

Polystyrene–Gelatin Composites Prepared via a Gel Pathway

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SYNOPSIS

Composite polymers of polystyrene and gelatin have been prepared using a gel pathway. The gels have been obtained by mixing at 50°C an aqueous solution containing gelatin and a surfactant (SDS) with styrene containing an initiator (AIBN). The obtained emulsions have the appearance of gels and are very stable both at room temperature and at 50°C. At 50°C, these gels are liquidlike with high viscosity; at room temperature, solidlike gels are formed when the gelatin content is sufficiently high. Polymerization of the gels can be achieved in several days at room temperature and in 24 h at 50°C. Composite polymers with different water-absorbing capacities have been produced by controlling the polymerization temperature and duration. These composite polymers are insoluble in water, ethanol, octane, and cyclohexane, but exhibit some swelling in these liquids. Additional thermal treatment at relatively high temperatures increases the mechanical strength of the composites. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

In previous papers, it was reported that an emulsion pathway can be used for (a) the preparation of gelatin-based composite polymers at 50°C¹ and (b) for the gelatin cross-linking at room temperature.² Emulsions with the appearance of gels have been prepared by mixing mechanically at 50°C an aqueous solution containing gelatin and a surfactant (sodium dodecylsulfate, SDS) with a monomer (methyl methacrylate, MMA) containing an initiator (AIBN). However, a difficulty has arisen because of the phase separation that occurred during the storage and polymerization of the emulsions at 50°C. Intensive stirring within the first hour of polymerization was needed to prevent phase separation.

In this paper, a different monomer, styrene, instead of MMA is used. The preparation procedure of the emulsion gels is similar to that described in the previous papers.^{1,2} However, in contrast, the gels are now very stable and can be polymerized either at 50°C or at room temperature without phase separation. The high stability of these gels facilitates

their further processing by injection molding or casting. The obtained composite polymers are insoluble in water, ethanol, octane, and cyclohexane, but exhibit some swelling. Composite polymers with different water-absorbing capacities can be produced by controlling the temperature and the duration of polymerization.

EXPERIMENTAL

Materials

Styrene (Aldrich Chemical Co.) was purified by distillation under reduced pressure. The initiator, azobisisobutyronitrile (AIBN, Alfa Chemical Co.) was purified by recrystallization in methanol. Sodium dodecylsulfate (SDS, Aldrich) and gelatin (300 bloom, Alfa Chemical Co.) were used as received. Water was deionized and double-distilled.

The Swelling Test

Samples of dried composites were weighed and placed in glass tubes containing the respective liquid. The weights of the swollen samples were determined after 24 h. The swelling ratio of the samples was

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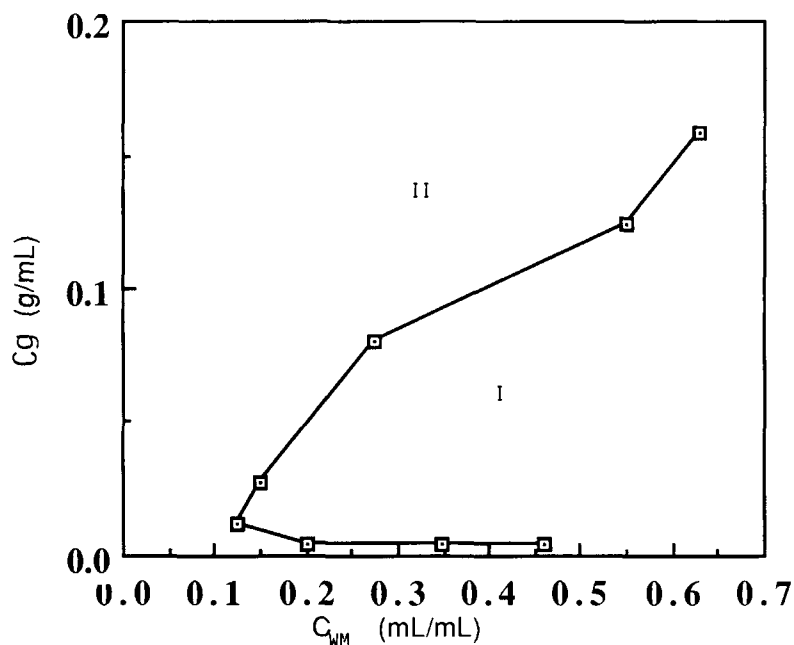


