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Applications of Gelatin in Food and Biotechnology

-Review-

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Abstract

Gelatin is a high molecular weight polypeptide derived from collagen, the primary protein component of animal connective tissues, which include bone, skin and tendon. Gelatin is usually produced from two different sources of raw materials(skins or bones) which are processed in two ways(lime or acid). According to this pretreatment, gelatin can be divided into gelatin type A(acid) and B(lime). The market is essentially driven by three demand sectors: food, pharmaceuticals(capsules) and photography. Although there is some potential threat in the photography sector, the other two sectors are well placed for further growth.

Key words: gelatin, pretreatment, demand sector, viscosity, gelatin type

INTRODUCTION

For more than 2000 years, connective tissues and products extracted from animals such as gelatin have been used at home and in food industry for their gelling properties, and also as technical products in the form of adhesives. When industrial scale gelatin manufacture appeared at the end of the nineteenth century, availability and product consistency were improved. Recently, an improved knowledge of collagen and gelatin, together with the introduction of modern production techniques, has made it possible to produce gelatin which is bacteriologically safe in accordance with international standards and rigid specifications(1,2).

Gelatin is defined in the US Pharmacopeia(USP) as a product obtained by partial hydrolysis of collagen derived from the skin, white connective tissues, and bones of animals. Collagen appears as white opaque fibres, constituting almost 30% of the total protein and surrounded by mucopolysaccharides and other proteins. The amino acid composition of the protein is constant and 18 of the 20 amino acids generally found in proteins are always present. A typical sequence of collagen is Gly-X-Y, where X is mostly proline and Y is mostly hydroxyproline. The unusual features of collagen that are reflected in the amino acid profile of gelatin(Table 1) include high proportions of glycine, proline and hydroxyproline, low contents of histidine, methionine, tyrosine and cysteine and an absence of tryptophan. The basic element in the configuration of collagen is tropocollagen, which consists of three chains, each left-handed, interwined like the strands of a cable and held together by hydrogen bonds(3,4). These three peptide chains form a slight, right-handed superhelix. The tropocollagen molecules are chemically linked to form fibrils. Fibres arise when fibrils line up alongside each other, and each one is shifted by one quarter of its length along its neighbouring molecule. These fibres are stabilized by intermolecular cross-linking between a lysine or hydroxyproline residue and a lysine(or hydroxylysine), forming a labile aldimine bond which becomes stable as the collagen ages(Fig. 1)(5-8). The complexity of the collagen structure, and the variety of collagen sources, such as hides, bones and pigskin and chemical and

Table 1. Approximate amino-acid composition of gelatin

	mol%	g/100g protein
Alanine	10.96	10.5
Arginine*	5.27	9.9
Aspartic acid	4.72	6.7
Cystine	0.29	0.4
Glutamic acid	7.39	11.7
Glycine	33.61	27.1
Histidine*	1.05	1.8
Hydroxylysine	0.52	0.9
Hydroxyproline	8.46	11.9
Isoleucine*	1.20	1.7
Leucine*	2.38	3.4
Lysine*	2.60	4.1
Methionine*	0.31	0.5
Phenylalanine*	1.13	2.0
Proline	12.91	16.0
Serine	2.96	3.3
Threonine*	1.68	2.1
Tryptophane*	–	–
Tyrosine	0.18	0.4
Valine*	2.38	3.0

*Those listed as essential amino acids in human nutrition

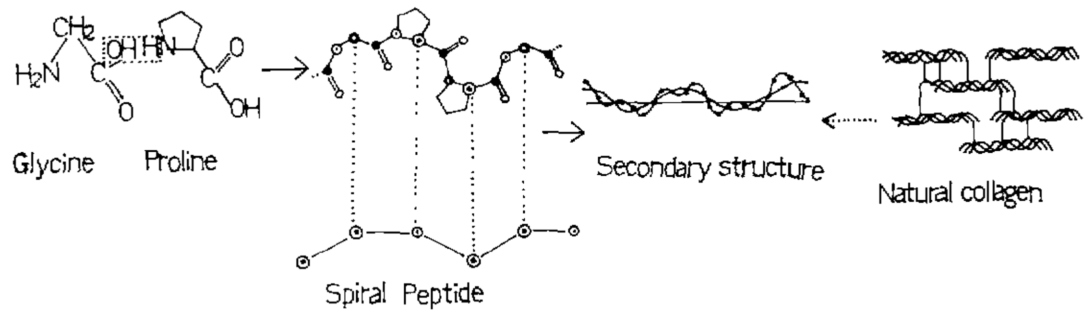

Fig. 1. Configuration of gelatin.

enzyme treatments that can be applied to the manufacture of gelatin, explain the existence of the great variety of gelatin types(9).

