

Role of styrene-based shrinkage reducing agent in polyester resin concrete

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Studies on the reduction of setting shrinkage of polyester resin concrete with and without the microfiller CaCO_3 by using a styrene/polystyrene shrinkage reducing agent are reported. The setting shrinkage of unmodified polyester resin concrete was quite considerable but could be reduced almost to zero by varying the shrinkage reducing agent content. At high shrinkage reducing agent content, expansion of the sample was observed instead of shrinkage. Some differences in the rate of shrinkage in the initial stages of curing were observed, which provides some insight into the role of the two components of the shrinkage reducing agent in the reduction of shrinkage. Reduction of shrinkage was accompanied by a reduction in compressive strength, which suggests the need for a proper compromise between these two properties for developing polyester resin concretes for specific applications.

Key words: concrete mixes; polyesters; compressive strength; shrinkage reducing agent

The use of polymeric binders for sand and aggregates has led to a new class of materials, known as polymer concretes. The development of polymer concretes is directed at high strength construction materials by combining conventional concrete technology with modern polymer technology. Polymer concretes, based on polyester resins, are finding applications in repairing airfield-runways, concrete pavements, bridge decks, protection to the concrete surfaces of hydraulic structures against erosion and cavitation, flooring in chemical industries and others.¹⁻⁴

Although polyester resin concrete (PC) possesses good resistance to various chemicals and better mechanical properties than conventional cement concretes, it is disadvantageous in having a large setting shrinkage, which can be four to five times greater than that of conventional concrete.^{5,6} This curing-shrinkage of PC restricts its applications and significantly affects the bondability of PC with old cement concrete.

The use of a shrinkage reducing agent (SRA) therefore becomes necessary wherever shrinkage mitigation is of prime importance. Ohama *et al*⁷ have reported studies of the effect of some commercial styrene-based SRAs on polymer concrete. This paper describes a study of the effect of a styrene-based, laboratory-prepared SRA on PC. Two types of PC sample were studied – one with siliceous sand and quartzite aggregates without any microfiller and the other with CaCO_3 microfiller.

Experimental

Materials

The resin used as the binder was a general purpose unsaturated polyester resin (UP) supplied by Crystic (India) Ltd. The catalyst and the accelerator were a 50% dimethylphthalate solution of methylethylketone peroxide and a 1% styrene solution of cobalt naphthanate added as 2% by weight of resin, respectively.

The SRA (prepared in the laboratory) was a 30% solution of additive-free polystyrene in laboratory reagent grade styrene. The specific gravity and viscosity of the SRA are compared with those of the resin in Table 1.

The microfiller used was calcium carbonate (CaCO_3) of laboratory grade, with a particle size in the range of 2.0 to 2.5 μm , and a specific gravity of 2.7. It comprised 6% by weight of the total mix.

The coarse (mineral) aggregates used were crushed quartzite with a specific gravity of 2.72, negligible moisture content and no organic impurities. The fine aggregates were siliceous sand (locally known as Badarpur sand) of specific gravity 2.6, with negligible moisture content and without organic impurities.

The maximum size of coarse aggregate was 10 mm. The fine aggregate was graded; it passed through a 1.18 mm sieve and was fully retained on a 150 μm sieve. The combined aggregate distribution, with grading modulus, $G = 6.42 \text{ mm}^{-1}$,

Table 1. Properties of unsaturated polyester resin and shrinkage reducing agent

| | Acid value (mg KOH/g) | Specific gravity at 25°C | Viscosity* at 25°C (cP) | Styrene content (%) |
|-----------------------------|--------------------------|--------------------------------|-------------------------------|---------------------------|
| Unsaturated polyester resin | 21.0 | 1.12 | 850 | 38 |
| Shrinkage reducing agent | — | 0.93 | 325 | 70 |

*Brookfield Viscometer LVF, 2/12 rpm

mean diameter, $D = 4.12$ mm and a fineness modulus 4.40,⁸ is shown in Table 2.

Method of preparation

The PC mix was prepared by mixing 12% by weight of binder (containing appropriate amounts of the resin, accelerator, catalyst and SRA) with 88% by weight of combined aggregate, into a homogeneous mix. Whenever microfiller CaCO₃ was included in the PC mix, the corresponding amount (6% by weight) of combined aggregate was replaced, keeping the binder content unchanged.

Beams of dimensions 25 × 25 × 250 mm were cast from the freshly prepared PC homogeneous mix, using specially prepared waterproof and greased wooden moulds for the length change experiments. Cylindrical specimens 50 mm in diameter × 100 mm high were cast from the same PC mix for compressive strength measurements.

