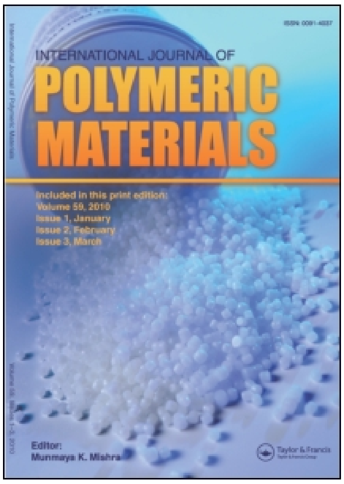

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Self-Crosslinking Gelatins with Improved Viscosity and Gel Strength

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Self-Crosslinking Gelatins with Improved Viscosity and Gel Strength

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The last fractions extracted in gelatin production have lower gel strength and viscosity than earlier fractions as result of thermal degradation during extraction. A method to improve the gel strength and viscosity of these fractions using a formaldehyde donor is presented. The improved gelatins present new properties: they are reactive, self-crosslinkable by drying and have an increase of 80–90% in viscosity and 10–15% in gel strength.

These new properties make them useful for sizing applications with improved water resistance.

Keywords: Gelatin; reactive gelatin; self-crosslinking gelatin; improved gelatin

INTRODUCTION

It is well known that the gelatin is a biopolymer obtained as a hydrolysis product of collagen which is a fibrous protein found in hides, skins and bones.

This natural water soluble biopolymer has a large number of applications in pharmaceuticals, medicine, food, photographical field and other allied fields.

It is well known that the last fractions extracted in gelatin production are of lower grade. It is very difficult to find useful application for them. The lower characteristics as Bloom gel strength and viscosity are determined by an advanced degree of degradation during multistage extraction accompanied by a reduction of the average molecular weight.

In order to improve the physical properties and to increase the value of these low grade gelatins, a method was proposed using a crosslinked gelatin by a recently patented [1] crosslinker. The M and H Hardener [1] is a stabilized formaldehyde donor with a composition similar to dimethylol-urea (DMU).

A direct use of formaldehyde as crosslinker for gelatins is usually associated with difficult technical problems such as insolubilization and environmental and health hazard. The use of M and H Hardener is much safer and the reaction parameters can be better controlled to meet the production requirements.

But the improvement of the viscosity and gel strength are limited by the condition to preserve the water solubility.

The gelatins obtained this way are able to further crosslinking during the drying process when they become partly insoluble. Due to this behavior, one can speak of "reactive" or "self-crosslinking" gelatins. This kind of gelatins can be used in processes involving a drying stage at higher temperatures, as in sand paper production or paper sizing.

MATERIALS AND METHODS

For the present study were used Miligan and Higgins gelatins and a M and H Hardener [1] (DMU).

The standard characteristics of the investigated gelatins are given in Table I.

These gelatins where crosslinked by heating the aqueous solution at 60°C with DMU. After reaction the gelatins were chilled and dried with hot air for 10 hours.

The crosslinked gelatins where characterized by standard methods [2] for viscosity and Bloom gel strength using 12.5 % aqueous solutions.

TABLE I The standard characteristics of gelatins used to obtain self-crosslinking materials by reacting with DMU

Gelatin	*Viscosity (mP)*	*Bloom gel strength (g)*
A	38	82
B	43	184
C	54	144
D	62	184

The viscosity of gelatin solution were measured with a Brookfield RTV Viscometer at 20 RPM.

RESULTS AND DISCUSSIONS

The viscosity increase on time of crosslinked type A gelatin is shown in Figure 1.

One can see a strong dependence of the viscosity increase on gelatin concentrations as well as on the DMU/gelatin ratio. From this kind of data, one can choose the proper conditions for reaching a certain increase in standard characteristics while preserving water solubility of the resulting dried gelatins.