Two methods are used in obtaining soluble gelatin from collagen. Acid process is suitable for less cross-linked raw materials, such as the bones of young cattle and pigskin. In lime process, ossein or bovine hides are soaked in an alkali bath for several weeks. Besides purification, an important purpose of the liming process is to destroy certain chemical cross-linkages still present in the collagen. During the preparation of gelatin, the acid or basic treatments hydrolyze amide groups to a greater or lesser extent, varying the isoelectric point between 9.4(no modification of amide groups) and 4.8(90~95% of free carboxylic acid groups)(10). Pig skin and lime hide gelatin predominate in the food sector, being lower cost products. Within the technical gelatin market, limebone gelatin is especially prized(11-13). The collagen in the pretreated raw materials is digested in tanks using successive

Pigskins → Acid treatment
Degreased bones → Ossein
Bovine hides → Liming

Washing

Water extractions(increasing temperature)

Filtration

Sterilization(ultra heat treatment)

Gelification

Extrusion, Drying, & Grinding

Blending & Packing

Fig. 2. Flow diagram for gelatin production.

water extractions, varying from 55°C to 90°C. Each extraction is carefully filtered in order to eliminate any impurities remaining in suspension(14). The solutions are then concentrated to 25~45% in vacuum evaporators. Once concentrated, the gelatin solution is subjected to a flash sterilization at 140°C. It is then rapidly cooled to be extruded in gel form. At the end of the drying process each successive extract is ground(Fig. 2). It may be possible that the collagen-containing material be irradiated to obtain shorter extracting times with a higher yield.

FUNCTIONAL PROPERTIES

Gelation mechanism

There is a wide variety of gelatin types which differ from each other in a number of aspects. These differences are important to the performance of the gelatin in use. The formation of heat reversible gels is the most important property of gelatin. Gelatin swells when placed in cold water, absorbing 5 to 10 times its own volume of water(15). When heated to temperatures above the melting point, the swollen gelatin dissolves and forms a gel when cooled. This sol-gel conversion is reversible and can be repeated(16-18). This is desirable in many foods. The gelation of gelatin can be considered to be a partial reformation of the collagen, and these reformed parts act as the junction zones of the gel(19,20). In a dessert jelly, the network constitutes only about 3% of the volume of gelatin. The liquid component allows for the free diffusion of oxygen, nutrients and other molecules, whereas the polymer network provides a structural framework that holds the liquid in place(21). There are several factors that affect the relationship between the gel strength and molecular weight distribution(22). There is also the effect of the distribution of intact pyrolidine groups along the chain and the proportion of chains(23-25).

Bloom index

Gelatins have long been used for their gelling and thickening properties, and therefore the primary determinants of quality are their gelling strength(in units of Bloom) and viscosity(in millipoise)(26,27). The Bloom indicates the resilience of a jelly sample of known strength tested under standard conditions(28). The gel strength is the weight in grams, called bloom index, which, when applied to the surface of a gel, by means of a piston 12.7 mm in diameter, produces a depression 4mm deep. The jelly must be contained in a standard flask at a concentration of 6.67% and have matured at 10℃ for 16~18hrs (29-33). The price of gelatin with high bloom strength is higher than that of low bloom gelatin, but on the other hand, a smaller quantity of high bloom gelatin is required to produce a jelly of the same rigidity(34-37). In the technical sector, 200 to 250 bloom gelatins are used in photo and hard shells, 150~200 blooms in soft shells, and lower blooms in micro-encapsulation. For food applications, bloom indices vary greatly, depending on the application and degree of 'set' required. As an example, in the production of gelatin desserts, higher gel strength grades offer advantages of improved clarity and colour development as less gelatin is required to produce jelly of a required setting strength. Higher gel strength allied with low pH gelatin can provide significant economic advantages in the manufacture of jelly products. For products where there is a high sugar and/or glucose syrup level, the most economic use of gelatin is often obtained with a grade of moderate gel strength(34). Changes in pH will affect the shape and charge of gelatin molecules and their interaction with each other, water, and phenomena which influence the strength of the gel.

Solution properties

Gelatin is relatively insoluble in cold water but readily soluble in warm water. Gelatin is soluble in polyhydric alcohols such as propylene glycol and glycerine if sufficient water is present as a co-solvent, but is largely insoluble in acetone, alcohol and non polar solvents such as carbon tetrachloride(38,39). Powdered gelatin is brought into solution by adding it to the correct weight of cold water-stirring as the powder is added to prevent balling, immersing the container in a warm water batch at a temperature of 60℃ and then stirring gently until the gelatin is seen to be completely dissolved and clear(40-42). Gelatins in the liquid phase can be used for their surface-

