

Interpenetrating Hydrogel Networks. I. The Gelatin–Polyacrylamide System*

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Synopsis

In situ polymerization of acrylamide–bisacrylamide mixture in concentrated aqueous gelatin solutions followed by the subsequent crosslinking of gelatin itself with glutaraldehyde yields interpenetrating hydrogel networks. The surface morphology, swelling, and thermal behavior of the samples of different composition were investigated. The swelling characteristics of the hydrogel could be manipulated by varying gelatin and acrylamide ratio.

INTRODUCTION

Gelatin and polyacrylamide are water-soluble macromolecules, capable of forming gels independently. Sufficiently concentrated warm aqueous solutions of gelatin set to a gel upon cooling. Inter- and intrachain hydrogen bondings are responsible for this gelation. Consequently, these gels are thermoreversible, exhibiting the sol \rightleftharpoons gel transition.¹ Polyacrylamide yields stable gels by chemical crosslinking.^{3–5} Free radically triggered polymerization of acrylamide in presence of small amounts of bisacrylamide (< 4%) leads to the formation of a clear, macroscopically homogenous network which can swell extensively in water. Since the network is the result of permanent bonds, crosslinked polyacrylamide gels do not exhibit sol \rightleftharpoons gel transition, but they can be dehydrated and rehydrated.

Swelling characteristics of a network are influenced by the conditions under which the network has been formed. de Boer et al.⁶ made the observation that solution-crosslinked polyethylenes could swell to higher proportions than bulk-crosslinked samples. It was suggested that when crosslinked in solution, the macromolecular chains may assume the most probable extended conformations and, as a result, in the dehydrated, shrunken state the average end to end distances will be shorter than in the “as crosslinked state.” Poh et al.^{7–9} refers to the overwhelming tendency of such networks in dry state to get solvated. He describes them as “high free energy networks” or “hungry networks.”

Here we report the formation from solution of a series of full and semi interpenetrating hydrogel systems based on gelatin and polyacrylamide as the two components and glutaraldehyde and bisacrylamide as the respective and exclusive crosslinking agents. The abbreviations listed in the Table I shall be used throughout the text.

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TABLE I
Abbreviations and Symbols

Aam	Acrylamide monomer
APS	Amonium persulfate
Bis Aam	<i>N,N</i> -methylene-bisacrylamide
Gel	Gelatin, uncrosslinked
Gelx	Crosslinked gelatin
PAam	Polyacrylamide, uncrosslinked
temed	Tetramethyl ethylenediamme
<i>The IPNs</i>	
[Gelx-PAamx]	Full IPN where gelatin and polyacrylamide are fully and independently crosslinked with GLA and Bis Aam, respectively
[Gelx-PAam]	Semi-IPN where only gelatin is crosslinked
[Gel-PAamx]	Semi-IPN where only polyacrylamide is crosslinked

EXPERIMENTAL

Materials and Methods

Aam, bisAam, temed, APS, gelatin, and glutaraldehyde (25% aqueous solutions) were supplied by Loba Chemicals (Bombay, India). Nitrogen-bubbled double-distilled water was used for all polymerizations.

Preparation of Hydrogels

Full IPNs: The [Gelx-PAamx] Series

The initial step is the preparation of the gelatin solution of required concentration in oxygen-free distilled water. Then calculated quantities of acrylamide, bisacrylamide, and APS are dissolved in this solution. Temed is then injected from a syringe; the solution is stirred well quickly to avoid lumping and then set aside undisturbed (overnight). The firm gel is then carefully dislodged from the walls of the container and immersed in 1% GLA overnight, to crosslink the gelatin chains. The gels are then washed extensively with water to remove water soluble moieties.

Semi-IPNs: [Gelx-PAam] and [Gel-PAamx] Series

The procedure adopted is the same as for full IPNs, except that in the [Gelx-PAam] series BisAam is deleted and in the [Gel-PAamx] series GLA treatment is omitted.