In the case of PC with CaCO₃ mix, some extra styrene was also added to maintain the workability of the mix. The binder formulation and a description of the various PC samples used in this study are given in Table 3.

Measurement of properties

Length changes were measured at 25°C using a Demec strain gauge, of gauge length 203.2 mm (8 in) with a total range of 2500 × 10⁻⁵ strain units, over two Demec points which were fixed on the PC beams at the time of casting. The accuracy of measurement of the gauge was 10 × 10⁻⁶ strain units per division. Measurements were made at intervals of ten minutes for the first hour after adding the catalyst and the accelerator to the polyester resin and later at one hour intervals for a total of 26 hours.

The compressive strength of PC was measured on a Universal compression testing machine, the load being applied at a rate of 11.8 MN/m² per min, as per IS standard.

Table 2. Grading of combined aggregate used in PC

| Sieve size | % weight retained | Cumulative % passing |
|------------|-------------------|----------------------|
| 10 mm | 0 | 100 |
| 4.75 mm | 45.00 | 55 |
| 2.36 mm | 18.33 | 37 |
| 1.18 mm | 3.66 | 33 |
| 600 μm | 7.33 | 26 |
| 300 μm | 16.50 | 9 |
| 150 μm | 9.18 | — |

Table 3. Composition of PC test samples

| Sample number | Description of samples | Binder formulation (by weight) | | |
|---------------|-----------------------------------|--------------------------------|-----|-----|
| | | UP* | SRA | St† |
| 1 | PC-SRA (0) | 100 | 0 | |
| 2 | PC-SRA (15) | 85 | 15 | |
| 3 | PC-SRA (25) | 75 | 25 | |
| 4 | PC-SRA (30) | 70 | 30 | 0 |
| 5 | PC-SRA (35) | 65 | 35 | |
| 6 | PC-SRA (50) | 50 | 50 | |
| 7 | PC/CaCO ₃ -SRA (0) | 100 | 0 | |
| 8 | PC/CaCO ₃ -St-SRA (0) | 100 | 0 | |
| 9 | PC/CaCO ₃ -St-SRA (15) | 85 | 15 | |
| 10 | PC/CaCO ₃ -St-SRA (25) | 75 | 25 | |
| 11 | PC/CaCO ₃ -St-SRA (30) | 70 | 30 | 8 |
| 12 | PC/CaCO ₃ -St-SRA (35) | 65 | 35 | |
| 13 | PC/CaCO ₃ -St-SRA (50) | 50 | 50 | |

*Unsaturated polyester resin, catalyst, accelerator mix; †styrene

Testing was carried out on 4 or 5 specimens of each composition and the average value is reported. The coefficient of variation was 4-7%.

Results

Length change as function of curing time is shown in Fig. 1 for PC without microfiller, and in Fig. 2 for PC with CaCO₃ microfiller samples. Negative values of shrinkage denote expansion in the specimen length. Samples 6 and 13, which have the highest SRA-content, show expansion over the whole range of curing time, whereas all other samples show shrinkage.

These shrinkage vs curing time curves show an increase of shrinkage with curing time in the 'early cure' stage, and thereafter a constant (or independent of curing time) value of shrinkage which will be called the 'ultimate shrinkage' or 'setting shrinkage'. The 'early cure' stage may be described as the region of curing time less than 20 h up to which the shrinkage of PC without SRA (*ie*, samples 1 and 7) increases with time, though in the other samples, this limit is about 10 h or less.

However, at the very start of the curing, *ie* in the region of curing time less than 2 h, a little expansion is apparent in some samples (samples 5, 11 and 12), while such an effect in the other samples may not be ruled out owing to

