

## **RHEOLOGICAL EVALUATION OF THE IRRADIATED PECTIN/GELATIN MIXED SYSTEMS**

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### **ABSTRACT**

The main biopolymers used in the edible films production are polysaccharides and proteins. Pectin is a heterosaccharidic polymer derived from the vegetal cell wall. Gelatin is a heterogeneous mixture of water-soluble proteins of high average molecular mass derived by hydrolytic action from animal collagen. The aim of this research was to evaluate the effect of ionizing radiation on either the biopolymers alone or on the mixed systems prepared with high- and low-methoxyl pectin and gelatin in solution and mixed gel. The results showed that gelatin viscosity remained almost unaffected by the irradiation with doses from 1 to 15 kGy, with a slight increase at 3 kGy. On the other hand, there was a sharp decrease of viscosity values of all pectin solutions upon irradiation, being this behavior predominant when both polysaccharides and proteins were present in a mixed system. The gel hardness and gel brittleness of the gelatin were affected by the increase of radiation dose.

### **1. INTRODUCTION**

Pectin is a heterosaccharide derived from the cell wall of higher terrestrial plants of considerable interest for food industry. It is mainly used as a gelling agent in jams and jellies. Today it is also used in fillings, sweets, as a stabilizer in fruit-juices and milk-drinks and as a source of dietary fiber in foods.

Gelatin is an irreversibly hydrolyzed form of collagen. Cattle bones, hides, pigskins, and fish are the principle commercial sources. As such, it may come from either agricultural or non-agricultural sources. Gelatin is also used as a fining agent in wine, and as a stabilizer, thickener, and texturizer for a range of products. Gelatin can be used as either a processing aid or an ingredient. In some cases, gelatin will comprise over 5% of a food. It has been commonly used in food, pharmaceutical, photography, and cosmetic manufacturing [1]. Structure-forming polysaccharides and protein provide desired functional properties to a wide range of foods such as gel confectionery products, milk products and fat replacers.

Edible packaging and coatings based on various mixes of proteins and polysaccharides could be the basis for the next innovative wave in food packaging [2,3].

Radiation processing can cause a variety of modifications, all of which have found useful industrial applications. These modifications include: cross-linking, in which polymer chains are joined and a higher molecular mass network is formed. Cross-linking usually brings about an improvement in mechanical properties, chemical resistance, thermal stability and other important properties [4,5]. Radiation can also induce polymeric degradation, in which the

molecular mass of a polymer is reduced through chain scissioning. With the reduction of molecular mass, the melt flow of the polymer increases and particle size can be reduced [6,7].

Different edible polysaccharides shown to be easily degraded by ionizing radiation due to free radical induced scission of the glycosidic bonds [8].

There are many characteristics of a material that can indicate its quality or performance in its intended use. The knowledge of a material's rheological characteristics is valuable to predict its pourability, its performance in a dipping or coating operation or the ease with which it may be handled, processed or used [9]. Viscosity measurement can be a powerful tool in product design, as well as quality and engineering applications providing food products with quantifiable attributes. Viscosity methods had been used to determine the efficiency of hydroxyl radical induced chain breaks generation in macromolecules. Inamura and Mastro [10] working with citric pectins showed the high radiosensitivity of this plant polysaccharides.

In the present work samples of pectin with different degree of methoxylation and gelatin were employed in order to study their radiation sensitivity by means of viscosity measurements of either the biopolymers alone or on the mixed system.

## **2. MATERIAL AND METHODS**

### **2.1. Material**

Citrus high methoxyl pectin (HMP), degree of esterification about 72%, was provided as a courtesy from CPKelco do Brasil S/A.- Pectin GENU® type B rapid set-Z (lot: L54013) and low methoxyl pectin (LMP), degree of esterification < 50%, was provided as a courtesy from Plury Química Ltda – Citrus Pectin GENU BTM Type 8002 (lot: L42056). Bovine powder gelatin was provided by GELITA do Brasil Ltda, 240Bloom/6mesh – lot: LF21658 05. Assays were done by dissolving the samples at different proportions in distilled water in a water bath at proper temperature and under vigorously stirring.

### **2.2. Irradiation**

Samples solutions at different concentrations contained in glass recipients were irradiated with doses of: 1; 3; 5; 10 and 15 kGy in a <sup>60</sup>Co Gammacell 220 (AECL) source, dose rate about 3 kGy/h, dose uniformity factor of 1.13.

