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Interpenetrating Hydrogel Networks. 2. Swelling and Mechanical Properties of the Gelatin–Polyacrylamide Interpenetrating Networks†

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ABSTRACT: In situ polymerization of acrylamide–bisacrylamide mixtures in a gelatin medium with subsequent cross-linking of gelatin chains using the bifunctional reagent glutaraldehyde yields interpenetrating networks (IPNs) of the two polymers. Here we report the swelling characteristics and mechanical properties of these networks. The matrix being nonionic, the swelling is not affected by electrolytes. The isotropic swelling of the full IPNs emphasizes the randomness of network formation and hence extensive interpenetration of the two networks at the mesh level. Mechanical properties of these IPN films, like the ultimate strength and elongation at break, show compositional dependence.

Introduction

Interpenetrating polymer networks (IPNs) come under the unique category of molecular blends. In an attempt to develop materials that perform like synthetic polymers, yet degrade like natural polymers, we have been investigating several combinations of these two classes of macromolecules. We were particularly interested in developing a two-component hydrogel matrix, wherein the degree of swelling can be effectively controlled by simply varying the composition. In this context, we have already reported the synthesis and characterization of hydrophilic/hydrophobic graft copolymers of cross-linked gelatin.[1] However, compositional variations are not easy to achieve in graft copolymers, because the heterophasic graft copolymerization is a cumulative result of a variety of kinetic parameters. This prompted us to explore the possibility of developing interpenetrating hydrogel networks. We selected the gelatin–polyacrylamide system for several reasons. Gelatin and polyacrylamide are water soluble and can form binary solutions over a very wide compositional range. The water solubility of gelatin, acrylamide, bisacrylamide, ammonium persulfate, and glutaraldehyde, together with the specificity of glutaraldehyde for gelatin and bisacrylamide for acrylamide, makes the formation of gelatin–polyacrylamide IPNs possible. Another advantage of this nonionic hydrogel system is that this could be easily converted into the ionic form through partial hydrolysis of the amide groups. The most desirable feature, however, is the simplicity of the reactions, which can be carried out at room temperature. In an earlier report, we discussed the chemistry of IPN formation between gelatin and polyacrylamide.[2] The macromolecular chemistry of gelatin has been dealt with in detail by Veis.[3] The glutaraldehyde cross-linking of gelatin includes Michael type adducts in addition to aldimine linkages (Figure 1).[4,5]

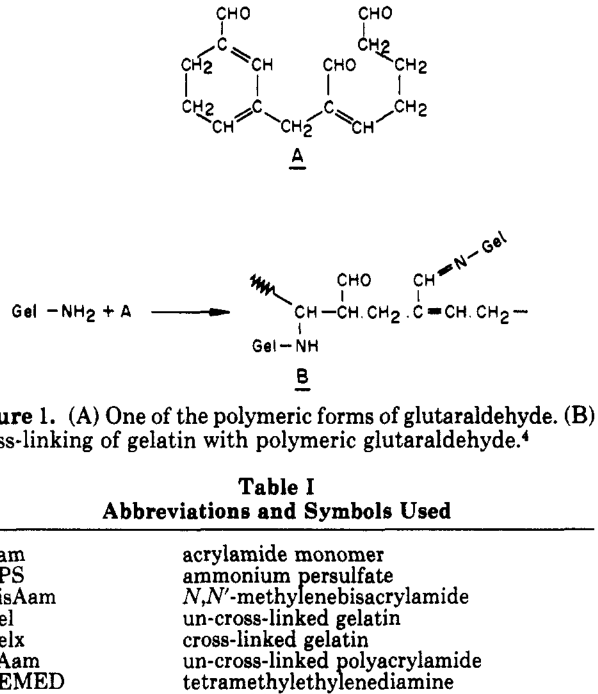

Figure 1. (A) One of the polymeric forms of glutaraldehyde. (B) Cross-linking of gelatin with polymeric glutaraldehyde.[4]