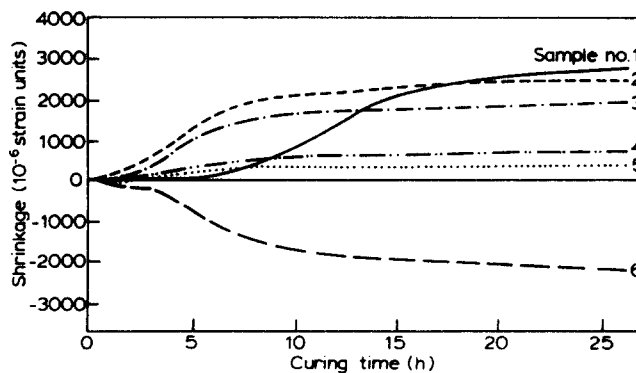


Fig. 1 Variation of shrinkage with curing time for PC without microfiller

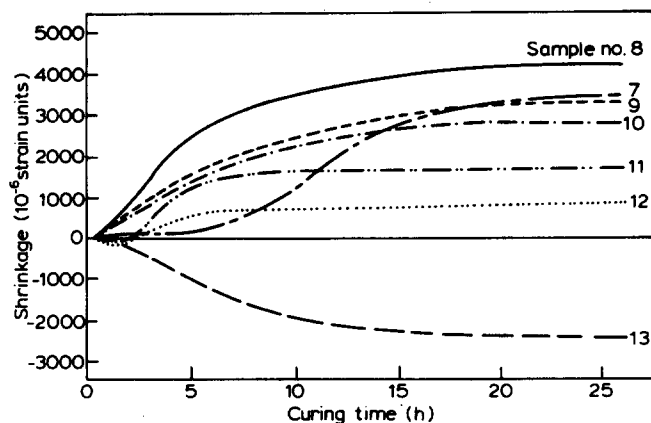


Fig. 2 Variation of shrinkage with curing time for PC with CaCO_3 microfiller

the difficulty in its detection for such a low magnitude of expansion. Similar expansion at the very start of the curing process has been reported by Ohama and Komiyama⁷, who attributed it to the possible loosening of compaction due to setting retardation of the polymer resin concrete.

Effect of CaCO_3 microfiller and styrene on shrinkage

Samples 1, 7 and 8, which do not contain the SRA, are the most appropriate systems for illustrating the roles of styrene and the CaCO_3 microfiller on the shrinkage of PC, without any interference from the effect of SRA. As shown in Table 3, samples 1 and 7 differ only in CaCO_3 microfiller content, while other samples 7 and 8 differ only in styrene content. The shrinkage curves for these three samples are presented in Fig. 3. The following points emerge from this comparison.

- 1) The use of CaCO_3 microfiller results in an increase of ultimate shrinkage, as well as the shrinkage in the early cure stage, as apparent from the difference of the shrinkage data for samples 1 and 7. Ultimate shrinkage is 3500×10^{-6} strain units for the PC sample with CaCO_3 microfiller (sample 7), and 2550×10^{-6} strain units for the PC sample without microfiller (sample 1).
- 2) The addition of styrene as a component of the binder produces an increase in the ultimate shrinkage in both PC without microfiller (compare samples 1 and 8) and PC with CaCO_3 microfiller (compare samples 7 and 8). Ultimate shrinkage of the sample 8 is 4200×10^{-6} strain units.
- 3) The effect of addition of styrene as a component of the binder is also apparent in the early cure region. Shrinkage

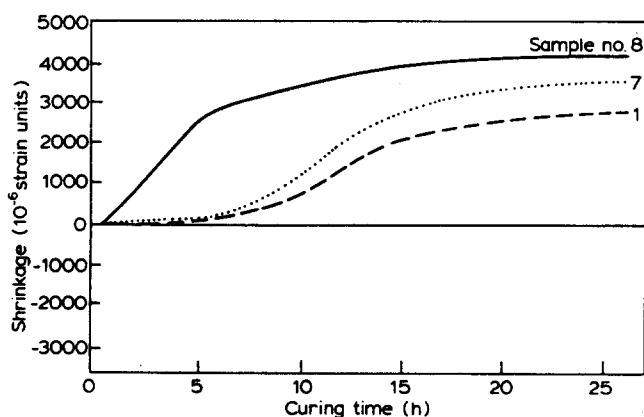


Fig. 3 Variation of shrinkage with styrene content for PC with and without CaCO_3 microfiller

of the sample containing additional styrene (*ie* sample 8) increases at a faster rate in the initial 5 h of curing time, whereas the shrinkage of the other two samples (*ie*, samples 1 and 7) increases inappreciably in this duration.

Effect of SRA on shrinkage

Early cure stage

In the early cure stage, the shrinkage profiles of the PC samples without SRA (*ie* sample 1 in Fig. 1 and sample 7 in Fig. 2) differ from those of the PC samples with SRA (*ie*, samples 2-5 in Fig. 1 and samples 8-12 in Fig. 2). During the initial 5 h of curing time, the PC samples without SRA show almost no shrinkage, while the PC samples with SRA show a rapid increase of shrinkage in this region of curing time. The expansion profiles of samples 6 and 13 (which show expansion instead of shrinkage) also show a rapid increase of expansion in this region. Shrinkage of the PC samples without SRA increases slowly with curing time and approaches its ultimate value only after about 20 h, while in the PC samples with SRA the ultimate values are reached in 10 to 15 h.

