

Mechanical Properties of Products of Thermocatalytic and Radiolytic Styrene–Acrylonitrile Copolymerization

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Synopsis

The mechanical properties of styrene (S)–acrylonitrile (AN) mixtures, ranging from 20 to 80 wt % S, polymerized by thermocatalytic and radiolytic techniques were studied. Maximum compressive and tensile strength was obtained for the mixture containing 60 wt % styrene. The hardness increased with styrene concentration up to 40 wt % and then remained nearly constant. Radiolytic copolymerization gave stronger copolymers than thermal copolymerization since irradiation enhances crosslinking. For the same composition, as the dose increases, the strength increases to a maximum and then decreases due to competing rates of crosslinking and degradation.

INTRODUCTION

Styrene (S)–acrylonitrile (AN) copolymers and their formation reactions were the topic of many publications since 1947.¹ They deal with the relationship between the composition of the monomer mixture and the composition of the copolymer obtained. Several authors^{1–5} found that a homogeneous copolymer can be obtained only from an azeotropic monomer mixture consisting of about 76 wt % S. Since neither of the homopolymers is soluble in the copolymer S–AN, heterogeneous mixtures are produced. Hence, the properties of the copolymers obtained depend directly on the S/AN monomer ratio. When the monomer mixture is enriched with AN, a polyacrylonitrile is formed, while mixtures rich in S form polystyrenes.

Free-radical polymerization can be carried out either by irradiation or by thermal catalytic techniques. It should be noted that radiolytic polymerization can be done at low temperatures.² On the other hand, in the thermal method a catalyst is used to initiate the reaction which needs a high temperature. The copolymerization of S–AN is highly exothermic, making it difficult to control the reaction temperature. This difficulty can result in a weak and brittle low molecular weight copolymer.² In this study, the effect of S/AN ratio in the monomer mixture, the effect of the free-radical bulk copolymerization techniques and the operating conditions on the mechanical properties of the obtained copolymers are discussed.

STARTING MATERIALS AND EXPERIMENTAL TECHNIQUES

Starting Materials

Pure S ($C_6H_5CH=CH_2$) and AN ($CH_2=CHCN$) monomers were supplied

by "Prolabo." Pure benzoyl peroxide supplied by "Knight Light" was used as an initiator.

Polymerization Techniques

Polymerization was carried out by radiolytic and thermal catalytic methods. Radiolytic polymerization uses a high strength Co-60 gamma irradiation unit with a 3000-Ci activity, which gives a constant intensity of 1.8×10^5 rads/h. Specimens were irradiated uniformly at atmospheric temperature and pressure. In thermal catalytic polymerization, the monomer mixtures, with 1% benzoyl peroxide as a catalyst, were heated in an electric furnace for 8 h. To minimize the thermal runaway problem, the furnace was held at 80°C. It should be noted the specimens temperature cannot be maintained exactly at 80°C due to finite rate of heat transfer and exothermic nature of the reaction, but the operating conditions were selected in view of Sebastian and Biesenberger⁶ results, who reported an increase in temperature of less than 20°C when a mixture of 70% S was used with 1.25% benzoyl peroxide and the surrounding temperature was kept at 100°C.

Mechanical Property Measurements

The compressive and tensile strength were tested using the standard universal hydraulic testing machine, the "Amsler." The machine was equipped with a dynamometer to control the equipment operation and to simultaneously plot the stress-strain relations.

The compression tests were performed on discs 15 mm in diameter by 10 mm in height and a loading rate of 6.89 N/mm²-min was used. Tension tests were conducted on rods 15 mm in diameter by 100 mm in length and a loading rate of 3.345 N/mm²-min was used. The fracture load (F) was recorded and the strength (S) was calculated from the relation.

$$S = F/A$$

where A is the specimen cross-sectional area.

The Brinell hardness test was conducted on discs 15 mm in diameter by 10 mm in height after grinding the surfaces. A hydraulic hardness tester, the "Amsler", with a 2.5 mm diameter steel ball under a constant weight of 15.625 kg was used.

