

Influence of the Ratio of Styrene and Acrylonitrile in Crosslinked Polymeric Binders for Use in High-Temperature Polymer Concrete Composites

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Synopsis

The feasibility of using a monomer composition based on a styrene-acrylonitrile copolymer as a binder in high-strength and chemically resistant polymer concrete was demonstrated earlier. From this work it is clear that properties of the polymer concrete composite are dependent on the styrene/acrylonitrile ratio. This paper deals with the study of the effect of the styrene/acrylonitrile ratio in styrene-acrylonitrile-acrylamide-trimethylolpropane trimethacrylate monomer formulations on the thermomechanical properties of polymer concrete composites.

INTRODUCTION

Styrene-acrylonitrile copolymers are thermoplastic polymers, which are prepared from commercially available monomers such as styrene ($C_6H_5CH=CH_2$) (St) and acrylonitrile ($CH_2=CHCN$) (ACN). These strong and rigid copolymers with excellent dimensional stability are suitable for applications requiring contact with oil, gasoline, etc.

The copolymerization reactions involving styrene and acrylonitrile have been studied extensively. As a result, St-ACN copolymers have found wide industrial application. The ability to utilize this copolymer as a construction material will result in many new applications. The properties of the copolymer obtained are directly proportional to the St-ACN ratio in the monomer mixture. The activity ratio of both monomers is such that the curve for the copolymer composition has the appearance shown in Figure 1,¹ where it is seen that a homogeneous copolymer can be obtained only in the case of azeotropic composition of the monomeric mixture consisting of St and ACN. The amount of ACN in the azeotropic mixture varies between 36 and 40 mol %. When the ACN concentration is higher than that in the azeotrope, the monomeric phase is enriched by acrylonitrile. On polymerization, the conversion to copolymer will be ~80%, with the remainder polyacrylonitrile. At this time, however, a large fraction of the St is spent and the ACN/St ratio in the copolymer increases rapidly. If, however, the initial concentration of ACN exceeds 60 mol %, then a pure polyacrylonitrile will be produced at the end of polymerization. The same situation applies to styrene. If the initial concentration of ACN is <27-30 mol %, then a pure polystyrene is formed at the end of polymerization. Since neither of the homopolymers mixes with the copolymer, mixtures of the monomers that are outside these limits yield a heterogeneous product.

The feasibility of using the monomer mixture based on St-ACN with different

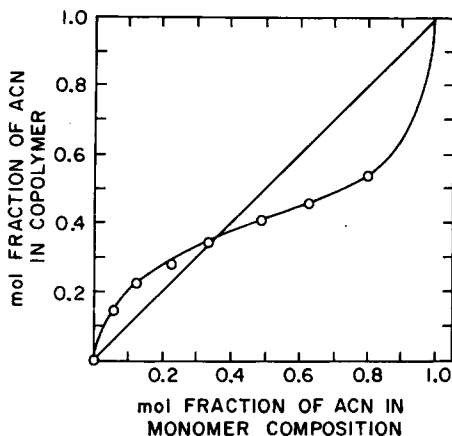


Fig. 1. Monomer-polymer composition curve for St-ACN bulk polymerization.

chemical additives in conjunction with inorganic fillers such as sand, portland cement, carbon black, mica, etc., was demonstrated earlier.²⁻⁴ The characteristic properties of this composite are its thermal, hydrolytic, and chemical stabilities.

In the practical sense, thermal stability is the ability of a material to maintain the required mechanical properties at a given temperature. A high melting or softening point is one of the requirements for a thermally stable polymer. The use of many polymers is limited by changes in the physical characteristics at elevated temperatures, rather than by breaking of the chemical bonds (i.e., they retain their chemical structure, but become weak, soft, and finally fluid). The melting point of polymers can be increased by introducing different amounts of polar substituents such as $C\equiv N$. It has also been shown that the melting point can be increased by hydrogen bonding with groups such as amides. Up to a certain concentration, the presence of bulky substituents such as methyl groups also increases the melting point by decreasing the mobility of the chain.

The chemical factors determining thermostability are also very important: for example, the formation of intramolecular bonds on heating, which produce crosslinked structures. Polymers may be crosslinked to yield melt-resistant structures. Although the use of thermoplastic materials is often limited by their softening point, thermoset materials are limited by the temperature at which bonds begin to break. Therefore, good heat-resistant polymers must have bonds of high dissociation energy. Unfortunately, the prediction of relative thermal stabilities of polymers involves more than a comparison of bond strengths. For example, ~ 78 kcal/mol is required to break the first bond in the chain of some vinyl polymers. The products formed in this step are highly reactive free radicals. In the second step, the chain further degrades to yield a monomer molecule and a shorter chain still bearing an odd electron. The energy required to break the carbon-carbon bond is supplied, at least partially, as a result of formation of a double bond in the removed monomer unit. Therefore, the thermal energy required to degrade the vinyl polymers to monomers is less than the sum of the bond energies of the broken bonds.

