting strength at elevated temperature, psi	1810.0	1900.0	1840.0	1990.0
strength deterioration, %	15.5	13.2	15.2	13.0
elastic flexural strength, psi	1600.0	1750.0	1550.0	1650.0
modulus of rupture, psi	2230.0	2600.0	2610.0	2620.0
flexural modulus of elasticity, 10^6 psi	2.4	2.7	2.7	2.0

Table 7. Derived values* of coefficients of thermal expansion for different aggregate-PC mixes.

used aggregate	k ₁	k ₂
G	4.4	6.0
L	3.8	5.2
B-1	4.0	5.7
B-2	3.6	5.7

*Given values are in $10^{-6}/F^{\circ}$.

Table 8. Different resin formulations used in the optimization of curing conditions.

resin formulation	ST %	TMPTMA %	DMA %	A-174	BFF-50%	PST %	DTBP %
1	54.0	36.0	1.0	1.0	4.0	3.4	0.5
2	54.3	36.2	1.0	1.0	4.0	3.4	-
3	56.0	37.3	1.0	1.0	4.0	-	0.5
4	56.4	37.6	1.0	1.0	4.0	-	-

Table 9. Splitting strength results for four different resin formulations.

used resin formulation	1	2	3	4
splitting strength at ambient temperature, psi	2920.0	2760.0	2300.0	2220.0
splitting strength at elevated temperature, psi	2500.0	2300.0	1920.0	1910.0
strength deterioration, %	15.0	17.0	16.0	14.0

Table 10. Effect of curing temperature and the addition of DTPB on strength.

Group No.	1	2	3	4	5	6
Curing temp, °F	75	210	300	350	75	210
Splitting strength, psi	2095	2825.0	2800.0	2800.0	2150.0	2730.0
Compressive strength, psi	12340.0	16770.0	16530.0	16730.0	-	-

Table 11. Effect of different curing conditions on strength deterioration.

Test temp., °F	75			210			300		
Group No.	1	2	3	1	2	3	1	2	3
splitting strength, psi	2780	-	2930	2120	-	2260	1960	-	1970
compressive strength, psi	-	16735	-	-	13265	-	-	11225	-

Table 12. Effect of curing times and temperature on strength for precasting.

Group	curing time, hrs	curing temp, °F	splitting strength, psi	
			at room temp.	at 210°F temp.
1	0.0	-	2040	2195
2	1.0	210	2830	2210
3	2.0	210	2910	2220
4	4.0	210	2855	2215
5	6.0	210	2820	2290
6	8.0	210	2890	2280
7	24.0	210	2860	2400
8	4.0	300	2840	2230
9	8.0	300	2900	2340

Table 13. Strength development for casting in place at 210°F.

curing time at 210°F	splitting strength, psi	compressive strength, psi
8 hr	2270	13265
48 hr	2590	13060
7 days	2550	13140
*8 hrs	2260	-
*48 hrs	2580	-

*Mixes without DTBP.

Table 14. Effect of fiber type and content on splitting strength.

type of fiber	fiber content, %	splitting strength, psi, at		
		75°F	210°F	300°F
1-1/2 in. corrugated	8	2920	2500.0	-
1.0 in. hooked	8	3040.0	2510.0	1990.0
1.0 in. hooked	4	2270	1880.0	1630.0

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Fig(8) Setting strains and exotherm of different resin formulation - mixers.

Fig. 1 Splitting strength - Mix richness relationship for

a) $I = 0.4$, b) $I = 0.6$, c) $I = 0.8$

FIG(2). Interchangeable mix variables relationships :

[a] x-y , [b] y-splitting strength & [c] x-R .

Fig(3) Temperature-thermal expansion relationships for the two families of curves d & e.

Fig(3) Temperature-thermal expansion relationships for the three families of curves, h.s.c.

Fig(6) Average load-deflection curves for different aggregate type-mixes in Flexure.

—	B-2	mix
- - -	B-1	mix
.....	GF	mix
- - - -	GF	mix

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