EXPERIMENTAL RESULTS AND DISCUSSION

Effects of Monomer Composition on the Mechanical Properties

Different ratios of S to AN were prepared. Polymerization was performed as previously mentioned using a dose of 5×10^6 rads for radiolytic copolymerization and 80°C for 8 h for thermal catalytic polymerization.

The results obtained by plotting the compressive strength vs. the amount of S in the monomer mixture for (a) thermal catalytic polymerization and (b) radiolytic polymerization are shown in Figure 1. From this figure one can observe that the compressive strength increases with S concentration up to a composition

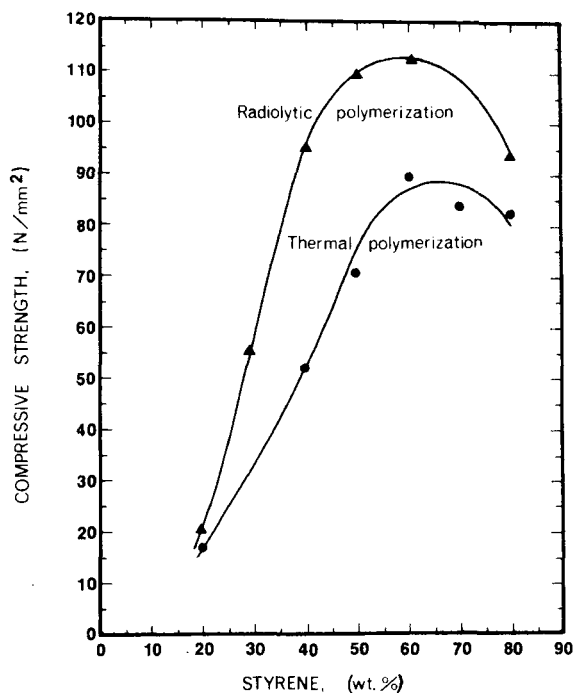


Fig. 1. Variation of copolymer compressive strength with composition of S/AN mixture.

containing 60% S and 40% AN. After that, increasing S concentration decreases the compressive strength. It is also shown that, for the same composition, radiolytic polymerization produces a higher strength than thermal catalytic polymerization.

Figure 2 shows the change of tensile strength as a function of the amount of S in the monomer mixture for (a) thermal polymerization and (b) radiolytic polymerization. It is evident that the effect of the composition on the tensile strength is exactly the same as that described for the compressive strength.

On plotting the hardness against the S concentration in the monomer mixture, Figure 3 was obtained. It shows two curves one for thermal catalytic polymerization and the other for radiolytic polymerization. This figure shows that the hardness increases as the S content increases up to about 40%. Above this composition, insignificant changes in hardness were observed. Radiolytic polymerization produces a harder copolymer than thermal catalytic polymerization.

The azeotropic mixture of 76 wt % S and 24 wt % AN, which produces homogeneous copolymer in this system, did not exhibit the highest strength. The highest strength was observed in a heterogeneous polymer which contains 15 wt % polyacrylonitrile and 85 wt % copolymer S-AN.

On the other hand, the highest mechanical properties of radiolytic polymerization may be due to the crosslinking occurring during the copolymerization by γ -rays as no crosslinking agents were added in the thermal process. When organic polymers are irradiated, simultaneous crosslinking and degradation of the chain occur due to the formation of free radicals on the polymer backbone.² The higher strength obtained here implies that crosslinking prevails.