Research performed at Brookhaven National Laboratory (BNL) has demonstrated the feasibility of using crosslinked polymeric binders such as St-

ACN-acrylamide (Aa) trimethylolpropane trimethacrylate (TMPTMA) in the polymer concrete (PC) composites. The material has strength and durability characteristics far superior to those of portland cement and may find application as a construction material. Formation of this composite requires mixing of an inorganic aggregate with a monomer, which is subsequently polymerized in place. The technology used is similar to that used for portland cement. In this study the influence of ACN concentration on the properties of the PC composite material has been investigated and the results are presented.

STARTING MATERIALS AND SAMPLE PREPARATION

The physicochemical properties of the monomers used in the development of PC composite materials were described earlier.² It has also been shown^{2,5} that a silica sand mixture that is part of the aggregate composition consisting of 50 parts by weight of sieve opening 1180 μm , 25 parts of 600 μm , and 25 parts of 150 μm has the proper particle size distribution for producing a high-quality PC with a minimum polymer content. Type III portland cement is added to this mixture to enhance the resistance to brine and steam. The monomers are mixed in a glass beaker and polymerization free radical initiator azobisisobutyronitrile (AIBN) is added and dissolved. When the small quantity of Aa is added to the monomer mixture to increase the thermostability of the copolymer, the mixture is heated to 45–50°C prior to the addition of free radical initiator AIBN in order to dissolve the solid monomer. The formulation is mixed with the sand-cement aggregate and placed in a glass tube coated with a release agent. Vibration is used to compact the PC. The samples are cured in an oven at polymerization temperature. After cooling, the samples are removed from the mold, cut to a length/diameter ratio of 2, and dried at 100°C.

RESULTS AND DISCUSSION

The thermal stability of polymers depends on the molecular weight, which in turn is related to the reaction temperature. It is known that copolymerization of St-ACN is highly exothermic, which makes it difficult to control the reaction temperature. Boundy⁶ showed that high reaction temperature yields a low-molecular-weight copolymer, which is weak and brittle. Thus PC samples have poor mechanical properties. On the other hand, a high-molecular-weight product is formed at low reaction temperature, but because of different reactivities of monomers, a partly nonuniform product is produced. Jones et al.⁷ found that optimum products are obtained when the monomer system is polymerized in bulk at a reaction temperature in the range of 130–180°C. The introduction of a small amount of Aa in the molecular chain is more reactive than St but less reactive than ACN, and also a trifunctional crosslinking agent TMPTMA, which has polymerization characteristics similar to those of St, changes the St/ACN ratio at which only copolymer of a constant composition is produced, as well as the reaction temperature.

Without determining the parameters of copolymerization on the basis of theoretical suppositions,⁸ we conducted a series of experiments to determine the effect of ACN concentration in a St-ACN-Aa-TMPTMA mixture on the properties of PC. Figure 2 shows the weight loss of a polymer measured in ni-

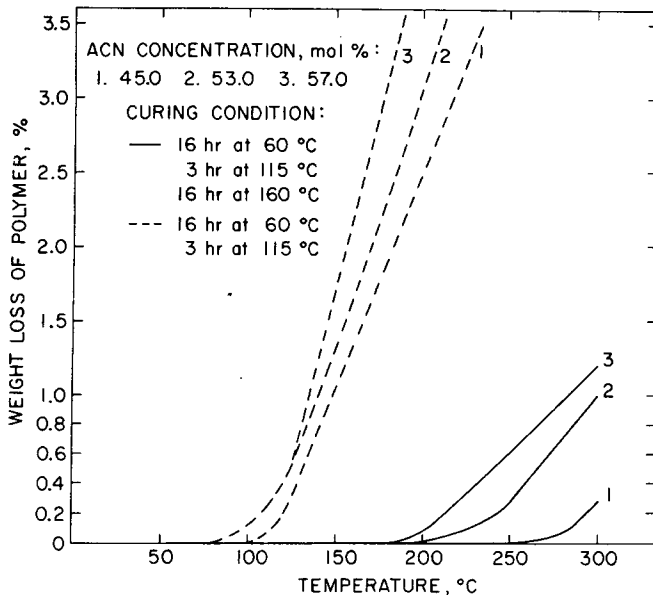


Fig. 2. Weight loss of polymer at elevated temperature.