Ultimate shrinkage or setting shrinkage

After crossing the limit of early cure stage, the shrinkage curves flatten out showing constant (time independent) values of shrinkage. The shrinkage values at 24 h curing time are taken as the ultimate shrinkage or setting shrinkage of the respective samples. Variation of setting shrinkage with SRA content for PC without microfiller and PC with CaCO_3 microfiller is shown in Fig. 4, where the negative values represent the setting expansion (of samples 6 and 13). Setting shrinkage decreases continuously with increasing SRA content in both the sets of samples. PC with CaCO_3 microfiller showed greater shrinkage than PC without microfiller over the entire range of SRA content studied (including the 0%, *ie*, the samples without SRA), except in the case of the samples with highest SRA loading.

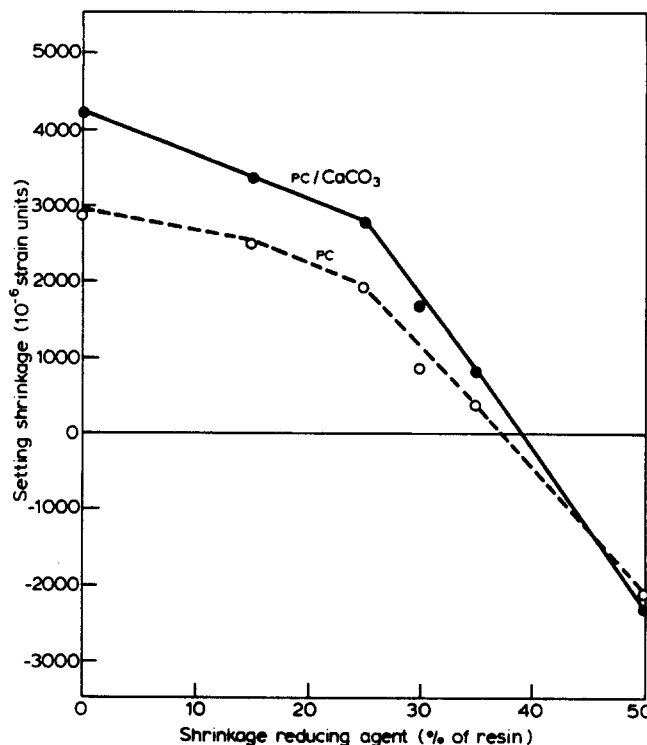


Fig. 4 Variation of setting shrinkage as function of SRA content for PC with and without CaCO_3 filler

The decrease of shrinkage is somewhat slower up to about 25% SRA content, as apparent from the lower slopes of the curves (Fig. 4) in this range.

The SRA loading required for minimizing the setting shrinkage in PC is about 35 to 40% by weight of the resin, for the present SRA. However, a proper optimization of the SRA loading would depend on a desired compromise between shrinkage and mechanical properties.

Effect of SRA on mechanical properties

Variation of compressive strength with SRA content of these samples is shown in Fig. 5. Compressive strength decreases with increasing SRA content for both PC without microfiller and PC with CaCO_3 microfiller. At low SRA contents, up to about 15%, the decrease of compressive strength is relatively slower than that at higher SRA content, as apparent from the slopes of the curves in these two regions (Fig. 5). Furthermore, though these variations of compressive strength are qualitatively similar for both the sets of PC samples, the values of compressive strength are higher for PC with CaCO_3 microfiller than PC without microfiller at identical SRA content. The highest values of compressive strength achieved at 0% SRA loading, viz 57.8 MPa (for PC with CaCO_3 microfiller) and 45.1 MPa (for PC without microfiller) decrease to 31.9 and 25.5 MPa respectively at the 50% SRA loading. These low values are not poor in comparison with the compressive strength of conventional cement concrete viz 19.6–29.4 MPa.

The qualitatively similar nature of the variations of the shrinkage and compressive strength with SRA content (Figs 4 and 5) is noteworthy. The samples showing higher compressive strength (ie PC with CaCO_3 microfiller as compared with PC without microfiller) show higher shrinkage also. Reduction in the ultimate shrinkage is accompanied by a loss of compressive strength. Hence it may be recommended that the SRA and CaCO_3 microfiller loadings have to be chosen optimally to avoid undue loss of compressive strength while achieving a reasonable reduction of ultimate shrinkage.