Figure 1 Phase diagram of the system composed of styrene and an aqueous solution of SDS and gelatin plotted as gelatin concentration (C_g) in the gel against the volume ratio (C_{WM}) of aqueous solution of dispersant (SDS) to styrene. I is the gel region and II is the two-phase region. The concentration of the aqueous solution of SDS is 0.25 mol/L.

calculated using the expression $S = (W_s - W_0) / W_0$, where W_s and W_0 are the weights of the swollen and dried (after swelling) samples, respectively.

Gel Preparation

For the preparation of the two stock solutions, weighted amounts of surfactant (SDS) and initiator (AIBN) were dissolved in water and monomer (styrene), respectively. The aqueous solutions of SDS were introduced in glass tubes containing gelatin. The glass tubes were placed in a water bath at 50°C for 30–90 min and stirred continuously with a mechanical mixer until the solution became homogeneous. The monomer containing AIBN was then introduced in the glass tubes. Gels were finally obtained by the intensive stirring of the aqueous solution of gelatin and SDS with the monomer under heating at 50°C for about 15 min.

Instruments Used

Scanning electron microscopy (SEM, Amray 100A) was used to investigate the morphology of the composite polymers.

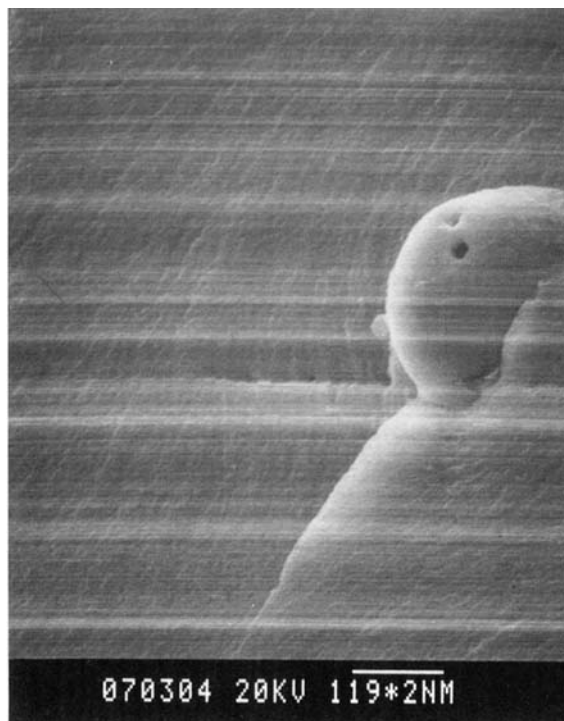
RESULTS AND DISCUSSION

The phase behavior of styrene–gelatin gels is similar to that of MMA–gelatin gels. Figure 1 is a phase diagram for gel formation in which the concentration of gelatin in the entire system, C_g (g/mL), is plotted vs. the volume ratio, C_{WM} (mL/mL), of aqueous solution of SDS to monomer (styrene) at a constant SDS concentration, $C_{SDSW} = 0.25$ mol/L. The gels formed in region I are very stable at room temperature and at 50°C. As noted in a previous paper,¹ a minimum amount of gelatin is needed to generate a