Table I
Abbreviations and Symbols Used

Aam	acrylamide monomer
APS	ammonium persulfate
BisAam	*N,N'*-methylenebisacrylamide
Gel	un-cross-linked gelatin
Gelx	cross-linked gelatin
PAam	un-cross-linked polyacrylamide
TEMED	tetramethylethylenediamine
GLA	glutaraldehyde
IPN	interpenetrating polymer network
(Gelx–PAamx)	interpenetrating polymer network where gelatin and polyacrylamide are fully and independently cross-linked with GLA and BisAam, respectively
(Gelx–PAam)	semiinterpenetrating polymer network where only gelatin is cross-linked
(Gel–PAamx)	semiinterpenetrating polymer network where only polyacrylamide is cross-linked
SIPN	semiinterpenetrating polymer network where only one component is cross-linked
FIPN	fully interpenetrating polymer network where both components are independently cross-linked

Experimental Section

The abbreviations used throughout the text are defined in Table I.

Aam, BisAam, APS, TEMED, gelatin, and glutaraldehyde (25% aqueous solution) were supplied by Loba Chemicals, Bombay, India. Doubly distilled water was used for all reactions.

Blocks of full IPNs, the (Gelx–PAamx) series, were prepared by adding calculated quantities of Aam, Bis, and APS to a gelatin solution of the required percentage. TEMED was then added from a microsyringe (100 μL), the solution was stirred well quickly to avoid lumping and then poured over rectangular perspex molds, and the molds were allowed to set overnight. The firm gels were then carefully dislodged and immersed in 1% GLA overnight to cross-link the gelatin chains. The gels were then washed extensively with water to remove all water-soluble moieties.

The same procedure was adopted for the preparation of semi-IPNs, except that in the (Gelx–PAam) series, BisAam was deleted and in the (Gel–PAamx) series, GLA treatment was omitted.

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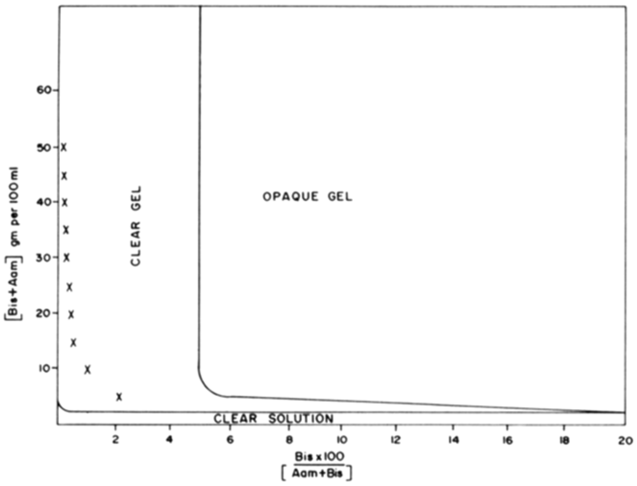

Figure 2. Gelation of the cross-linked acrylamide–bisacrylamide copolymerization systems investigated.

Films of the respective IPNs were prepared by casting the solutions onto perspex sheets and allowing them to dry at room temperature for several days. Here the required amount of GLA together with 0.25% glycerol as plasticizer was added to the casting solution itself. Since moisture also was found to have a plasticizing effect on the film, the humidity values are also reported. The thicknesses of the films were measured with a micrometer. In all cases the extent of gelatin cross-linking was assessed by amino acid analysis.[6]

Swelling studies were performed by immersing dry blocks of average size 3 × 3 × 0.75 cm^3 in a water/saline medium. The swollen gels were then lifted, patted dry, and weighed at defined intervals. From swollen and dry weights of the samples, the extent of swelling was calculated.[7] The initial and final dimensions of the blocks were measured in each case.

