Influence of dissolution processing of PVA blends on the characteristics of their hydrogels synthesized by radiation—Part I: Gel fraction, swelling, and mechanical properties

M.T.S. Alcântara [a,*], A.J.C. Brant [a], D.R. Giannini [a], J.O.C.P. Pessoa [a], A.B. Andrade [a], H.G. Riella [b], A.B. Lugão [a]

[a] Instituto de Pesquisas Energéticas e Nucleares, IPEN/CNEN-SP, Av. Professor Lineu Prestes 2242, Cidade Universitária, CEP 05508-000 São Paulo, SP, Brazil
[b] Departamento de Engenharia, Universidade Federal de Santa Catarina, UFSC Campus Universitário, CP 476, CEP 88040-900 Florianópolis, SC, Brazil

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ABSTRACT

In this work several hydrogels were obtained with two different poly(vinyl alcohol)s/PVAs as the main polymer in aqueous solutions containing 10% of PVA, 0.6% of agar, and 0.6% of κ-carrageenan (KC), cross-linked by gamma-rays from a ^{60}Co irradiation source. The PVAs tested have different degrees of hydrolysis and viscosities at 4% with values closed to 30 mPa s. The aqueous polymeric solutions were prepared using two distinct processes: the simple process of heating–stirring and that of making use of an autoclave. The purpose of this study was to evaluate the influence of the dissolution process by means of both methods on the hydrogels' properties obtained. These were investigated by means of degree of cross-linking/gel fraction, degree of swelling in water, and some mechanical properties. The results that are obtained for hydrogels synthesized from solutions of PVA, agar, KC, and blends thereof prepared by both dissolution processes showed higher degrees of swelling for hydrogels from the autoclaved polymer solutions than those from the solutions prepared by simple heating–stirring process. Furthermore, their hydrogels containing totally hydrolyzed PVA displayed higher tensile strength and lower elongation properties.

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1. Introduction

Hydrogels can be described as cross-linked hydrophilic polymers which swell in the presence of water or biological fluids (Peppas, 1987). Poly(vinyl alcohol)/PVA hydrogels have found numerous biomedical and pharmaceutical applications once PVA is a hydrophilic synthetic polymer, filmogenic, non-toxic, biocompatible, and biodegradable, besides showing some very interesting mechanical properties (Stasko et al., 2009). Synthetic and natural polymers can be combined with polysaccharides such as agar and carrageenan among others to produce hydrogels with desirable properties. Addition of carrageenan to PVA, for instance, favors the increase of the equilibrium degree of swelling of the resulting hydrogel (Dafader et al., 2009).

The degree of hydrolysis (DH) and the molar mass of poly(vinyl alcohol)(PVA) are the main parameters to define its physicochemical properties such as solubility in water, viscosity, adhesion to hydrophilic surfaces, elongation strain, etc. These parameters are important to choose its successful employ in diverse scientific and technological areas. PVA solubility in water commonly is not immediate. Heating effect on PVA solubility is related to the break of intra- and intermolecular hydrogen bonds. By raising temperature, intra- and intermolecular forces are diminished, disrupting the hydrogen bonds and enabling therefore an increase of its solubility in water (Wang et al., 2004). Numerous studies on aqueous PVA solutions have been reported, demonstrating their behavior in terms of spinodal decomposition, which still is not totally explained. Due to this behavior, evaluation of physical properties of such solutions, gels and membranes thereof requires hence a much deeper study on this subject and use of more sophisticated techniques to accomplish it (Takeshita et al., 1999).

Hydrogels can be prepared by chemical and physical methods. In the former, cross-linking reactions occur via covalent bonds' formation involving a cross-liker at least. The success of the reaction depends upon the chemical nature of both polymer (or monomer) and cross-linker, besides being influenced by other important parameters such as concentrations of reagents, catalyst action, temperature and time established in order to the reaction occur until reach a desirable degree of cross-linking, etc. By physical processes, there are numerous options such as electrostatic interactions (Li et al., 2011), hydrophobic interactions (Tuncaboylu, et al., 2011), hydrogen

* Corresponding author. Tel.: +55 11 97480697; fax: +55 11 3133 9249.
E-mail addresses: maratalcantara@uol.com.br, mtsalcan@ipen.br (M.T.S. Alcântara).