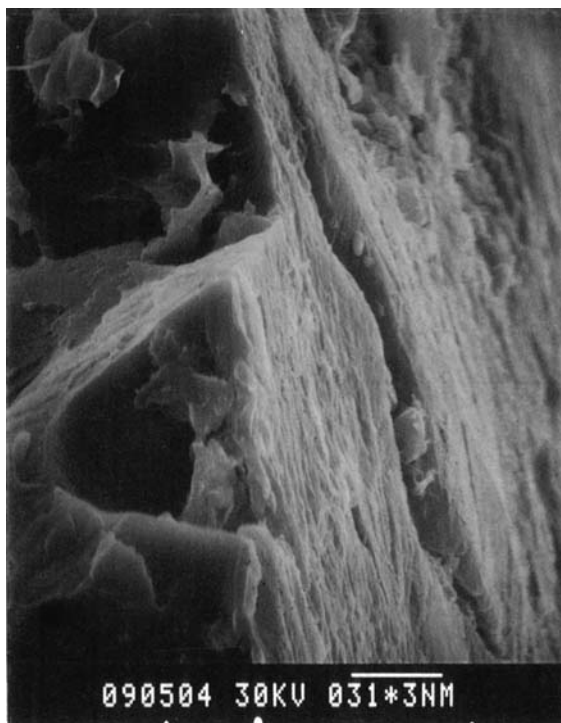
Table I The Swelling of Composite Polymers Polymerized for 24 h at 50°C

	Sample (S)					
	1	2	3	4	5	6
Water	0.32	0.33	0.33	0.34	0.41	0.41
Ethanol	0.31	0.32	0.34	0.29	0.22	0.24
Octane	0.32	0.30	0.22	0.21	0.21	0.14
Cyclohexane	1.07	0.38	0.33	0.28	0.28	0.20

The compositions of samples 1, 2, 3, 4, 5, and 6 are $C_g = 0.023$, 0.034, 0.045, 0.056, 0.079, and 0.102 g/mL, respectively; $C_{WM} = 0.5$ mL/mL, $C_{SDSW} = 0.25$ mol/L, and $C_{AIBN} = 0.25$ mol/L.



(a)



(b)

Figure 2 Electron micrographs of gelatin-based composite polymers: (a) composite polymer polymerized in sheet form for 24 h at 50°C; (b, c) composite membrane materials polymerized in sheet form for 24 h at 50°C and heated subsequently at 280°C under pressure. The compositions of (a), (b), and (c) are $C_g = 0.058, 0.023,$ and 0.067 g/mL, respectively; $C_{AIBN} = 0.25$ mol/L; $C_{WM} = 0.5$ mL/mL; and $C_{SDSW} = 0.25$ mol/L.

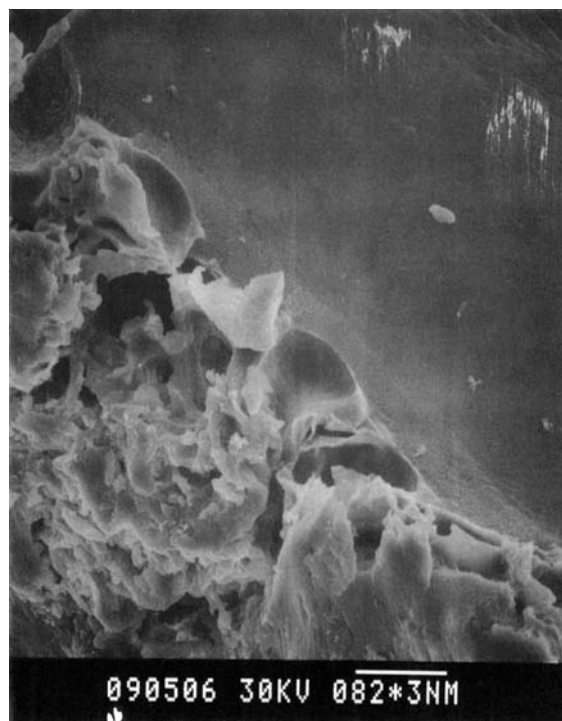


Figure 2 (Continued from the previous page)

gel and a too high gelatin concentration does not favor gel formation. Gels did not form in region II. The gels became liquidlike and could flow when they

were heated at 50°C. The gels with a sufficiently high gelatin content became solidlike and had viscoelastic behavior at room temperature.