The tensile properties of the films were measured as per ASTM D-638 in an Instron universal test instrument (Model 1026). Six tests were taken for each sample. The tensile strength at break was calculated as $f^* = F/A^*$, where F is the load in kilograms and A^* is the cross sectional area of the undeformed sample. The percentage elongation at break (ϵ) was given by $100\Delta L/L$, where ΔL is the increase in length and L is the original length. The extension rate is 1 cm min^{-1}.

Results and Discussion

The copolymerization of Aam with BisAam leading to network formation has been well explored.[8,9] Bansil and Gupta[8] point out the necessity to keep the concentration of BisAam below 4% of the total monomer concentration for transparent, macroscopically homogeneous gels. Figure 2 shows the range of acrylamide–bisacrylamide composition that we investigated superimposed over the Bansil–Gupta phase diagram for Aam–BisAam cross-linking.[8]

The concentration of gelatin employed in these investigations ranges from the gelling threshold (5%) to well above (25%). At these concentrations, there is a very high degree of overlapping and entanglement of gelatin chains.[3] The initiation of the copolymerization of a Aam–BisAam mixture leads to the formation of PAam networks trapping the gelatin chains within. This is the semi-IPN state. With GLA treatment the gelatin chains are also covalently cross-linked, yielding full IPNs.

The isotropic swelling of a gel network often reflects its macroscopic homogeneity. The equilibrium swelling of a network in a diluent is the result of a balance between the osmotic and the restoring elastic pressures. Figure 3 shows the (Gel–PAam) IPN blocks in the initial dry and final equilibrium swollen states. All of the hydrogel samples reported here are clear and transparent, indicating the absence of phase separation. However, the samples with gelatin in the cross-linked state ranged from pale brown to amber, depending upon the gelatin concentration. The cross-linking reaction between gelatin and glutaraldehyde, resulting in a Schiff base linkage, is accompanied by a definite color change.[1]

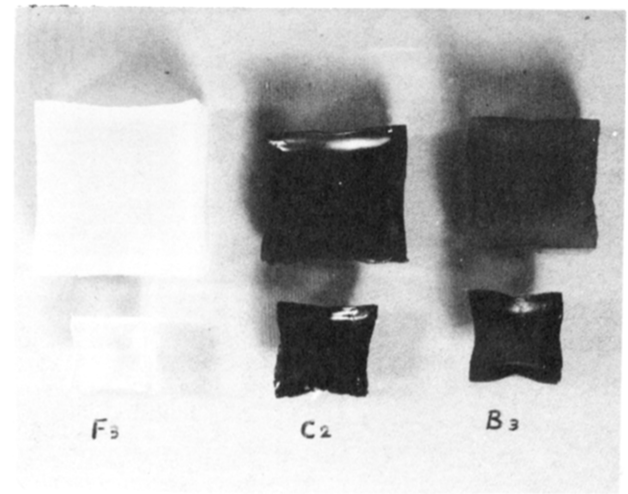

Figure 3. Dry (lower) and swollen (upper) IPN gels: F_3 = 1:3 (Gel–PAamx); C_2 = 2:1 (Gelx–PAam); B_3 = 1:3 (Gelx–PAamx).