### **2.3. Viscosimetry**

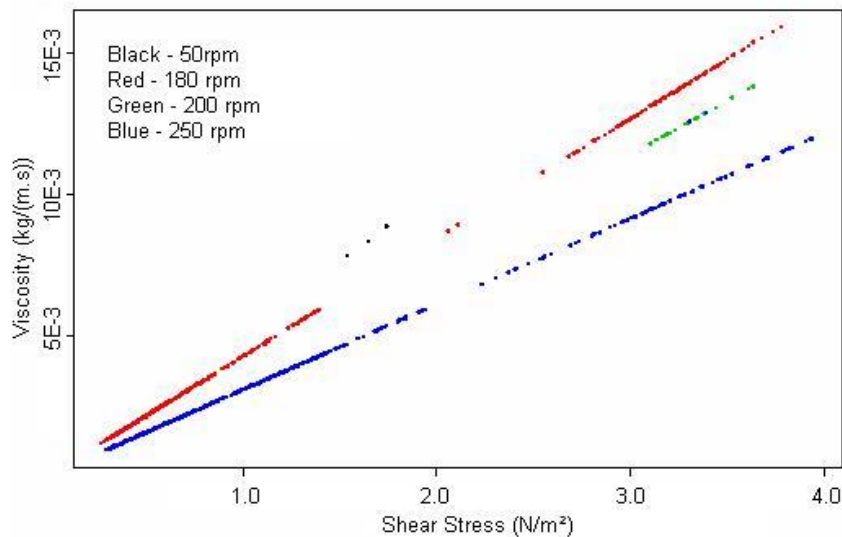
Radiation effects were measured following viscosity changes at 50, 60 and 70 °C using Brookfield viscometer; model LV-DVIII with small sample adapter (SSA), spindle SC4-18, with Rheocalc software and Neslab water bath model RTE-210, precision ± 0.1 °C. Viscosity measurements were performed according to our previous experience [8] and the results are the means of at least 5 readings. The viscosity unit used was kg m<sup>-1</sup>s<sup>-1</sup> - SI.

## 2.4. Texture Analysis

The measures of compression had been carried through using Texture Analyzer Stable Micro Systems TA-XT2 with capacity of compression of 25 kg. The used accessory was stainless steel cylindrical probe with a diameter of 35 mm (P/35) for all the samples. The samples had been compressed to a speed of 1mm/s generally until 6mm of compression.

## 3. RESULTS AND DISCUSSION

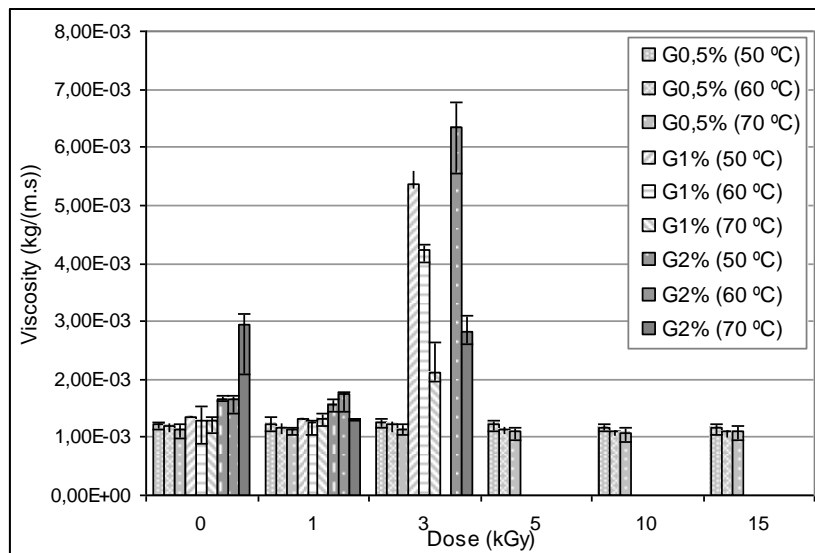
For a Newtonian fluid the viscosity depends only on temperature and pressure (and also the chemical composition of the fluid if the fluid is not a pure substance), not on the forces acting upon it. In this work all samples behaved as non-Newtonian fluids because the viscosity changes with the applied strain rate (Fig. 1).



**Figure 1. Relationship between viscosity and shear rate of all the samples employed.**

In an study on rheological properties of several food hydrocolloids where the samples were subjected to a programmed shear rate increasing linearly from 0 to 300 s<sup>-1</sup> in 3 min, followed by a steady shear at 300 s<sup>-1</sup> for 10 min and finally a linearly decreasing shear rate from 300 s<sup>-1</sup> to 0 in 3 min, gelatin but not pectin showed a Newtonian behavior [11].

Apparent viscosity of irradiated aqueous solution of gelatin is shown in Fig. 2. In general terms the viscosity diminished with the temperature and increased with the concentration; but remained almost unchanged with the increase of the irradiation dose, unless for the dose of 3 kGy where a viscosity increase is evident.