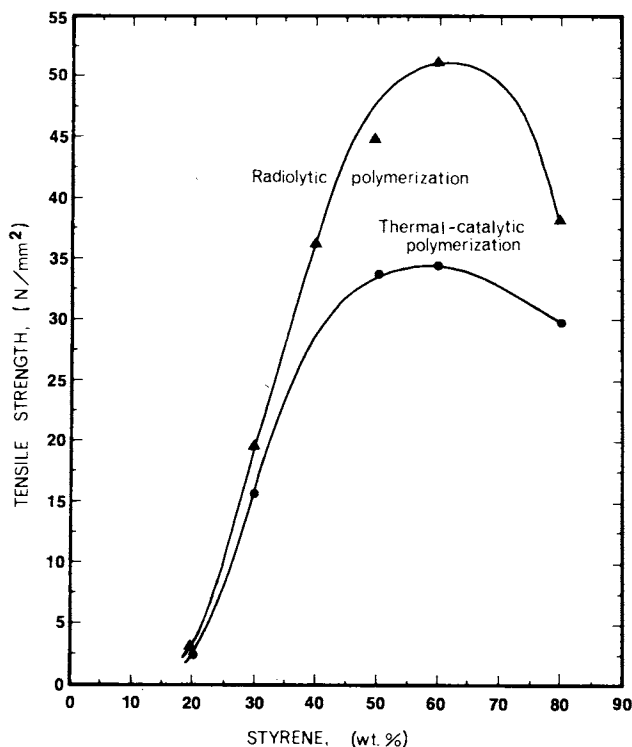


Fig. 2. Variation of copolymer tensile strength with composition of S/AN mixture.

Effects of Irradiation on the Mechanical Properties

Since the copolymer with the composition 60 wt % S and 40 wt % AN obtained by radiolytic copolymerization has the best mechanical properties, it was chosen to study the effects of irradiation dose on the mechanical properties. The doses

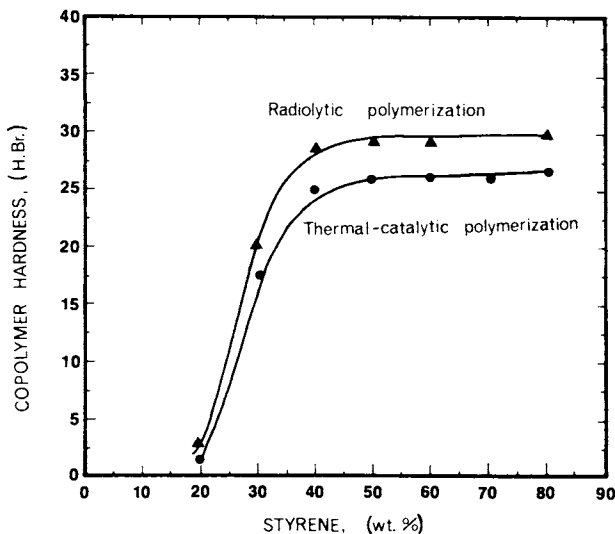


Fig. 3. Variation of copolymer hardness with composition of S/AN mixture.

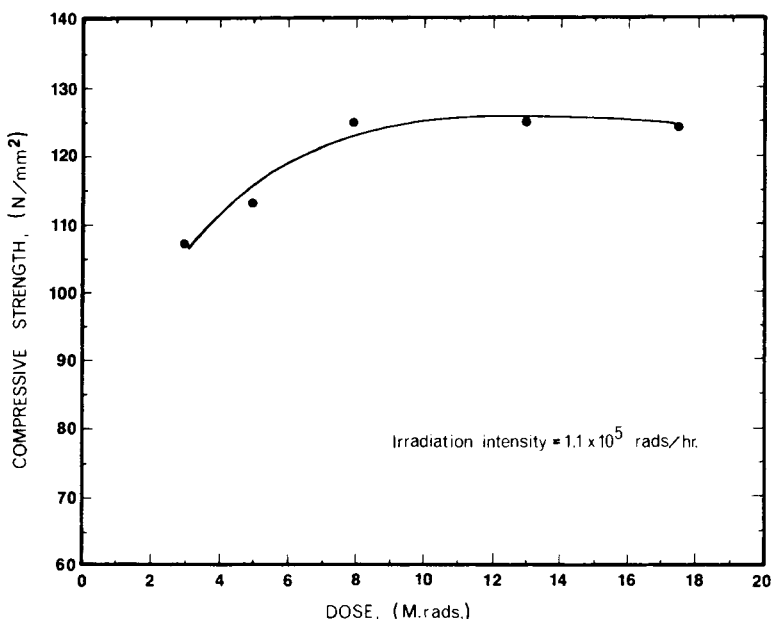


Fig. 4. Variation of copolymer compressive strength with irradiation dose.