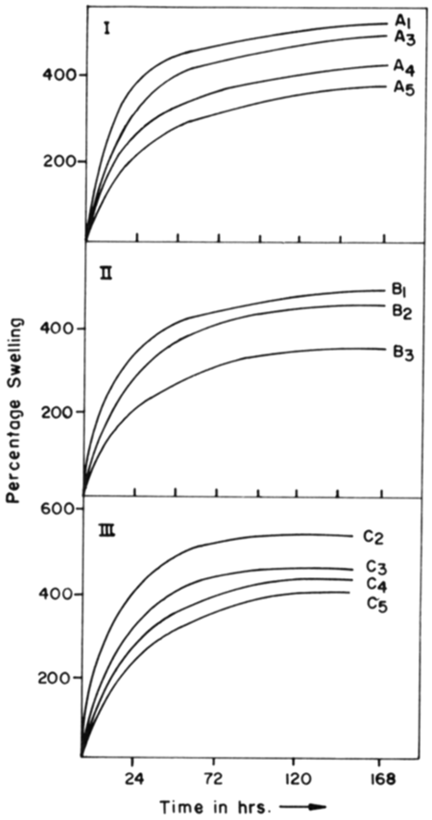

Figure 4. Swelling pattern of IPNs. I, (Gelx–PAamx): A_1 = 1:1 Gel:Aam, A_3 = 3:1 Gel:Aam, A_4 = 4:1 Gel:Aam, A_5 = 5:1 Gel:Aam; II, (Gelx–PAamx): B_1 = 1:1 Gel:Aam, B_2 = 1:2 Gel:Aam, B_3 = 1:3 Gel:Aam; III, (Gelx–PAam): C_2 = 2:1 Gel:Aam, C_3 = 3:1 Gel:Aam, C_4 = 4:1 Gel:Aam, C_5 = 5:1 Gel:Aam.

Typical swelling curves for several sets as a function of time are given in Figure 4. The networks being nonionic, the swelling ratio is not affected by the presence of electrolytes (Figure 5). The same behavior has been reported earlier for cellulosic gels and poly(vinylpyrrolidone) gels.[10,11] The most important result, however, is the data shown in Figure 6, where the initial dry dimensions of the blocks are plotted against the final dimensions in

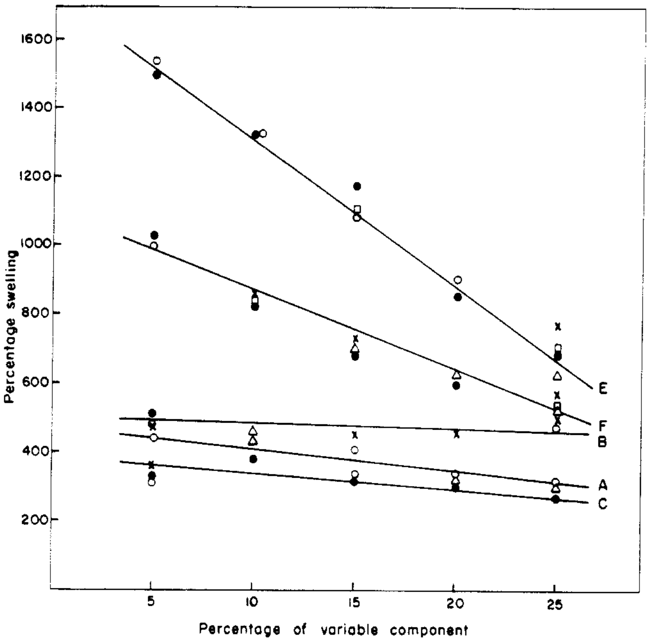

Figure 5. Swelling pattern of IPNs in water and sodium chloride solutions as a function of composition. A = (Gelx–PAamx), variable gel; B = (Gelx–PAamx), variable Aam; C = (Gelx–PAam), variable gel; E = (Gel–PAamx), variable gel; F = (Gel–PAamx), variable Aam. Various concentrations of NaCl solution are designated as follows: (×) 0.5 M NaCl; (○) 0.1 M NaCl; (△) 0.01 M NaCl; (□) 0.001 M NaCl; (●) distilled water.