**Figure 2. Viscosity as a function of radiation dose for 0.5%, 1% and 2% aqueous solution of gelatin at 250 rpm at 50°C, 60°C and 70°C.**

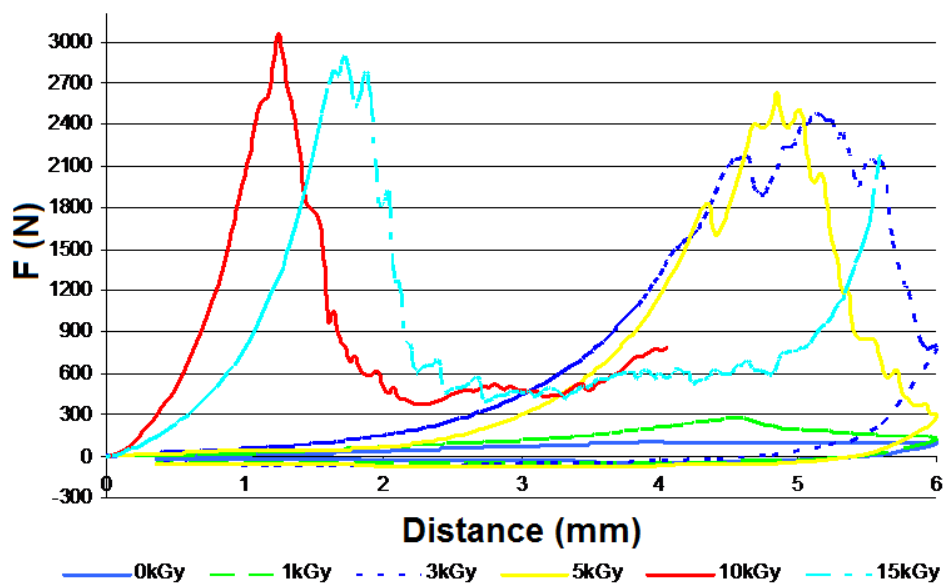
The gelatin gel formation is considered as endothermic and occurred gradually as the energy of the system is dissipated [12]. Then, chemical modifications produced by radiation-induced cross-linking can affect directly the physic-mechanical properties of gelatin [13]. Some food characteristics can be followed by texture analysis [14].

The texture of irradiated gelatin was quantified by instrumental techniques. A 1% gelatin gel was fractured in tension (Fig. 3). The unirradiated sample presented the most easily fractured gel. The maximum resistance to fracture was those of the 5 kGy irradiated sample. Gels irradiated with 10 and 15 kGy showed some retraction. This phenomenon was already reported by Cataldo et al. [15] - who irradiated at room temperature and in the absence of air - but that happening at much higher doses, above 50 kGy. They described that the gelatin hydrogels showed a curious shrinking phenomenon due to the relatively high crosslinking density level achieved, so part of the available water is squeezed out from the gel cage. In the present case, the fracture of the gel happened at the beginning of the compression showing a brittle gel.

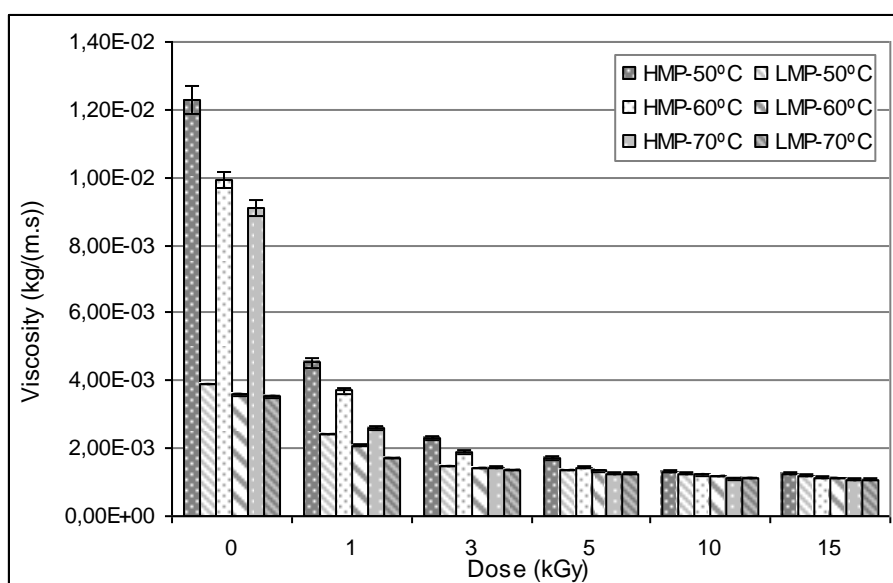
Kosaraju & Puvanenthiran [16] reported a thermo-irreversible gelatin formation at 60 °C, and by controlling the crosslinking reaction, they obtained gelatin with modified material properties.