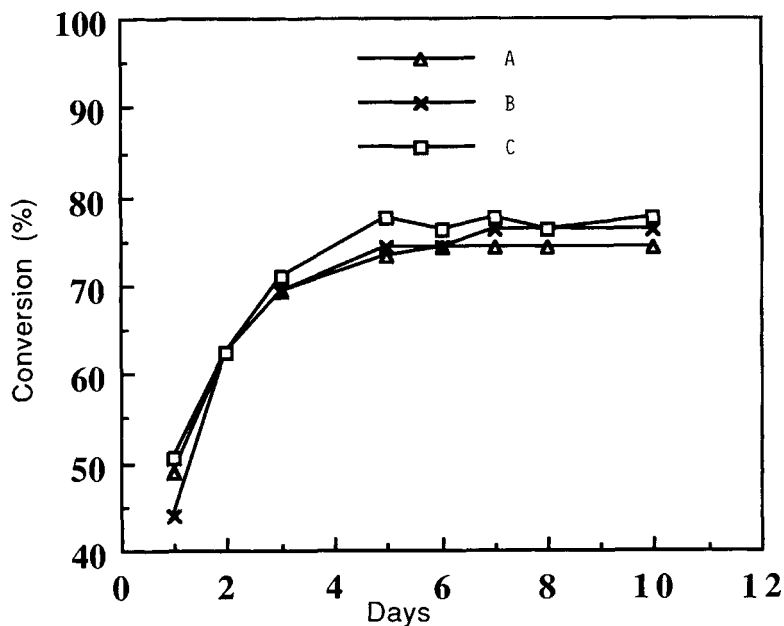


Figure 3 Conversion (%) of styrene polymerized at room temperature against the polymerization time before drying. Compositions: Samples A and B: $C_g = 0.068$ and 0.092 g/mL, respectively; $C_{WM} = 0.50$ mL/mL; $C_{SDSW} = 0.25$ mol/L; $C_{AIBN} = 0.25$ mol/L. Sample C: $C_g = 0.102$ g/mL; $C_{WM} = 0.67$ mL/mL; the other concentrations are as for samples A and B.

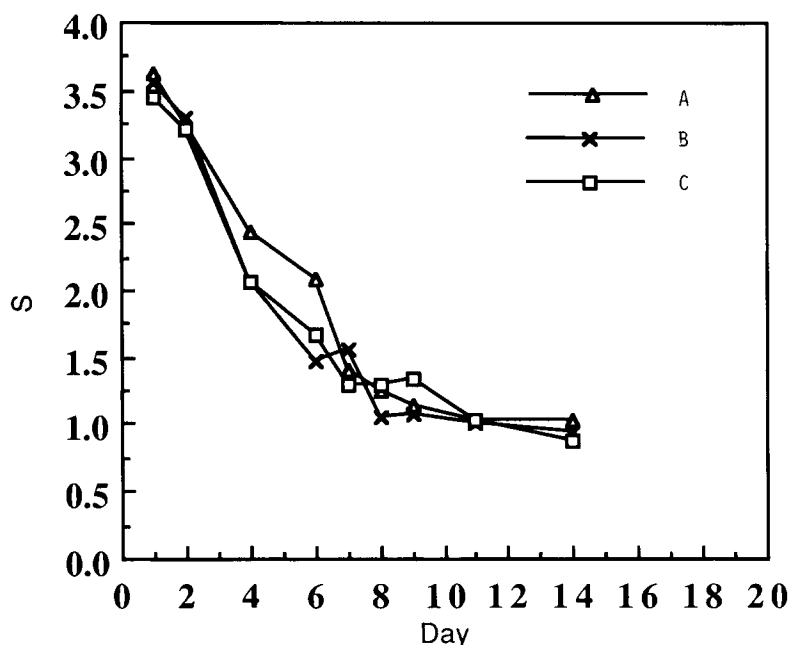


Figure 4 The swelling of undried composite polymers polymerized at room temperature against the polymerization time. The compositions of samples A, B, and C are as in Figure 3.

The high stability of these gels constitutes an advantage in their processing. For the MMA-gelatin gels, intensive stirring had to be employed within the first hour of polymerization at 50°C. In contrast, the polymerization of the styrene-gelatin gels could be performed at 50°C without stirring. The composite polymers are insoluble in water, ethanol, octane, and cyclohexane, but have some swelling in these liquids (see Table I). The high stability of these gels allows us to make any desired form by injection molding or casting. Membrane composite polymers have been prepared using these gels. The gels were first heated at 50°C and poured into aluminum dishes in sheet form of 2–5 mm thickness. As shown by the SEM picture of Figure 2(a), the composite sheets have a condensed structure.