bonding (Mutsuo et al., 2008), ionizing radiations (Ajji et al., 2008; Felinto et al., 2007; Zulli et al., 2010), UV radiation (Felinto et al., 2007; Lopérgolo et al., 2003), technique of thermal cycles (Hassan et al., 2000), and many others to accomplish polymer cross-linking. Ionizing radiations, mostly gamma-radiation and electron beam (EB), have been used widely in attainment of hydrogels. Such radiations have advantages of not compulsorily demanding cross-linkers and catalysts, which usually are toxic substances, to perform cross-linking in polymer systems. Moreover, through their use, it is possible to simultaneously combine cross-linking and sterilization of the hydrogel to be attained, therefore they are called as "clean processes". In these, radiation induces free-macroradicals' formation, generated from scission reactions on polymer chains. The generated macroradicals mutually recombine and cross-link. Solvent radiolysis usually occurs in this process (Güven, 1982). If water is the solvent, diverse reactive intermediates can be generated to enhance the cross-linking reaction: H*, OH*, etc. (Samuel and Magee, 1953). The inter- and intramolecular covalent bonds formed in the polymer networks mainly depend upon the concentration of the polymer or polymers involved and the radiation dose applied.

This work aimed to the synthesis and characterization of hydrogels from PVA–κ-carrageenan–agar mixtures dissolved in water by two different processes (simple heating/stirring and autoclave), next submitted to gamma-radiation in order to evaluate the impact of the two different dissolution processes on the hydrogels' properties obtained from four PVAs of distinct degrees of hydrolysis and molar masses used in the mixtures.

2. Materials and methods

2.1. Materials

The solutions were prepared using PVA-A (Celvol 325-$\overline{M_w}$ ca. 85,000 g mol^{-1}, viscosity ca. 30 mPa s at 4 °C, DH ca. 98%) from Celanese/Dermet Agekem; PVA-B (Mowiol 26-88 $\overline{M_w}$ ca. 160,000 g mol^{-1}, viscosity ca. 26 mPa s at 4 °C and, DH ca. 88%) from Clariant; natural polysaccharides agar–agar (Agar no. 1) from Oxoid and kappa-carrageenan (KC) from Agargel; and reverse-osmosis water (ROW) as the solvent.

2.2. Methods

2.2.1. Preparation of hydrogels

The polymers were used without further purification, and the aqueous solutions were prepared with final concentrations of 10% (wt/wt) PVA, 0.6% (wt/wt) agar, and 0.6% (wt/wt) KC by two different processes.

In process 1 (*heating and stirring*), the PVAs were added to the ROW in a glass beaker and let to be heated to 90 °C under mechanical stirring on a heating plate until complete dissolution of the polymer after ca. 1 h. Similarly, the agar and KC were separately dissolved at 80 °C in ca. 10 min. In process 2 (*autoclaved*), pure PVAs and their blends with the polysaccharides were suspended in ROW in a glass flask, sealed and brought to an autoclave, where they were kept at 120 °C and 1 kgf cm^{-2} for 15 min. All solutions/mixtures prepared were then cast in molds, thermosealed and, next, irradiated with gamma-ray from a Co-60 source using a dose of 25 kGy at a rate dose of 1.98 kGy h^{-1}. The irradiated PVA samples were aged at 50 °C for 24 h in packed sealed to complete any post-irradiation cross-linking.

2.2.2. Viscosity

Apparent viscosity measurements of all solutions were performed on an analogical Brookfield viscometer RVT at 32 ± 1 °C, 20 rpm, spindle 2 and 45 ± 1 °C, 20 rpm, spindle 3. The read results were multiplied by the corresponding factors of speed and spindle used in the viscosity measurements, and the values given in m Pa s.

2.2.3. Gel fraction

Samples of each hydrogel were taken and dried at 60 °C until constant weight; then, packed in stainless steel screen (500 meshes), immersed in distilled water and kept in an autoclave at 120 °C for 2 h. Next, the samples were dried until constant weight; thereafter, the % gel fraction was calculated according to Eq. (1), and the final result takes into account the average value of the assays based on the triplicate:

$$\text{Gel fraction } (\%) = \frac{W_d}{W_i} \times 100 \qquad (1)$$

where W_d is the mass of the dried sample after extraction and W_i is the mass of the dried sample before extraction.