Swelling Studies

The freshly prepared water washed gels are immersed in distilled water for 48 h, with frequent changes of water. The swollen gels are then lifted, patted dry, and weighed. They are then oven-dried till constant weights are maintained. From the swollen and dry weights of the samples the extent of swelling is calculated.¹⁰

Thermal Behavior

Differential thermal analysis of the full and semi-IPNs were carried out in a Leeds Northup unit at 12.5°C/min heating rate up to 900°C. The reference used was alumina.

Scanning Electron Micrographs

The surface morphology of the full and semi-IPNs were inspected using 5520 Hitachi Model scanning electron microscope. The samples were gold coated in the usual manner prior to examination.

RESULTS AND DISCUSSION

Physical mixtures of Gelx and PAamx are conspicuously incompatible either in the solid state or in the aqueous phase. But in the uncrosslinked, linear state both gelatin and polyacrylamide can form binary solutions in water over a very wide composition range. Secondly, under a given set of conditions, GLA and BisAam are mutually exclusive crosslinking agents for gelatin and polyacrylamide, respectively. This precisely is the possibility we exploited to get interpenetrating hydrogel system based on these macromolecules.

The concentrations of gelatin employed in these investigations range from the gelling threshold to well above (5–30%). Under these conditions the gelatin solutions are quite concentrated and the individual chains can be considered

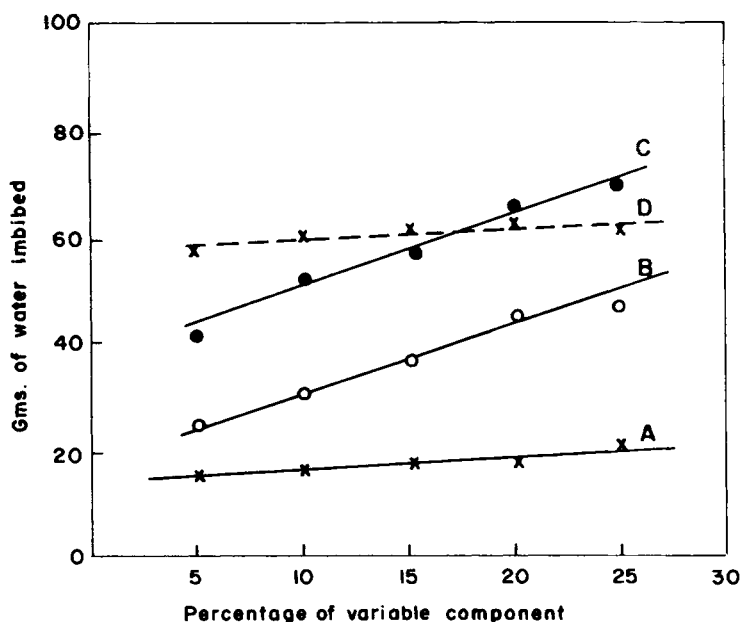


Fig. 1. Swelling behavior of the IPNs: (A) [Gelx-PAamx] full IPN: acrylamide constant at 5%, gelatin varied from 5 to 25%; (B) [Gelx-PAamx] full IPN: gelatin constant at 5%, acrylamide varied from 5 to 25%; (C) [Gelx-PAam] semi-IPN: Gelx constant at 25%, acrylamide varied from 5 to 25%; (D) [Gel-PAamx] semi-IPN: PAamx constant at 25%, gelatin varied from 5 to 25%.

TABLE II
Swelling Characteristics of [Gelx-PAamx] Full IPNs

Sample	Gel % (w/v)	Aam % (w/v)	Total polymer % (w/v)	Total amount of water imbibed (g)	Percentage
Co	5	—	5	Gluey mass did not set	
A1	5	5	10	20.8	100
C2	5	10	15	28.0	93
C3	5	15	20	36	90
C4	5	20	25	45	90
C5	5	25	30	52	88
Ao	—	5	5	17	170
B2	10	5	15	18.5	62
A3	15	5	20	18.0	60
A4	20	5	25	20.0	63
A5	25	5	30	20.0	63

to be overlapping and entangled.¹ This is the situation we begin with. The polyacrylamide network is then built over and around the gelatin chains, thus reducing their mobility. The system gels with the progress of the polyacrylamide network. Subsequent crosslinking of the protein chains with glutaraldehyde interlocks both the networks inseparably. The concentrations of acrylamide and bisAam are also meticulously chosen so as to avoid phase separation. Bansil and Gupta² point out that, in order to obtain clear homogenous gels, the concentrations of the bifunctional reagent must be kept low. In our experiments we have varied the acrylamide concentration from 5 to 30% and accordingly the bisAm content has ranged from 2 to 0.1%.