Viscosity of 1% aqueous solutions of pectin with high degree of methoxylation decreased sharply with the radiation dose remaining almost constant from 5 kGy. Pectin with low degree of methoxylation presented initially lower values of viscosity and the radiation-induced decrease was also pronounced (Fig. 4).

Viscosity measurements decreased with the increase of the temperature applied for both kinds of samples for those unirradiated and irradiated with low doses.



**Figure 3. Typical textural profile of irradiated gelatin 1%.**

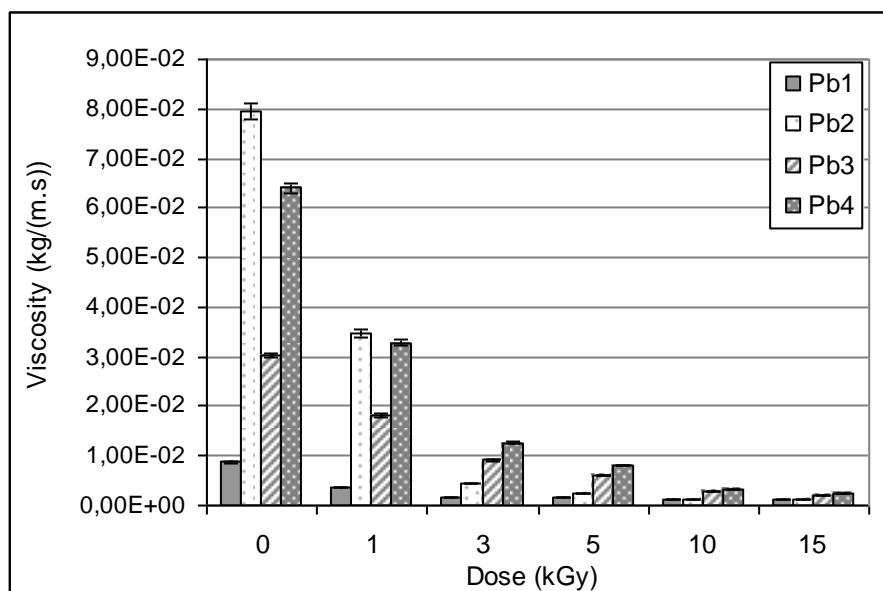


**Figure 4. Viscosity vs radiation dose for 1% LM Pectin and 1% HM Pectin at 250 rpm at 50, 60 and 70 °C.**

The effect of radiation induced chain breaks generation in pectin molecules was evident through the viscosity reduction of irradiated pectin solutions although the viscosity presented diverse values depending of the degree of methoxylation of carboxyl groups in the backbone of polysaccharide macromolecules.

Some data from the literature also described that different polysaccharides are differently affected by radiation [17].

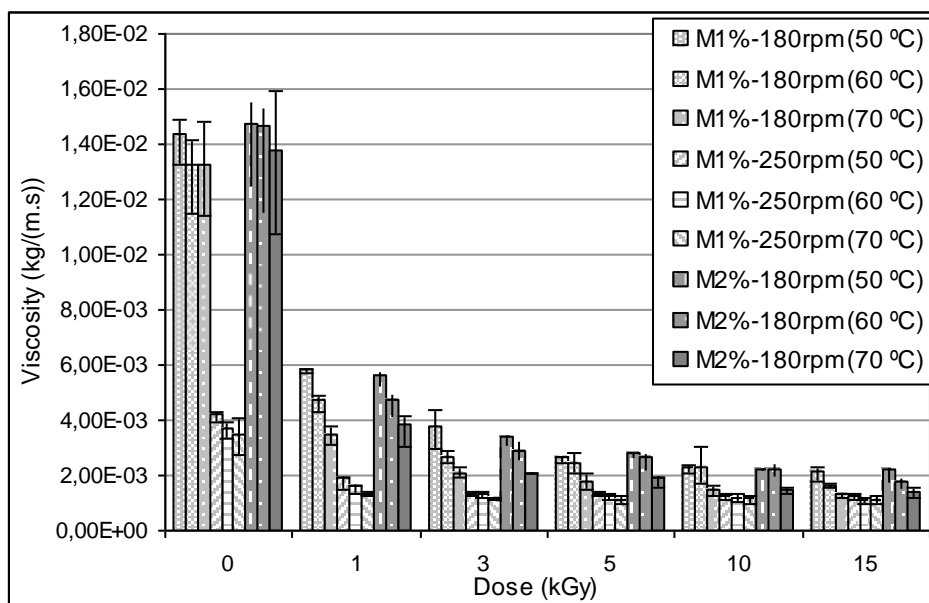
Fig. 5 showed the effect of the addition of  $\text{Ca}^{2+}$  on the pectin gel formation. Sample Pb2 - LMP 1% +  $\text{CaCl}_2$  0.075%; presented the highest values of viscosity. All the samples presented similar pattern in relation to the radiation effect, following a similar decrease with the radiation dose. The presence of  $\text{Ca}^{2+}$  ions induced a web formation and consequently the gel formation [18].