2.2.4. Swelling in reverse osmosis water

The swelling assays were performed by immerging each previously weighed specimen into ROW at 30 ± 1 °C and evaluating its weight after different periods of immersion time (from 30 min to 24 h or beyond this time, if necessary) until the sample reachs the equilibrium swelling. Before weighing each swollen specimen, this was withdrawn from the solvent and quickly blotted with an absorbent paper to remove excess of superficial water. The swelling percentage was calculated according to Eq. (2), and the final result takes into account the average value of the assays based on the triplicate of specimens,

$$\text{Swelling } (\%) = \frac{W_s - W_d}{W_d} \times 100 \qquad (2)$$

where W_s is the mass of the swollen hydrogel and W_d is the mass of the dried sample before immersion in the water.

2.2.5. Mechanical properties

Tensile stress at rupture (σ_R), elongation at rupture (σ_R), and elasticity module (E) of the hydrogel membranes were measured on a texturometer—TA.XT*Plus* Texture Analyzer according to ASTM D882, 1995 but with some adjustments (the original rectangular specimens with 100 mm × 25 mm sizes after cross-linked in thermoformed packages and, later, conditioned for 48 h at 18 °C). The analyzed membranes showed thickness of 20 ± 5 mm. The matrices were stretched at a deformation rate of 8.33 mm s^{-1}. Tensile stress was calculated on the basis of the area of the transversal section of each sample, and elongation on the basis of deformation of the sample in relation to the percentage of its initial length ($L_o = 60$ mm) according to Eq. (3):

$$\text{Elongation at break}(\%) = \frac{L_b - L_o}{L_o} \times 100 \qquad (3)$$

3. Results and discussion

3.1. Viscosity

Throughout the measurements one observed shear-thinning behavior at 32 °C and 45 °C in all aqueous polymer solutions, mainly in those of the polysaccharides kappa-carrageenan (KC) and agar. This, after cooled to room temperature (25 °C), tends to become a smooth gel. The viscosities of all polymer solutions dropped by increasing the temperature.

The profiles of Figs. 1 and 2 show a trend of the pure polymers directly dissolved by autoclaving to present higher viscosity, mainly that of the polysaccharides. Taking into to account both dissolution processes, the discrepancies of the viscosity values
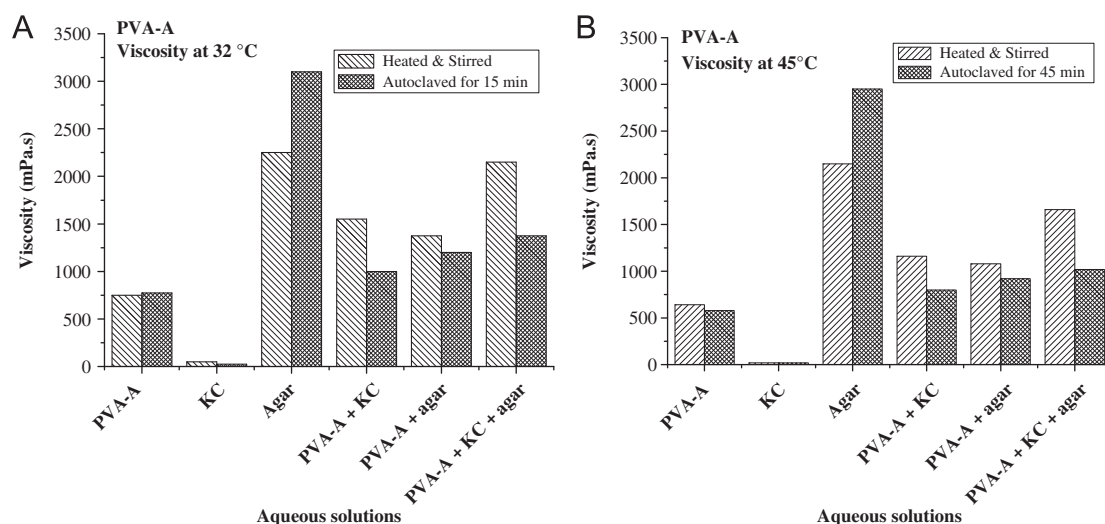
Fig. 1. Apparent viscosity of non-irradiated aqueous polymer solutions based on PVA-A and its blends, prepared by heating–stirring and autoclave processes and measured at two different temperatures.
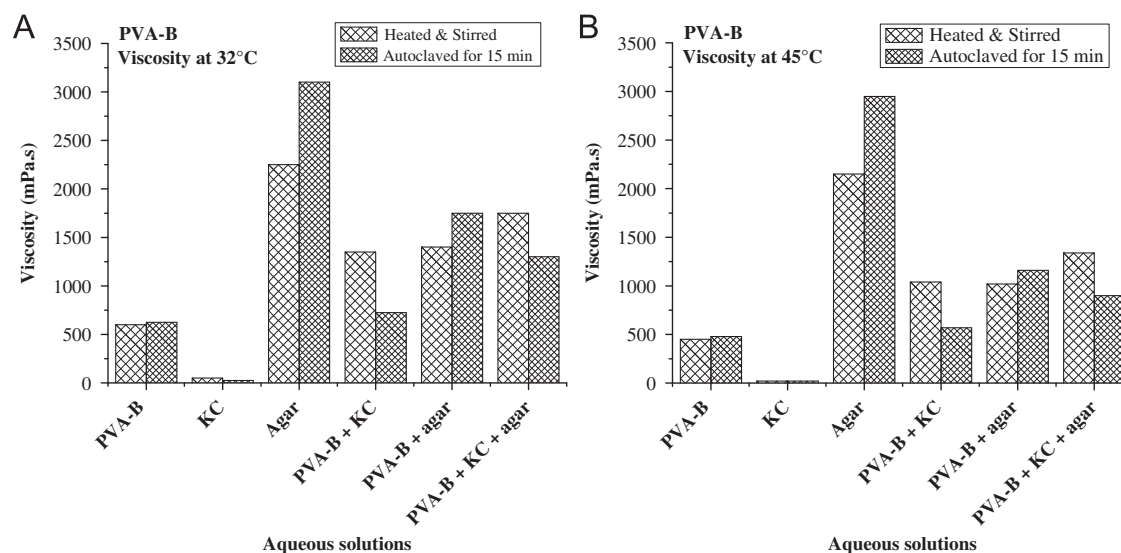
Fig. 2. Apparent viscosity of non-irradiated aqueous polymer solutions prepared by heating–stirring and autoclave processes and measured at two different temperatures.