ranged from 1×10^6 to 17.5×10^6 rads using a source of intensity of 1.8×10^5 rads/h. It was noted that a dose of 1×10^6 rads was not sufficient to initiate polymerization reactions and accordingly, doses higher than 3×10^6 rads were used. For each dose at least three specimens were tested for compression, and three were tested for tension.

In plotting the irradiation dose against the compressive strength (Fig. 4), it was observed that the strength increases with the dose up to about 9×10^6 rads. Beyond this value, the compressive strength decreases slightly with the increasing dose.

The effect of the dose on the tensile strength is shown in Figure 5. It shows that after the tensile strength increases to a maximum at about 9×10^6 rads, it decreases rapidly with the increasing dose.

As polymers are irradiated, simultaneous crosslinking and degradation of chains occur due to the formation of the free radical. The change in both compressive and tensile strength with the dose is a resultant of both crosslinking which increases strength and degradation which decreases the strength. The above results show also that the tensile strength is more sensitive to degradation than compressive strength. This is a characteristic property for nonductile materials. Degradation of a polymer causes cracking to start resulting in a stress concentration and accelerating fracture under tension. Such cracks can carry a compressive load without failure, and this explains the rapid drop in tensile strength.

CONCLUSIONS

1. The addition of AN to S monomer increases the tensile and compressive strength. Maximum strength was observed by the monomer mixture containing 60 wt % S and not by the azeotropic mixture of 76 wt % S.

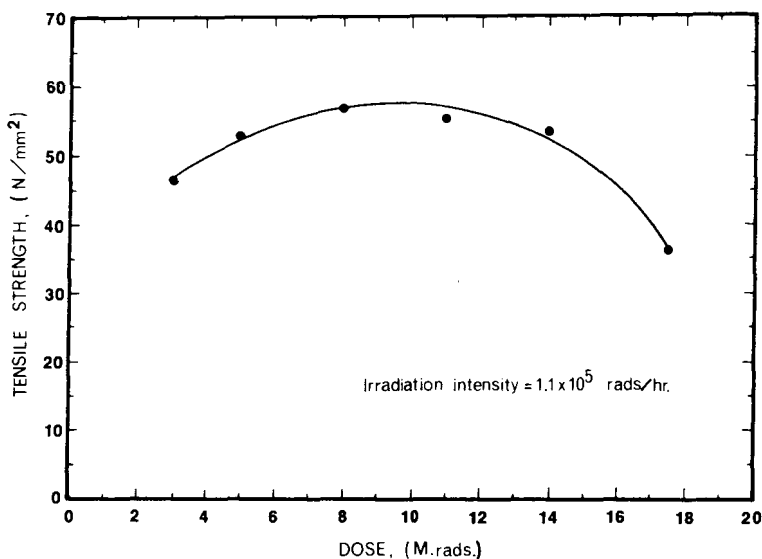


Fig. 5. Variation of copolymer tensile strength with irradiation dose.

2. The copolymers produced by radiolytic polymerization were stronger than copolymers produced by thermal catalytic polymerization. This is attributed to the crosslinking formed during polymerization by γ -ray radiation.

3. The strength of a copolymer increases with an irradiation dose up to 9×10^6 rads; however, beyond this dose the compressive strength decreases slightly and the tensile strength decreases sharply due to polymer degradation, creating cracks which propagate quickly under tension. The behavior is a resultant of two simultaneous processes: crosslinking, which increases strength, and degradation, which decreases it.

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