When acrylamide content is held constant at 5% and gelatin content varied over 0–25%, the amount of water imbibed remains constant [Fig. 1 (A), Table

TABLE III
Swelling Characteristics of Semi-IPNs [Gelx-PAam] and [Gel-PAamx]

Sample	Gel % (w/v)	Aam % (w/v)	Total polymer content % (w/v)	Total amount of water imbibed (g)	Percentage
<i>[Gelx-PAam]</i>					
Do	25	—	25	30.8	60
D1	25	5	30	36.3	60
D2	25	10	35	52.3	74
D3	25	15	40	—	—
D4	25	20	45	65.3	74
D5	25	25	50	68.9	69
<i>[Gel-PAamx]</i>					
Eo	—	25	25	57.4	115
E1	5	25	30	59.2	100
E2	10	25	35	61.0	87
E3	15	25	40	63.2	79
E4	20	25	45	64.7	72
E5	25	25	50	62.0	62

II]. Figure 1(B) depicts the behavior of [Gelx-PAamx] system where gelatin content is held constant and acrylamide content varied. Water absorption increased with increasing acrylamide content.

The two semi-IPN sets, [Gelx-PAam] and [Gel-PAamx], also exhibit a similar trend. The [Gelx-PAam] series where gelatin content is held constant at 25% and acrylamide content varied from 0 to 25% resembles the corresponding [Gelx-PAamx] set [Fig. 1(C), Table III]. The [Gel-PAamx] set where acrylamide content is held constant at 25% and gelatin varied from 0 to 25% [Fig. 1(D), Table III] correlated very well with the corresponding [Gelx-PAamx] set except at higher gelatin contents. We observed that such samples, where gelatin content was above 20%, suffered extensive weight losses on successive water washings and finally the residual weight roughly leveled off at the PAam content. Figure 2 presents the correlation curve between the theoretical weights of the samples and the actual experimental (oven-dried to constancy) weights.

The behavior of the full and semi-IPNs is consistent with the swelling behavior of the individual networks. Depending upon the concentration, cross-linked PAamx networks can imbibe larger quantities of water than Gelx under the same conditions (Fig. 3). Thus the swelling characteristics of PAamx could mask those of Gelx. The thermal behavior of the IPNs reinforce this aspect. The individual decomposition traits of Gelx and PAamx overlap and yield com-