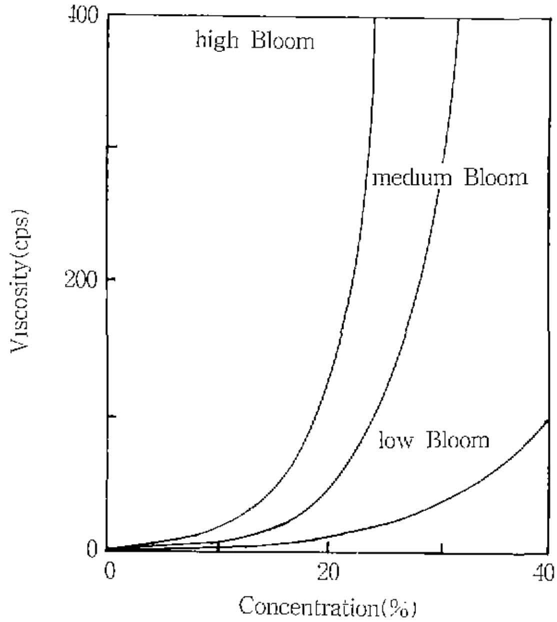

Fig. 3. Viscosity behaviour as a function of gelatin concentration.

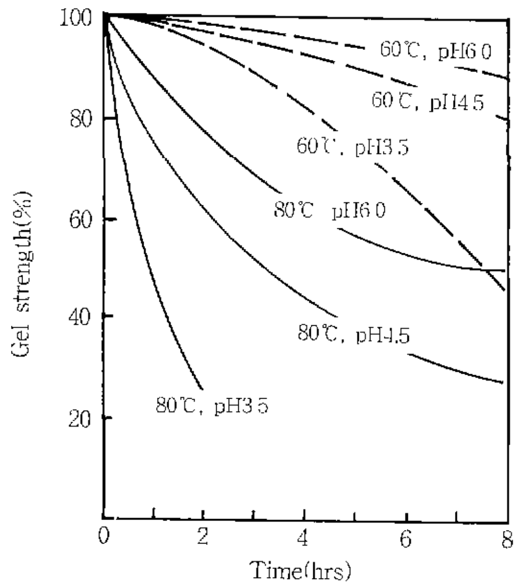

Fig. 4. The rate of loss of gel strength as a function of temperature and pH.

active properties, either as stabilizers and emulsifiers or as polyelectrolytes. Besides gel strength, viscosity in water is an important property of gelatin for some product applications. Gelatin viscosity is dependent upon pH, temperature and concentration(43). Higher viscosity gelatins give higher melting temperatures, while those of lower viscosity can be prepared in a much higher concentration without causing problems due to tailing when depositing in moulds, etc.(Fig. 3). Also, lower-viscosity gelatins dissolve at a faster rate. Changes in molecular shape, charge

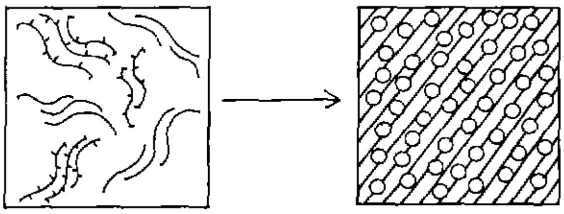

Fig. 5. Gelified gelatin beads in a viscous galactomannan matrix.

distribution, and degree of solvation result in changes in viscosity at different pH levels. The protective colloidal action of gelatin results from its orientation at the interface between the two phases where it forms a monomolecular film round the colloidal particles. It also increases the viscosity of the aqueous phase and assists the formation and stability of suspensions and emulsions. The gelatin should not be subjected to prolonged and excessive heat. Once in solution gelatin suffers a loss in gelling ability and viscosity when exposed to elevated temperature for any prolonged period of time. Loss of gel strength and viscosity is a result of hydrolysis of the gelatin molecules(44). The rate of hydrolysis is a function of temperature and pH of solution. Fig. 4 shows the rate of gel strength loss as a function of temperature and the considerable influence of pH. To avoid unnecessary hydrolysis, the addition of acid to a product formulation should be delayed until the latest possible time in the process. Minimum viscosity is at the pH equivalent to the isoelectric point of the gelatin. Since many of the same factors influence the gel strength and viscosity, generally speaking, a high bloom gelatin has a high viscosity and a low bloom gelatin, a low viscosity. Microbiological quality is strict in food and pharmaceutical applications. However, the gelatin manufacturing processes include heating the material to a temperature which destroys the contaminating agent.