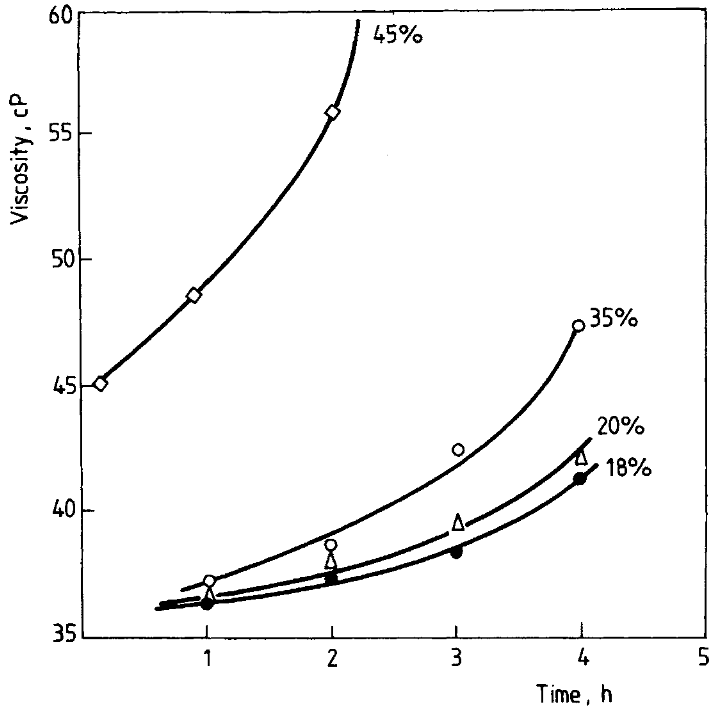


FIGURE 1 The increase of viscosity of gelatin A heated at 60°C with DMU: ●–0.6 g DMU/g gelatin; Δ–0.75 g DMU/g gelatin; O–0.10 g DMU/g gelatin; □–1.5 g DMU/g gelatin.

In Figures 2 and 3 show the increase of the viscosity and Bloom gel strength of the A, B, C and D gelatins using 12.5 % solutions and different DMU/gelatin ratio.

For initially higher grade gelatins (C and D) only a maximum of 25 % solutions can be used in order to preserve the water solubility of the new reacted gelatins.

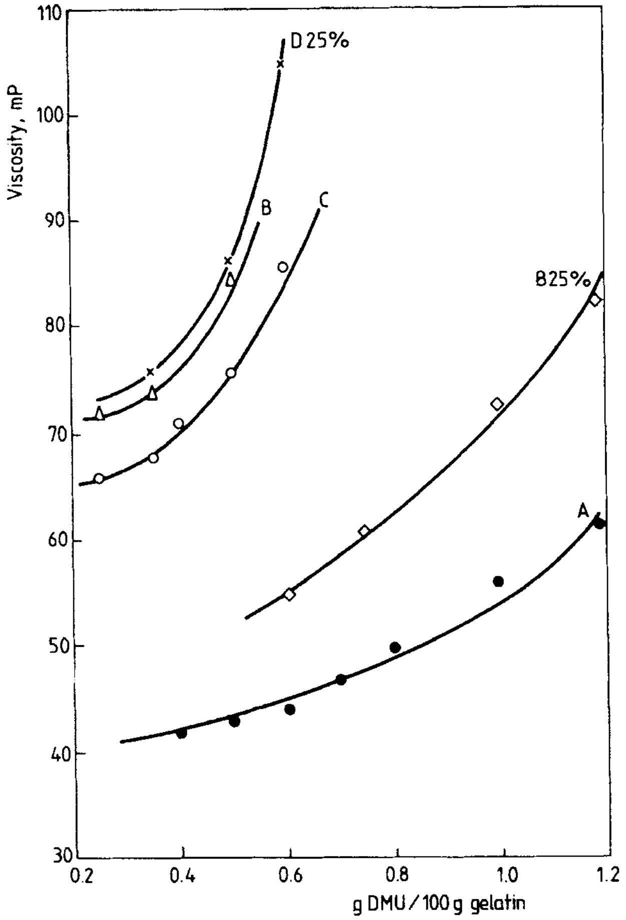


FIGURE 2 Standard viscosity of gelatins obtained by reaction with DMU for 1 hr at 60 C and 45 % concentration of gelatin.