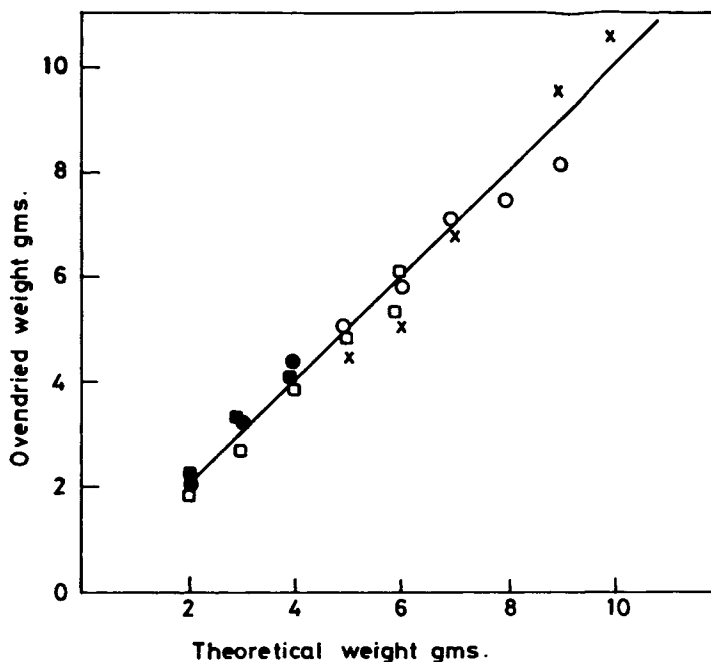


Fig. 2. Correlation between the theoretical weights and experimentally obtained weights. The solid line is the theoretical curve. The details of experimental points are as follows: (\square , \blacksquare) full IPN, variable gelatin; (\bullet) full IPN, variable acrylamide; (\times) semi-IPN, variable acrylamide; (\circ) semi-IPN, variable gelatin.

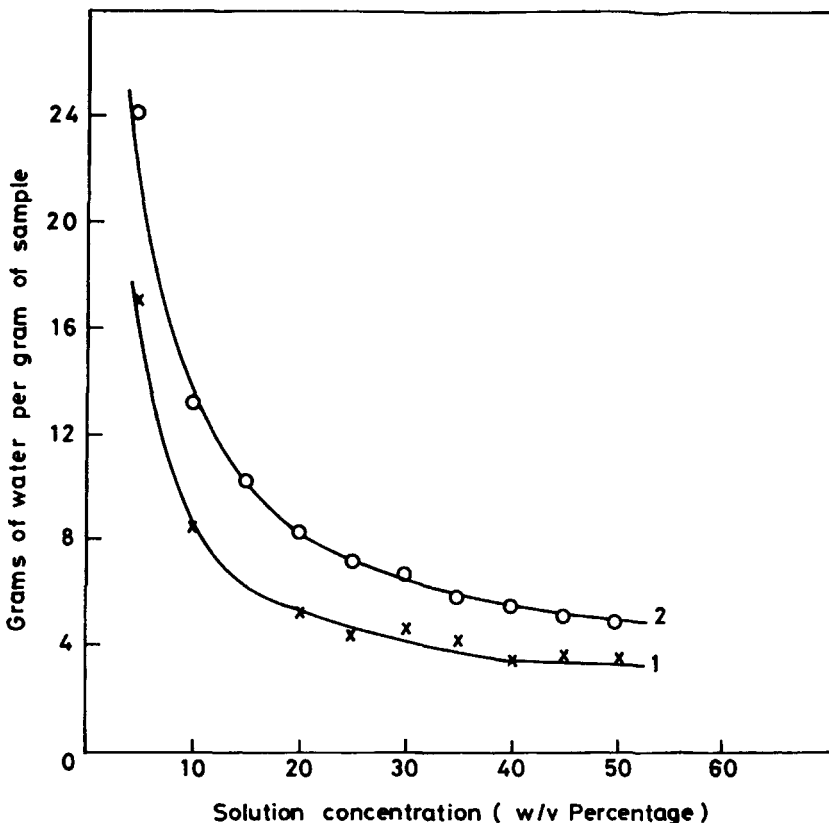


Fig. 3. Swelling characteristics of Gelx (1) and PAamx (2) samples over a period of 48 h.

posite thermograms (Fig. 4). The scanning electron micrographs reflect the surface morphology of the various samples (Fig. 5).

For semi-IPNs, we selected such concentrations of Gel and Aam, which would yield firm gels. The situation here is analogous to those discussed by de Gennes¹¹ and Poh et al.⁸ with reference to the dynamics of the linear macromolecules entrapped in a crosslinked matrix. Taking into consideration the molecular weight M of the linear polymer, the average molecular weight between crosslinks (M_x) and the average molecular weight (M_e) between physical entanglements of the matrix three probabilities were envisaged. The free draining stage where the dimensions of the linear polymer are so inconsequential in comparison with the M_e and M_x values, that it can easily get leached out of the network. For values of M , intermediate between M_e and M_x (i.e., $M_e < M < M_x$) the lateral mobility of the linear chain will be restricted; however, it can still diffuse along its own length by way of reptation.¹¹ When $M > M_e > M_x$ the linear macromolecule gets totally entrapped within the meshwork. We can equate these situations to those prevailing in the semi-IPNs. In the [Gelx-PAam] set, Gelx provides the matrix in which linear PAam chains lay entrapped. The low swelling tendency of Gelx matrix prevents the PAam chains from