trogen by thermogravimetric analysis (TGA) at different curing conditions and ACN concentrations. The broken lines indicate that the weight loss of the polymer increases rapidly with temperature independently of ACN concentration if the maximum curing temperature of the reaction is 115°C. As shown earlier,³ this weight loss is attributable to unreacted monomer. An increase in the reaction temperature to 160°C decreases the weight loss. As can be seen, the system containing 45 mol % of ACN in the monomer composition has a minimum weight loss. An increase in the ACN concentration increases the weight loss of the polymer, which can result in a partial formation of pure polyacrylonitrile at the end of the copolymerization reaction.

We reported earlier that PC samples have high durability and thermostability when a crosslinking agent is used to obtain a three-dimensional polymer structure. The concentration of the crosslinking agent affects not only the properties of PC, but also the required ACN concentration (Fig. 3). The PC samples which were exposed to air at 240°C for 30 days showed a high degree of resistance to thermo-oxidation when the concentration of the TMPTMA crosslinking agent is in the range of 1.15–1.70 mol % and the ACN concentration is in the range of 45–55 mol %. An increase in the concentration of TMPTMA increases its ability to thermo-oxidize with increasing ACN concentration. Results of the study of the compressive strength of PC samples after their preparation and exposure to air and to a simulated geothermal brine solution at 240°C for 30 days are shown in Figures 4–6.

When the concentration of the crosslinking agent is in the range of 1.15–1.25 mol %, the compressive strength of the composite after preparation varies from 177 to 183 MPa. This also occurs when the ACN concentration increases from 40 to 55 mol % (Fig. 4). Exposure of these samples for 30 days to the geothermal brine solution and to air at 240°C decreases its strength no more than 20% at an ACN concentration of 40–45 mol % and up to ~50% at ACN concentrations in

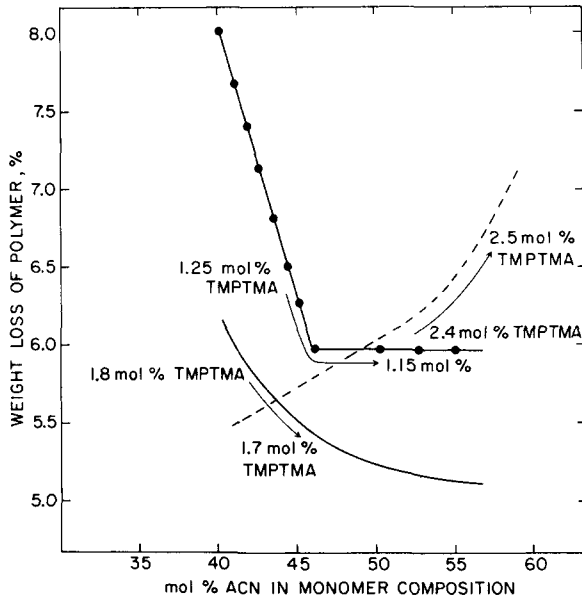


Fig. 3. Weight loss of polymer in polymer concrete versus ACN concentration after exposure for 30 days to air at 240°C.

the range 45–55 mol %. An increase in the concentration of the crosslinking agent from 1.7 to 1.8 mol % (Fig. 5) improved the durability of the samples to thermo-oxidation, although after exposure to brine, the strength decreased rapidly (~50%) at an ACN concentration of 40 mol % and continued to decrease with increasing ACN concentration. The same behavior was observed when the concentration of the crosslinking agent is increased to 2.6 mol % (Fig. 6). The

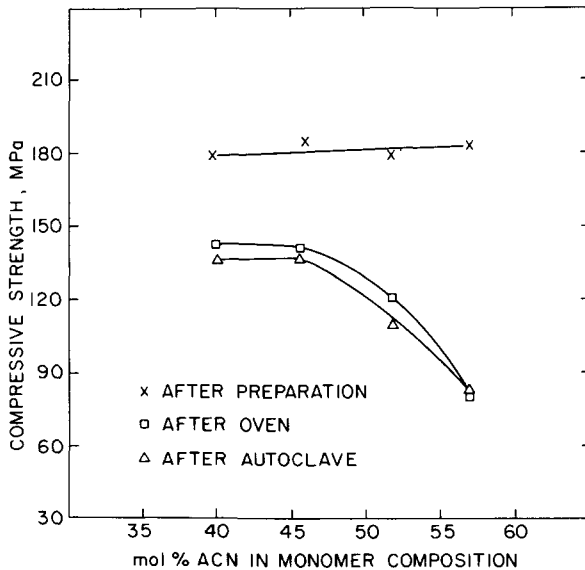


Fig. 4. Compressive strength of polymer concrete versus ACN concentration. Monomer load, 13 wt.%; sand/cement ratio, 7:3; crosslinking agent, 1.15–1.25 mol %; acrylamide, 5.5 mol %.