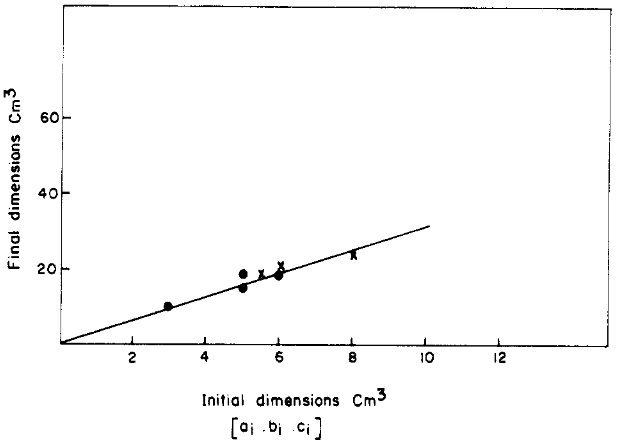

Figure 6. Plot of initial dry dimensions vs final equilibrium swollen dimensions of rectangular blocks of (Gelx–PAamx) full IPNs.

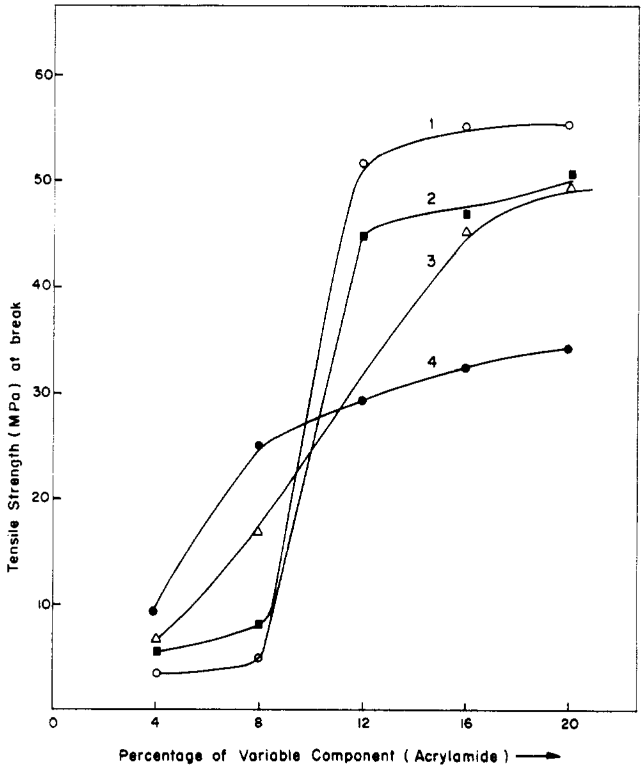

Figure 7. Tensile strength of IPNs as a function of composition. Gelatin constant at 4%. (1) (Gel–PAamx); (2) (Gelx–PAam); (3) PAamx; (4) (Gelx–PAamx). Humidity 91%.

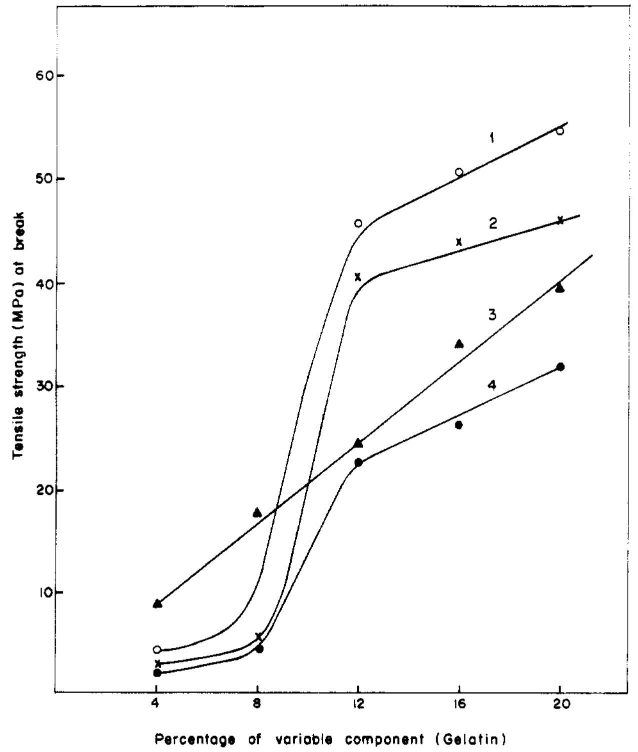

Figure 8. Tensile strength of IPNs as a function of composition. Acrylamide constant at 4%. (1) (Gel–PAamx); (2) (Gelx–PAam); (3) Gelx; (4) (Gelx–PAamx). Humidity 91%.