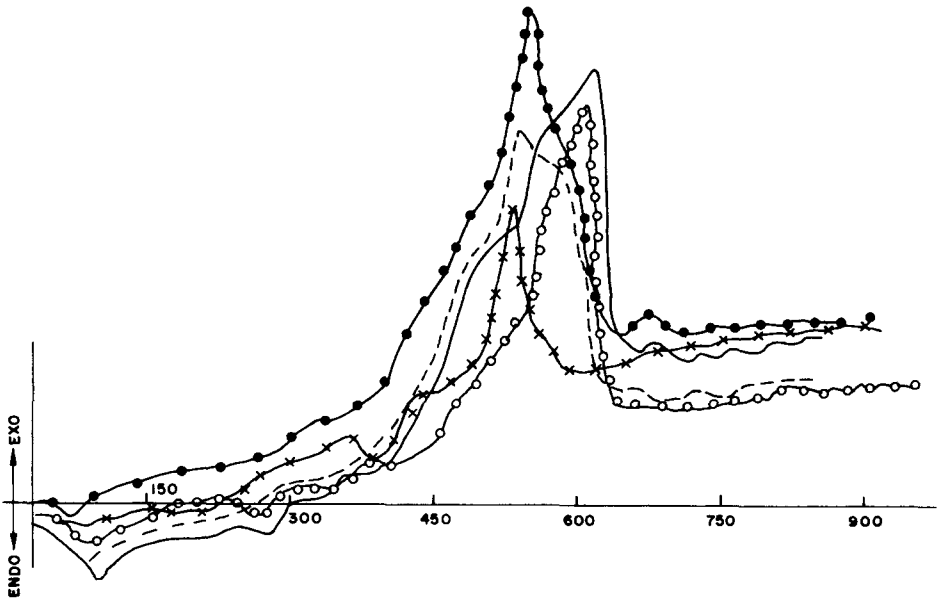


Fig. 4. Thermal behavior of the IPN samples: differential thermal analysis was carried out as described in the text: (×) Gelx; (○ — ○) PAamx; (—) Gelx-PAamx (1 : 1); (● — ●) Gelx-PAam (1 : 1); (- - -) Gel-PAamx (1 : 1).

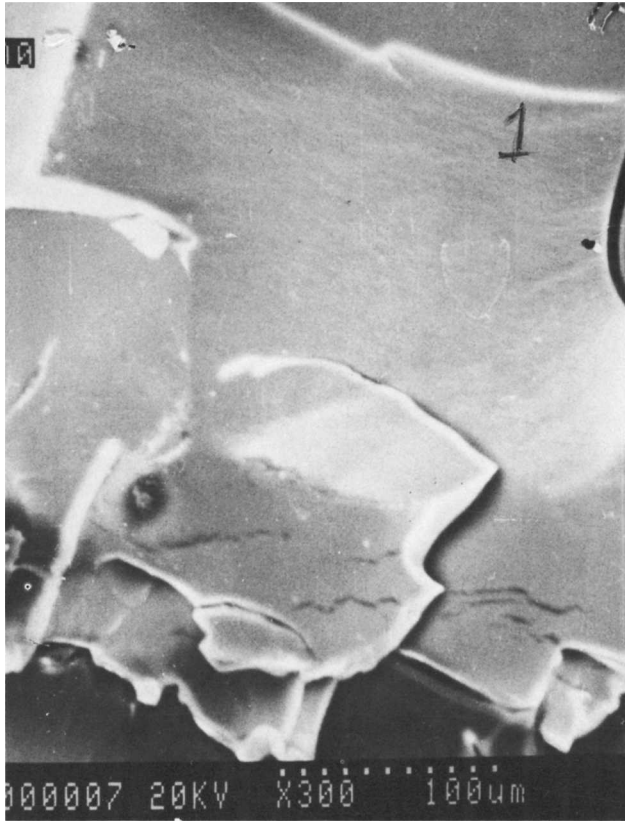


Fig. 5. Scanning electron micrographs of: (1) Gelx; (2) PAamx 3; [Gelx-PAamx] (1 : 1); (4) [Gelx-PAam] (1 : 1); (5) [Gel-PAamx] (1 : 1).