measured for the dissolved PVAs are rather unmeaning, whereas this is not true for κ-carrageenan and agar, mainly for the latter. PVA dissolution process involves hydrogen bonds' breaking of the polymer, either intermolecular or intramolecular, by the solvent and temperature increase. Its linear chains are easily distended by water under heating and stirring. Concerning κ-carrageenan and agar, these polysaccharides are dissolved in water at 80–100 °C. Even at low concentrations they can form double helices in aqueous solutions (Varshney, 2007). Such double helices in turn aggregate in three-dimensional structure arrangements capable of retaining water in their interstices and form thermoreversible gels.

3.2. Gel fraction

KC solutions showed to be liquid before and after irradiated at 25 kGy, whereas agar solutions showed to be as a physical gel before irradiated and a liquid after irradiated at this same dose. Both polysaccharides exhibited viscosity drop on their irradiated solutions due to a probable predomination of scission reactions over cross-linking reactions on the polymer chains. Abad et al.

(2009) observed degradation of KC in 1% aqueous solutions irradiated even at 2 kGy dose. Thus, it was not possible to evaluate their gel fractions through the methodology used. Nevertheless, the solutions of pure PVAs and their blends cross-linked after irradiated at 25 kGy formed consistent membranes influenced by the PVA cross-linking as the main polymer in a system prone to form probable IPNs or SIPNs (interpenetrating polymer networks or semi-interpenetrating networks) as well as likely grafts of the polysaccharides onto the chains of the main polymer.