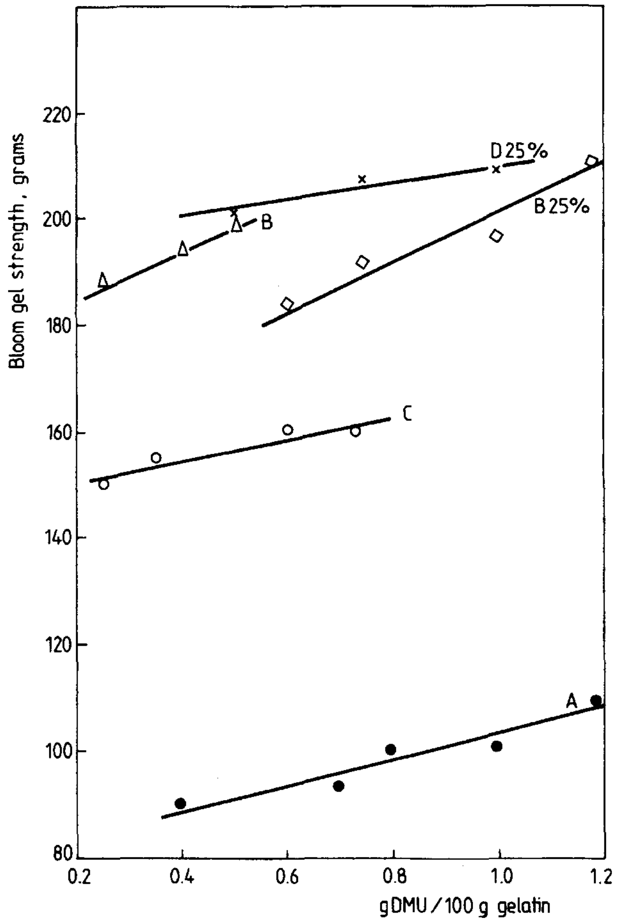


FIGURE 3 Standard Bloom strength of new gelatins obtained by reaction with DMU.

The increase of the viscosity comparative to the parent gelatins is the result of a crosslinking reaction between gelatin molecules assisted by DMU with the corresponding increase in the average molecular weight. If one looks at the DMU as a formaldehyde donor, than crosslinking could be the result of HCHO reacting with amino groups of protein:

$$\text{GEL-NH}_2 + \text{HCHO} \Leftrightarrow \text{GEL-NH—CH}_2\text{OH} \qquad (1)$$

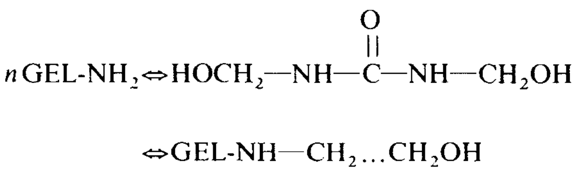
As shown before [3], the crosslinking efficiency with HCHO is much lower than expected from the HCHO reacted. It is likely that only a small part of HCHO reacts as proposed by Kormanek and Mandru [1] and contributes to crosslinking by reaction (2) as suggested by kinetic study of Davis and Tabor [4]:

$$2\mathrm{GEl\text{-}NH{-}CH_2OH} \Leftrightarrow \mathrm{GEL\text{-}NH{-}CH_2{-}O{-}CH_2{-}}$$

$$\mathrm{NH\text{-}GEL} + \mathrm{H_2O} \qquad (2)$$

It was also established that the crosslinks formed in reaction (2) are hydrolyzed at temperature higher than 60°C [4–5], a fact responsible for the observed behavior of these gelatins.