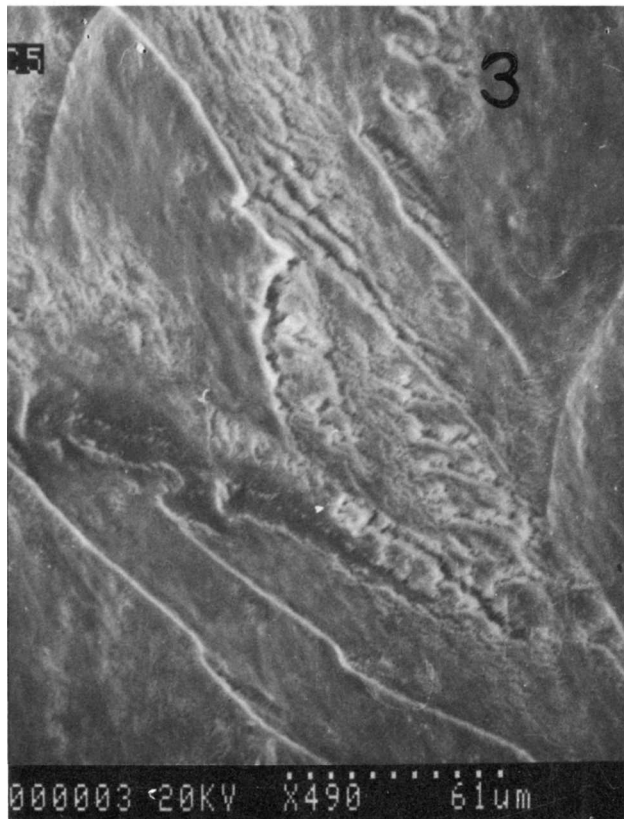
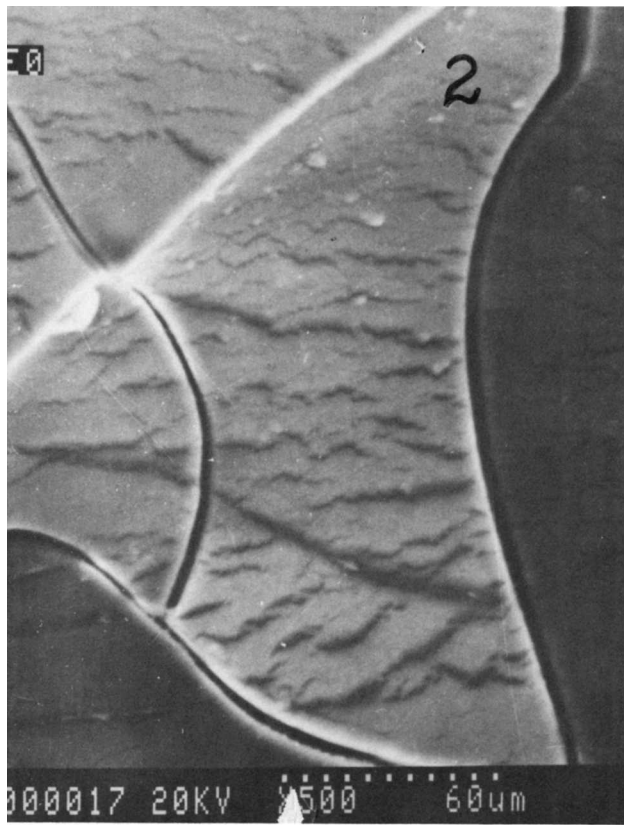