Fig. 3 clearly shows that the hydrogels from the PVA-A and PVA-B solutions and their respective blends generally exhibited gel fraction values very close (from 89.8% to 90.5%, PVA-A systems; from 89.6% to 92.3%, PVA-B systems), regardless the process of dissolution of the polymers. However, pure PVA-A and PVA-B solutions afforded hydrogels with slightly higher cross-linking than those from their blends. Therefore, when the PVAs are associated with KC, agar or KC+agar, the gel fractions of their blends slightly diminish or keep the values practically unchanged, suggesting that the cross-linking may mostly originate from the PVAs once these polysaccharides degrade under the test conditions. Moreover, considering the hydrogels prepared with PVA-B
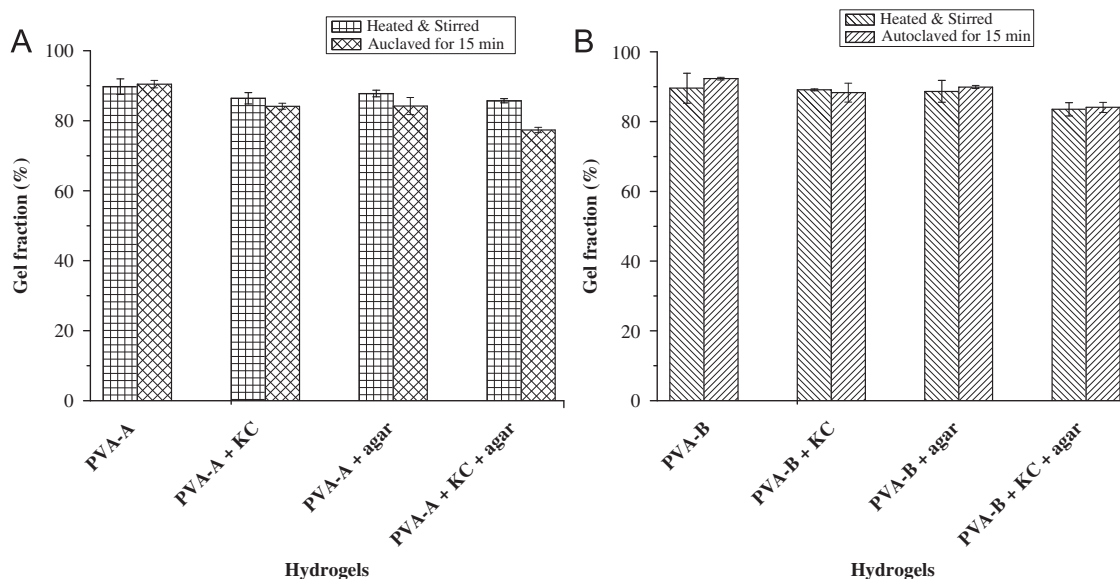
Fig. 3. Gel fractions of aqueous polymer solutions (A with PVA-A and B with PVA-B) prepared by two different dissolution processes, γ-irradiated at 25 kGy, next extracted in ROW after autoclaved for 2 h.
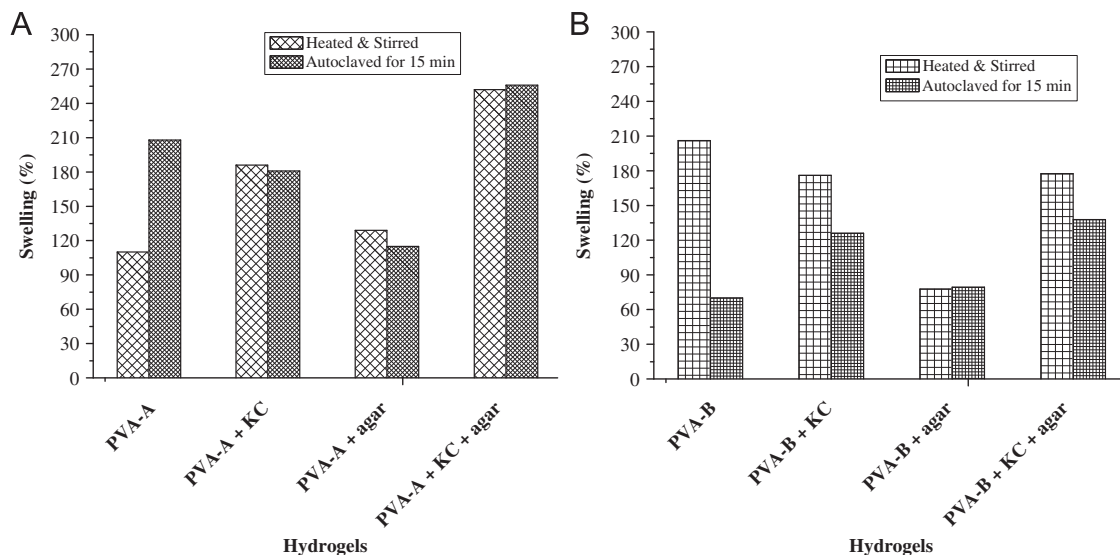
Fig. 4. Swelling (%) at equilibrium of aqueous polymer solutions (A with PVA-A and B with PVA-B) prepared by two different dissolution processes, γ-irradiated at 25 kGy, next immersed in ROW for a period until reach equilibrium (72 h).

and its blends with degrees of cross-linking higher than those of PVA-A and its blends, it suggests that that molar mass associated with degree of hydrolysis of PVA plays an important role in cross-linking induced by ionizing radiation. In summary, the data of gel fractions of the PVAs and their blends did not show significant discrepancies in the values, showing that, for this parameter, the influence of the polymer dissolution process is almost negligible.