**Figure 5. Viscosity of 1 and 3% LM Pectin solutions and  $\text{CaCl}_2$  addition in different concentration. Pb1 - LMP 1% +  $\text{CaCl}_2$  0.05%; Pb2 - LMP 1% +  $\text{CaCl}_2$  0.075%; Pb3 - LMP 3% +  $\text{CaCl}_2$  0.05%; Pb4 - LMP 3% +  $\text{CaCl}_2$  0,075%.**

In Fig. 6 are presented a comparison of diverse gelatin-pectin mixtures. In all the cases viscosity values are higher when pectin is predominant and also the radiation effect is mainly due to pectin presence. Also, the importance of hydrogel concentration is evident for any type of sample.

Strauss and Gibson [19] used plant-derived phenolic acids and flavonoids to prepare cross-linked gelatin gels in bulk and cross-linked gelatin-pectin coacervates in the form of microparticles for use as food ingredients. Gels cross-linked by these materials had greater mechanical strength, reduced swelling, and fewer free amino groups [20]. Dynamic light scattering analyses showed that such cross-linking results in denser polymeric networks and prevents extension of the peptide chains is when the pH is moved away from the isoelectric point. Coacervated gelatin-pectin microparticles when cross-linked became more lipophilic, and were stable at temperatures up to 200 °C, in contrast to un-cross-linked particles that coalesce and/or disintegrate on heating. These properties of cross-linked gelatin gels and gelatin-based coacervates have applications for the development of novel food ingredients.



**Fig. 6. Viscosity as a function of radiation dose for the aqueous gelatin-pectin systems 1% at 180 rpm and 250 rpm and 2% at 180 rpm at 50, 60 and 70 °C.**

Jo et al. [21] studied the mechanical properties and biodegradation of irradiated casting solutions of gelatin-pectin films. The film casting solution including the pectin and gelatin was irradiated at 0, 10, 20, and 30 kGy to investigate the irradiation effect on the mechanical properties of the film. The tensile strength of the 10 kGy-irradiated films was the highest among the treatments but the elongation at break, water vapour permeability, and swelling ratio were the lowest. Hunter color L\*-and a\*-values decreased but the b\*-value increased as the irradiation dose increased. The total organic carbon content produced from the *Paenibacillus polymyxa* and *Pseudomonas aeruginosa* also showed that the film of 10 kGy-irradiated was lower than those of 0, 20, and 30 kGy-irradiated films. In conclusion, irradiation of the film casting solution at 10 kGy increased the mechanical properties of the pectin and gelatin based film.

According to Wahba et al. [22] pectin is essentially a linear polyionic molecule which is sensitive to oxidative and hydrolytic scission by radiation and chemical means. The radiation effect induced chain breaks generation in pectin molecules was evident in the present work through the viscosity reduction of irradiated pectin solutions although the decrease in viscosity followed a diverse pattern depending of the degree of methoxylation of carboxyl groups in the backbone of polysaccharide macromolecules. Loeffgren et al. [23] studied the microstructure and rheological behavior of pure and mixed pectin gels. Mishra et al. [24] developed biocompatible pectin and polyvinyl pyrrolidone (PVP) blended hydrogel membranes (PEVP), with different pectin: PVP ratios.

De Mars and Ziegler [25] studied the texture of gelatin:high-methoxyl pectin gummy gels by instrumental and sensory techniques and their microstructure examined by light and transmission electron microscopy.

### 3. CONCLUSIONS

The increasing of radiation dose on pectin solutions caused an exponential decrease of viscosity, although LMP and HMP presented diverse values of viscosity depending of the degree of methoxylation of carboxyl groups in the backbone of polysaccharide macromolecules. Like other polysaccharides [26] the viscosity of pectin solutions showed a slight reduction with the increase of temperature in the range of 50-70 °C. When mixed hydrogels are prepared, pectin behavior is predominant and determines the radiation effect pattern of the mixture.

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