Fig. 5. (Continued)

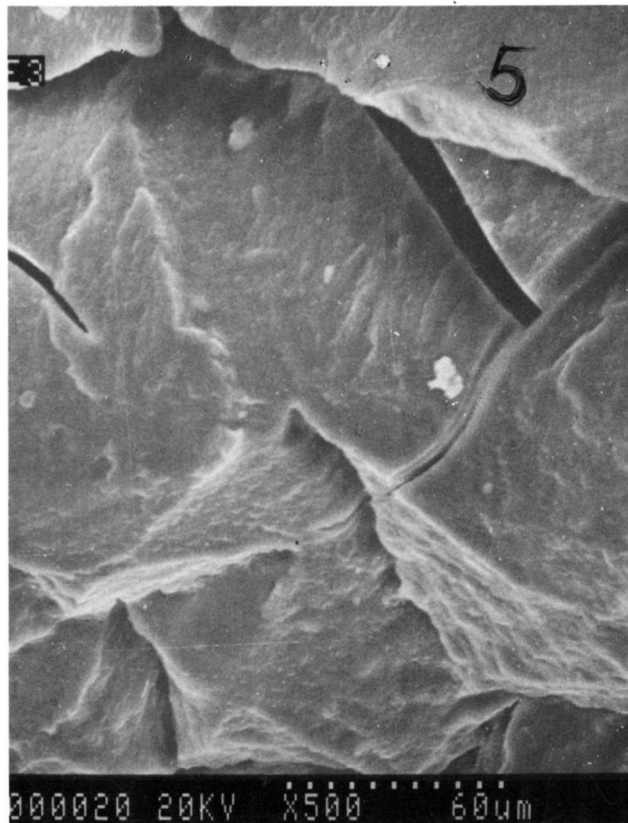
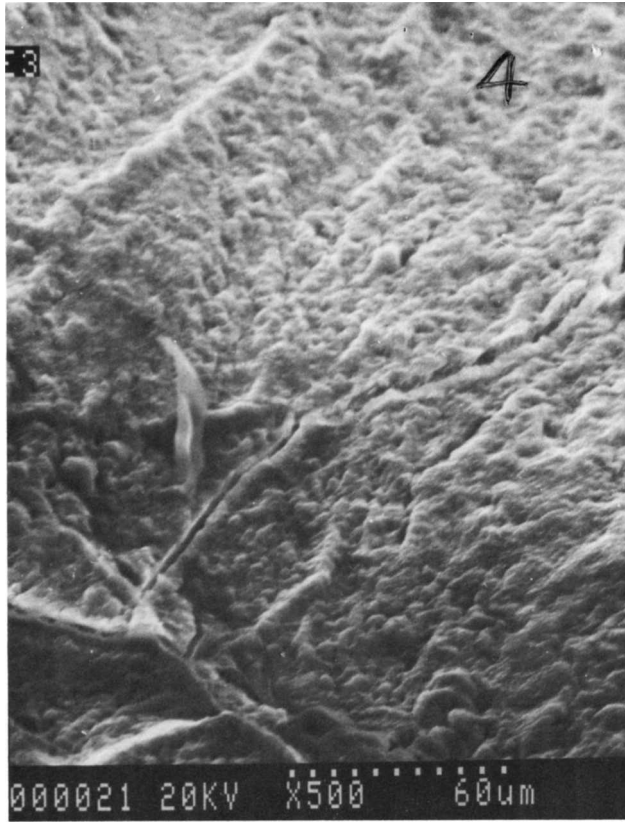


Fig. 5. (Continued)

escaping. In the [Gel-PAamx] set the PAamx provides the meshwork. The well-swollen PAamx matrix greatly facilitates the mobility of the water soluble gelatin chains. This will be more evident in cases where free gelatin content is very high. This precisely is our observation.

The synthetic and natural macromolecules complement each other in most of their properties. The possibility of forming IPNs between these two classes opens up a unique way of blending the two at the molecular level and yet preserving the identity of both.

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