Discussion

Since the cross-linking of the polyester resin during the

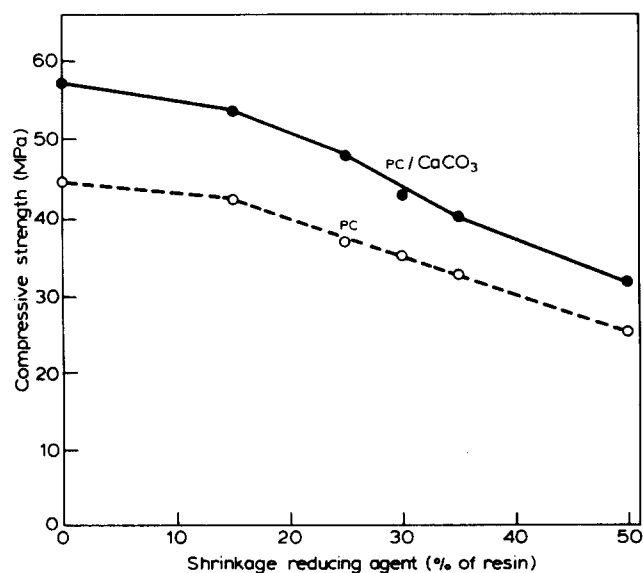


Fig. 5 Variation of compressive strength as function of SRA content for PC with and without CaCO_3 filler

course of curing gives rise to a change in the sample dimensions, the reduction in shrinkage in the presence of the SRA may occur due to either one or both of the following effects:

- 1) polystyrene (which is a component of SRA) may obstruct the cross-linking of the polyester at some of the sites of cross-linking; or
- 2) polystyrene may produce some space-filling effect by forming its own domains interspersed between the cross-linked polyester domains.

Both these events seem equally probable, as the reduction of compressive strength supports the obstruction of cross-linking at some sites (or an imperfectly cross-linked structure of the polyester), and the expansion of sample dimensions at extremely high SRA content supports the space-filling effect of bigger domains of polystyrene formed at such high SRA content.

The observed difference of shrinkage between the PC samples without SRA and the PC samples with SRA, in the early cure stage, suggests that the SRA facilitates cross-linking of the polyester and thus accounts for a greater rate of increase of shrinkage in the samples containing SRA.

In this early cure stage, the PC samples with SRA had an excess amount of styrene (as a component of the SRA) than the PC samples without SRA, which might be responsible for facilitating the cross-linking and thus producing shrinkage at a faster rate in the former class of the samples. Styrene, owing to its smaller molecules (than the molecules of the other components of the binder) might act as a diluent and thus provide greater mobility to polyester and polystyrene molecular chains (analogous to plasticization effect in polymers). This enhanced mobility of the molecular chains results in an ease of the pairing of the cross-linking sites of the polyester.

In the ultimate shrinkage region (ie at curing time greater than 20 h), some of the styrene may get involved in the cross-linked structure of the polyester⁹ and a part of it might evaporate away. Styrene content of the samples without SRA (ie samples 1 and 7) was only as much as was present in the commercial polyester resin used, whereas the other samples had additional amounts of styrene as a component of the SRA. The lower styrene content might be responsible for the lower plasticization effect and hence a lower rate of cross-linking (or lower rate of shrinkage increase) in the PC samples without SRA than the samples with SRA in the early cure stage.

Conclusions

The ultimate shrinkage of polyester resin concrete with and without microfiller CaCO_3 increases with curing time at room temperature and reaches a constant value after 15 to 20 hours. The addition of styrene enhances the setting shrinkage.

The ultimate shrinkage of the polyester resin concrete with and without CaCO_3 microfiller decreases markedly with increasing loading of the shrinkage reducing agent, up to about 40% loading. At higher loading of the shrinkage reducing agent, expansion occurs instead of shrinkage in both sets of samples (ie with and without the CaCO_3 microfiller).

Compressive strength of the polyester resin concrete is higher for the samples with CaCO_3 microfiller than the

samples without the microfiller. In both the sets of samples, the compressive strength decreases with increase in the loading of shrinkage reducing agent. The desired shrinkage reduction can be optimized with the acceptable level of compressive strength. The acceptable level of compressive strength depends upon the specific application, as for example its application in repairs of cracks in the old concrete structures and highway pavements would require not so high compressive strength while the shrinkage reduction is quite important for this application. In other structural applications some shrinkage reduction may be sacrificed for a desired gain in compressive strength.

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