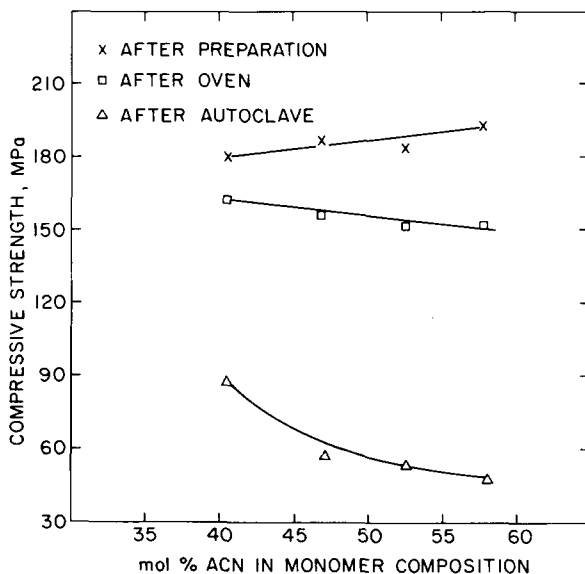


Fig. 5. Compressive strength of polymer concrete versus ACN concentration. Monomer load, 13 wt.%; sand/cement ratio, 7:3; crosslinking agent, 1.7–1.8 mol %; As, 5.75 mol %.

mechanical durability decreases with increasing ACN concentration, which results in the partial formation of ACN homopolymer. After the exposure of the samples to hot brine solutions at 240°C, this homopolymer leads to cyclic formation with evolution of gases and hence to the conjugation of the double bonds, which can be easily hydrolyzed during the exposure to hot brine. The cyclic formation increases with increasing ACN concentration.^{9,10} Because it cannot fit compactly, an increase in the concentration of the TMPTMA crosslinking

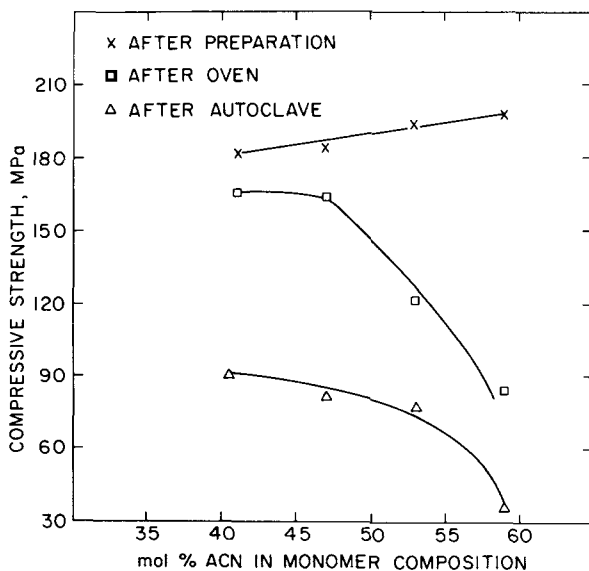


Fig. 6. Compressive strength of polymer concrete versus ACN concentration. Monomer load, 13 wt.%; sand/cement ratio, 7:3; crosslinking agent, 2.4–2.5 mol %; Aa, 6.0 mol %.

agent from 1.15 to 2.5 mol % decreases the mobility of the molecular chain. As a result, PC samples after exposure to air and to brine solution become weak and soft and lose their mechanical durability.

CONCLUSIONS

The results obtained show that the concentration of ACN is critical and is dependent on the concentration of other monomers. Thus at 40–45 mol % concentration of ACN, 5–5.5 mol % Aa, and 1.15–1.25 mol % TMPTMA, a true homogeneous copolymer is formed exclusively, which leads to the formation of highly stable, chemically resistant PC. Changes in the above concentration lead to changes in azeotropic conditions, and consequently the formed PC becomes thermochemically weak. The experimental results also indicate that the inclusion of small amounts of Aa and TMPTMA into the molecular chain of St–ACN copolymers shifts the azeotrope in the direction of increasing ACN concentration, but it still occurs in the area of 40–45 mol %, where the homogeneous copolymer product can be obtained.

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