the equilibrium swollen state. This indicates isotropic swelling of the IPN network, which is possible only if a certain degree of homogeneity exists at the mesh level.[12] This inference has interesting overtones. Here we have two distinctly different gelation processes occurring. One is the cross-linking of small acrylamide and bisacrylamide units, which conforms to the critical phenomena, while the other is the classical example of the vulcanization of gelatin chains through GLA cross-linking, which adheres to the Flory–Stockmayer model.[13,14] (Both processes can be explained sufficiently satisfactorily by percolation theory). It has been observed that if gelatin network formation is rapid or takes place at high polymer concentration, random chain orientations and excessive chain entanglements lead to the formation of fine network structures.[3] Consequently, this fact has to be taken into account when the structures of (Gelx–PAamx) full IPN networks are discussed. Though chemically these come under the category of sequential IPNs (because gelatin is cross-linked at a later state), they could as well be classified as simultaneous IPNs. The high gelatin concentrations employed cause a large number of chain entanglements that are simultaneously locked in position within the growing PAamx matrix; later, by GLA cross-linking, these random orientations are given a permanent lattice framework.

For a meaningful interpretation of the results in Figures 7–10, it is necessary to have an estimate of the elastically

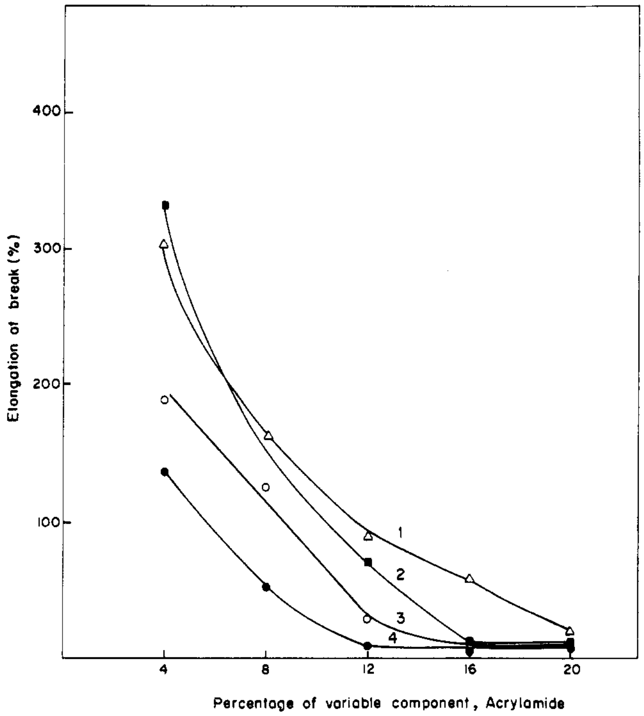

Figure 9. Percentage elongation as a function of IPN composition. Gelatin constant at 4%. (1) PAamx; (2) (Gelx–PAam); (3) (Gel–PAamx); (4) (Gelx–PAamx). Humidity 91%.