SUPPLY

Beyond the above analytical requirements, it has been a matter of research and development to determine which types and grades of gelatin suit particular applications, and then negotiation to establish the specifications that meet both the requirements of each industrial customer and the capabilities of the manufacturer. The worldwide supply of gelatin has a value of about one billion dollars, producing 140,000~160,000 tonnes per year. This represents a growth of 50% since the late 1980s(45). Although the gelatin supply situation is characterized by a sustained concentration with Sanofi and DGF Stoess, several changes have occurred in recent years. First, DGF expanded in the US when it bought Kind & Knox in 1994. Second, Intergel was formed from the fusion of Leiner-Davis activities. Third, Sanofi has lost relative position in the US. In the technical sector, the Japanese company Nitta and Kodak also share a significant portion of the market. In the food sector, Intergel, P. B. Gelatins and Kraft General Foods(KGF) joined the leading companies. Other significant suppliers with regionals include Weishardt, Croda, Grabek, Nippi and Miyagi. New construction is underway in India and China. World supply of gelatin will expand by a further 15% until the year 2000.

DEMAND

Gelatin is one of the hydrocolloids or water-soluble polymers that can be used as a gelling, thickening or stabilizing agent. It differs from other hydrocolloids because most of them are polysaccharides, such as carrageenan and pectins, whereas gelatin is a totally digestible protein containing all the essential amino acids except tryptophan. In addition, being a food product in its own right, it is perceived as being absolutely safe and serves to support diet preparations.

The major food sectors using gelatin are fruit dessert jellies, bakery items, meat products(jellied meats, aspic), fish products, confectionery(jelly babies, gummy bears etc.), ice cream, alcoholic and soft drinks, dairy products, and yellow fats(46,47). Gelatin gives them elasticity, the desirable soft, chewy consistency, and a long shelf-life as a recrystallization inhibitor. Cream fillings for cakes(if the cream contains gelatin) can be frozen and thawed simply without liquid seeping out, without turning soft, and without forming coarse, sandy structures(48,49). In the case of lightly aerated confectionery, such as marshmallows and chocolate coated candies, the gelatin makes the light fluffy foam possible and stabilizes the product for transport and storage. In conjunction with vegetable hydrocolloids, gelatin regulates the formation of crystals, the melting characteristics of various food items and their palatability(Fig. 5). Gelatin helps clarify wines and provides the mouthfeel in sparkling and fruity drinks. In low fat spreads, gelatin acts as a gelling and water binding agent(50).

Gelatin can be used to supplement other proteins to give a mixture with a higher protein value than individual component. When mixed with beef protein, the net protein value can rise from 84% to 99%. The caloric value of gelatin is only 3.5kcal/g. There is also a food based capsule application which may grow in importance, particularly in the field of flavour and vitamin encapsulation. Other pharmaceutical applications of gelatin include microencapsulation, tablet forming, suppositories and medicinal emulsions. An interesting development is the cold water soluble proteins/peptides made from pharmaceutical grade of gelatins by enzymatic hydrolysis. These proteins have the advantage of dissolving in cold water(whereas gelatin swells) and can be used in tablet formation, as growth media, as a protein protector and a surgical dusting powder. The use of hydrolyzed products also opens opportunities as a functional amino-acid source(binding and forming) competing with such products as whey protein concentrates and egg albumin(51).

Gelatin is known as a support material for enzyme immobilization Moreover, a simple and efficient process of whole cell immobilization using the radiation-modified gelatin gel as a carrier has been developed. The radiation-modified gelatin gel is insoluble and resembles collagen, the natural host matrix for enzyme complexation. Gelatin gel entrapped cells also grow well inside gel matrices, this growth being confirmed by the increases in oxygen uptake and cell number. The entrapment stabilizes markedly the viability and productivity of the cells(52-55).

The photography sector uses high technical specification gelatin for support of silver halides on both film and paper. Though there are fears of market loss to electronic imaging in the Western retail market, a combination of growth in Asia and the continued demand in print and the specialist sector as X-rays assures the future for gelatin. Technical gelatins are used in a variety of industrial processes. In the printing industry, gelatins are used in paper sizing and in photo-gravure, collotype and screen printing processes. Microencapsulated dyes, used in copy transfer papers, may be coated with gelatin through the formation of a coacervate complex with gum arabic. Gelatin is also widely used in electroplating, to ensure smooth deposition, and as a protective colloid in some polymerization reactions. Other miscellaneous uses include binders for special papers, such as bank notes, papers for bonds, securities and certificates. Gelatin is also used in matches to bond the match paste lower the density to give an even combustion, and to fasten abrasive particles on canvas or paper backing to produce abrasive papers. In chemistry and biochemistry, gelatin gels are employed in the analytic methods of chromatography and electrophoresis, where molecules are separated according to the speed with which they percolate through the pores of the gel.

PERSPECTIVES

Gelatin has a rosy future within the technical sector, as well as the food sector, both as a single gelling agent and in combination with other stabilizers such as pectin, agar, gum arabic, and other carbohydrate base hydrocolloids. because of its unique characteristics scarcely present in any competitive materials. The gelatin market worldwide is well placed for further growth in general, although there is some potential threat to its use in the photography sector.

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