Some of the polymerized composite sheets were additionally heat-treated by locating them between two metal plates under pressure, one of the plates being placed on a heater at about 280°C. Membranes of 0.5–1 mm thickness were thus produced. In the SEM pictures of Figure 2(b) and (c), one can observe a two-layer structure of the heat-treated membranes. One of the layers is more condensed and the other is porous. Contact-angle measurements show that the condensed layer is more hydrophobic (the contact angle with water is about 85°) and the porous layer is more hydrophilic (the contact angle with water is about 40°). The porous structure might have been generated by the water

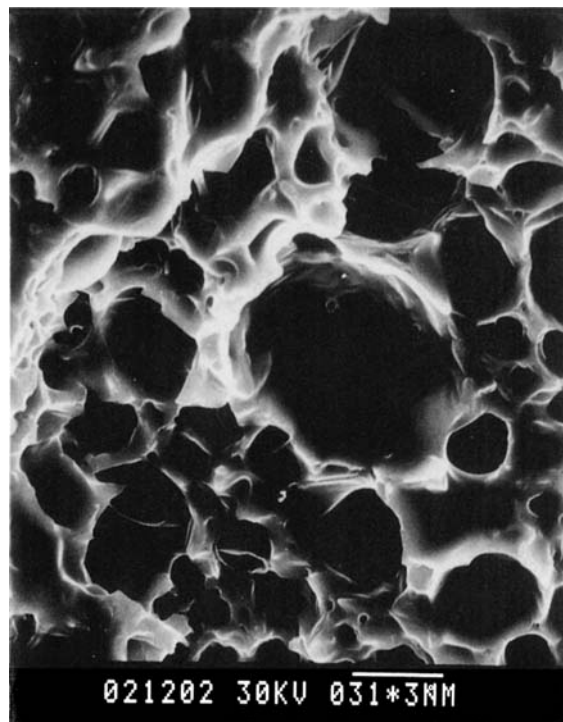
evaporation and decomposition of the gelatin during the heating of the composite at 280°C.

The polymerization of the gels could also be carried out at room temperature. The samples of polymerized composite polymers were first dried for 24 h at ambient temperature, followed by drying for 24 h at 40°C under vacuum. The extent of conversion of styrene into polystyrene after various polymerization times was determined by weighing the products and the gels. Figure 3 shows that the conversion of styrene into polystyrene varies within the first 5 days and reaches a constant value after 5 days. The constant conversion indicates that styrene can be only partially polymerized. The swelling in water test was used to follow the polymerization at room temperature. The swelling of the partially polymerized composites (see Fig. 4) strongly decreases

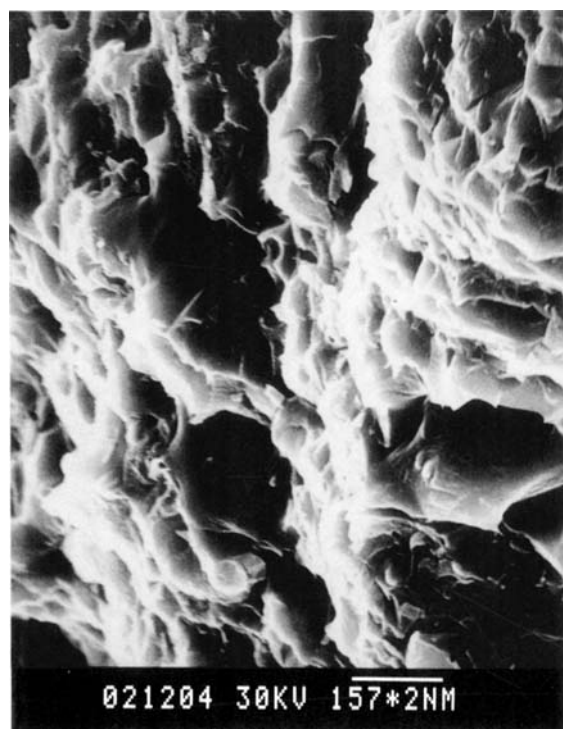
Table II The Swelling of Composite Polymers Polymerized for 10 Days at Room Temperature

	Sample (S)		
	A	B	C
Ethanol	0.166	0.033	0.066
Octane	0.023	0.036	0.038
Cyclohexane	0.079	0.056	0.049

The compositions of the samples are as in Figure 3.