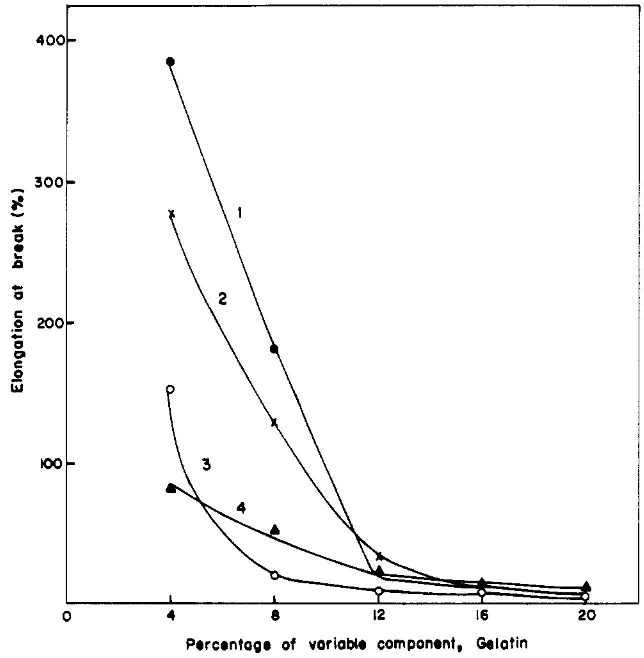

Figure 10. Percentage elongation as a function of IPN composition. Acrylamide constant at 4%. (1) (Gelx–PAamx); (2) (Gelx–PAam); (3) (Gel–PAamx); (4) Gelx. Humidity 91%.

efficient segments in the network. By definition, elasticity is the ability to sustain large reversible deformations without rupture. While a minimum number of cross-links between polymer chains is essential to impart and safeguard the property of elasticity, with an increase in cross-link density, the chains anchored at shorter distances, with a consequent decrease in the spacings between cross-links. This introduces an element of rigidity into the network.

The amino acid analysis of gelatin indicated ~7 nanomoles of lysine residues in 20 μg of the sample, and the data on IPNs showed 85–90% of the lysines tied up in cross-links irrespective of the gelatin concentration. This is not surprising in view of the following facts: (i) the swiftness and efficiency of the reactions and (ii) the large excess of glutaraldehyde employed. This nearly total modification of lysine residues in protein chains by glutaraldehyde has been the reason for the wide use of this reagent as a cross-linking agent in biochemical experiments.[4,5] The molecular mass of gelatin determined viscometrically[15] is 4.04×10^5 daltons. Theoretically this yields an average cross-link density of 136 links per mol (or 1.7×10^{-4} mol of cross-links/cm^3), with the average molecular weight between cross-links, M_x, definitely being a function of the gelatin concentration. We calculated the cross-link density of the PAamx networks in the semi-IPN and full IPN systems using the Flory–Rehner equation[16]

$$-\ln(1 - v_2) - v_2 - \chi_{12}v_2^2 = (\rho/M_x)V_sC_x^{2/3}(v_2^{1/3} - v_2/2)$$

where v_2 is the volume fraction of polymer in the gel swollen to equilibrium, χ_{12} is the polymer–solvent interaction parameter,[17] ρ is the density of the solvent, V_s is the molar volume of the solvent, M_x is the molecular weight between cross-links, and C_x is the concentration of the polymer as a volume fraction.

The values were of the order of $(2–5) \times 10^{-5}$ mol of cross-links/cm^3 with M_x values in the range $(4–10) \times 10^4$ daltons, depending upon the concentration of acrylamide employed. However, we believe these values have very little realistic significance for the gelatin–polyacrylamide IPN system because of the extremely large number of intra- and interchain hydrogen bonds formed by gelatin during gelation. Though it will be futile to even attempt to make a quantitative assessment of these hydrogen bonds, their overwhelming contribution toward the swelling and mechanical properties of the material cannot be overlooked. On the basis of Figures 7–10, the following order could be derived with respect to tensile strength and elongation at break: SIPN > PAamx > Gelx > FIPN.

This suggests that the cross-link density should also be in the same order. This assumption is logistically correct in light of the Flory–Rehner equation, which predicts that M_x is a function of polymer concentration for networks formed in solution. These IPNs are formed in solution and, in the case of SIPNs, the un-cross-linked polymer component functions as an effective diluent while, in the FIPNs, the two networks reinforce each other through interpenetration.

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