In using DMU as crosslinker, a direct reaction with α-amino groups of gelatin is also possible:



$$n\mathrm{GEL\text{-}NH_2} \Leftrightarrow \mathrm{HOCH_2{-}NH{-}\overset{\overset{\Large O}{\|}}{C}{-}NH{-}CH_2OH}$$

$$\Leftrightarrow \mathrm{GEL\text{-}NH{-}CH_2 \ldots CH_2OH} \qquad (3)$$

with formation of a reactive gelatin molecules that can undergo further crosslinking reaction similar to (2).

It was shown [5] that there is a critical degree of crosslinking of 0.03 mmoles crosslinker/g of gelatin where the melting point of the gel starts to increase dramatically, transforming the gelatin gels in a kind of mixed covalent and hydrogen bonded system.

The DMU/gelatin ratio used for viscosity and gel strength improvement is in the range of 0.016–0.1 mmole/g gelatin. It is very likely that only a small fraction of DMU leads to crosslinking at least in solutions of working concentrations. Reactions (2) and (3) are responsible for the characteristic behavior of these self-crosslinking gelatin. The equilibrium in the reactions (2) and (3) will move to the right by increasing gelatin concentration during drying process. If gelatin is redissolved in water and heated, the equilibrium will move to the left by hydrolysis and the viscosity of solutions is dropping (Fig. 4) as the result of decreasing molecular weight. This behavior is the proof that hydrolysis takes place.

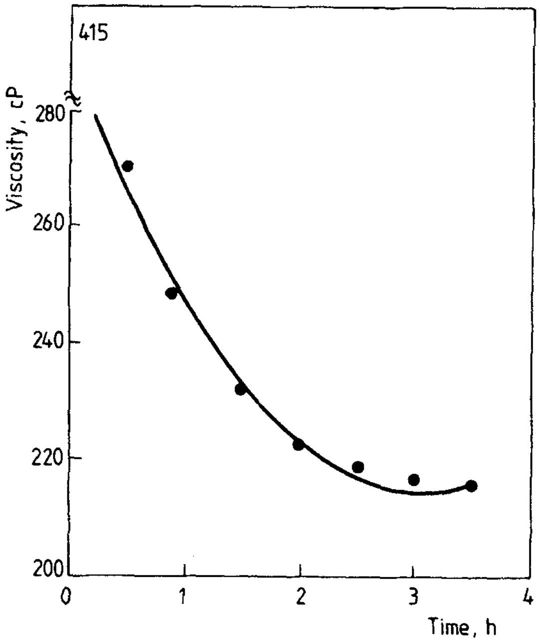


FIGURE 4 The drop in viscosity of self-crosslinking gelatins obtained from D gelatin with 0.7 g DMU/g gelatin with the time of heating at 60°C and 25% (determined with a Brookfield viscometer at 20 RPM).

CONCLUSION

The self-crosslinked gelatins by DMU have an increase of 80–90% in viscosity and 10–15% in Bloom gel strength.

The self-crosslinking capacity of this gelatins determined by nonreacted methylol groups in reactions (1) and (3) can be useful from practical point of view. In many application a certain degree of crosslinking is necessary in order to improve water resistance and thermo-mechanical properties of gelatin films. The on site addition of crosslinking agent leads to shorter pot life and technological difficulties in handling such reactive systems.

Incorporation of a potential crosslinker, like DMU Hardener [1], in gelatins structure will allow a practically unlimited pot life for the system.

The self-crosslinking gelatins have after drying a much lower swelling capacity in water in comparison with the parent gelatins [6].

The method of reacting gelatins with DMU Hardener creates the possibility of increasing the characteristic parameters specially of lower grade gelatins and in the same time to obtain self-crosslinking materials that can be crosslinked by advanced drying.

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