(A)



(B)

Figure 5 Electron micrographs of composite polymer samples A and B of Figure 3.

within the first 5 days and becomes constant after about 8 days of polymerization at room temperature. The swelling in water of the composites is much larger than that of the composites polymerized at 50°C. This indicates that gelatin-based composite polymers with different swelling capacities in water can be produced by controlling the polymerization time and temperature.

Comparing Figures 3 and 4, one can observe that the time at which the swelling and conversion become constants are different. In Ref. 2, it was reported that cross-linking of gelatin occurred at room temperature in the gels consisting of gelatin, water, SDS, MMA, and AIBN. In the present styrene-gelatin gel system, the polymerization of styrene and the cross-linking of gelatin probably occur simultaneously at room temperature within the first 5 days. The cross-linking reaction of the gelatin might, however, last longer than the polymerization and could be responsible for the reduction of the swelling of the composites after 5 days of reaction. The partially polymerized composite polymers are insoluble in ethanol, octane, and cyclohexane and absorb very small amounts of these compounds (see Table II).

The SEM pictures of Figure 5 show the porous structures of the dried composite polymers of gelatin and polystyrene prepared at room temperature. The porous structure might be a result of the evaporation of water and residual monomers (styrene) during drying.

The high stability of these gels and insolubility of the resulting composite polymers could be useful technologically. For instance, they may be used for repairing nicks and scratches. The gels can be heated to 50°C and injected into the nicks or scratches and then allowed to polymerize *in situ* at room temperature.

As suggested in Ref. 1, the gelatin-based composite polymers might have an interpenetrating network structure. The solution of gelatin generates a physical hydrophilic network dispersed in the hydrophobic monomer phase. The polymerization of these gels at 50°C or at room temperature generates a second, hydrophobic, polystyrene network that interpenetrates the former gelatin network. The gelatin network becomes cross-linked chemically via a radical process.² Polystyrene is soluble in cyclohexane, but the composite polymers of polystyrene and gelatin are insoluble. The hydrophilic gelatin network prevents the penetration of the solvent inside the composite polymers. As a result, the gelatin-based composite polymers become insoluble in organic, hydrophobic solvents, such as cyclohexane or

octane. Gelatin is soluble in water, but the composite polymers of polystyrene and gelatin are insoluble.

CONCLUSION

Stable emulsions with the appearance of gels have been prepared by mechanical mixing at 50°C of an aqueous solution of a surfactant (SDS) and gelatin with a monomer (styrene) containing an initiator (AIBN). The gels thus obtained are very stable and can be kept for a long time at room temperature and at 50°C. The gels are liquidlike and can flow at 50°C; those with a high gelatin content are solidlike and have a viscoelastic behavior at room temperature. Composite polymers can be produced by polymerizing the gels for 24 h at 50°C or for several days at room temperature. The composite polymers thus obtained are insoluble in water, ethanol, octane, and cyclohexane, but absorb these liquids to various extents. Composite polymers with different water-absorbing capacities can be produced by controlling the polymerization time and temperature. Membranes with a two-layer structure, with one layer more hydrophobic and compact and another more hydrophilic and porous, can be prepared by polymerizing the gels in sheet form for 24 h at 50°C, followed by their heating at 280°C under pressure. Porous structures have also been observed in the gelatin-based composite polymers polymerized at room temperature.

NOTATIONS

C_g	the concentration of gelatin in the entire gel (g/mL)
C_{SDSW}	the concentration of SDS in water (mol/L)
C_{AIBN}	the concentration of AIBN in monomer styrene (mol/L)
C_{WM}	the volume ratio of aqueous solution of SDS to monomer styrene (mL/mL)

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