3.3. Swelling in reverse-osmosis water

Fig. 4 presents swelling (%) at equilibrium of the synthesized membranes of PVAs and their blends with κ-carrageenan (KC) and agar.

Interestingly, PVA-A and PVA-B hydrogels showed degrees of swelling dependent on the dissolution process, but with contrary tendencies: higher swelling for autoclaved PVA with DH of 98% and for heating–stirring for PVA with DH of 88%. The hydrogels from the blend solutions based on PVA-A and the

polysaccharides presented swelling (%) values at equilibrium very close, what demonstrated that there is little influence of the dissolution process of the blends on the water uptake of the resulting membranes based on this polymer. On the other hand, the hydrogels based on PVA-B (DH of 88%) blend solutions, except for PVA-B+agar, exhibited more discrepant swelling values dependent on the preparation process of the original solutions. κ-Carrageenan contributed more for the PVA swelling than agar. Such a fact has been observed by our research group in preparation of hydrogels from their blends in diverse other experiments using the same concentrations of these polymers. In relation to swelling, cross-linking density of the PVA/KC/agar hydrogels prepared with PVA-A by the two processes may be smaller than that for the same blend prepared with PVA-B by the autoclave process. These results corroborate with those attained from the assays for determination of cross-linking degrees based on swelling. In view of that, generally, the lower the cross-linking density, the higher the degree of swelling at equilibrium

Table 1
Results of tensile stress at rupture (σ_R) obtained in mechanical assays of hydrogel membranes synthesized by gamma-radiation.

PVA	Process	Tensile stress at rupture (kPa)			
		PVA	PVA+KC	PVA+agar	PVA+KC+agar
PVA-A	Heating and stirring	12.00 ± 0.06	9.40 ± 0.92	10.90 ± 0.57	8.95 ± 0.21
	Autoclaved	8.47 ± 2.60	9.50 ± 1.32	11.70 ± 1.50	9.60 ± 0.96
PVA-B	Heating and stirring	17.00 ± 0.57	27.80 ± 5.27	54.58 ± 10.76	33.15 ± 6.20
	Autoclaved	19.23 ± 3.00	22.05 ± 6.19	54.40 ± 2.34	41.37 ± 9.76

Table 2
Results of strain at rupture (ε_R) obtained in mechanical assays of hydrogel membranes synthesized by gamma-radiation.

PVA	Process	Strain at rupture (%)			
		PVA	PVA+KC	PVA+agar	PVA+KC+agar
PVA-A	Heating and stirring	172 ± 7	238 ± 52	226 ± 9	248 ± 6
	Autoclaved	145 ± 16	204 ± 18	228 ± 9	296 ± 23
PVA-B	Heating and stirring	474 ± 7	325 ± 20	423 ± 5	409 ± 44
	Autoclaved	130 ± 2	205 ± 34	441 ± 14	374 ± 34

Table 3
Results of modulus of elasticity (Young's modulus) (E) of hydrogel membranes synthesized from gamma-irradiated aqueous PVA and PVA blend solutions.

PVA	Process	Modulus of elasticity (Pa $\times 10^{-4}$)			
		PVA	PVA+KC	PVA+agar	PVA+KC+agar
PVA-A	Heating and stirring	108 ± 5	93 ± 5	87 ± 2	55 ± 7
	Autoclaved	82 ± 19	75 ± 11	77 ± 11	44 ± 5
PVA-B	Heating and stirring	83 ± 10	121 ± 10	200 ± 27	134 ± 9
	Autoclaved	166 ± 9	173 ± 18	182 ± 15	151 ± 11

of the hydrogel once both these factors are inversely proportional to each other.

3.4. Mechanical properties

3.4.1. Tensile stress at rupture

The cross-linking density is one of the most important factors that affect gel fraction, water absorption ratio, and mechanical properties of hydrogels (Gwon et al., 2011). The results in Table 1 exhibit values with considerable discrepancies.

The apparent distortions in results can arise in such systems once they may present inhomogeneities on cross-linking density on their membranes. However, one must point out that the results to stress were obtained considering the transversal section values of the specimens before these having undergone deformation. Such values were not adjusted as soon as the specimens elongated, i.e. the variation of the cross-sectional area during the elongation was not considered because of limitations of the equipment, the methodology and kind of polymer employed. In this case, stress results may be rather controversial with significant discrepancies. Nevertheless, it is possible to observe that such results corroborate with their greater cross-linking density suggested from the results of swelling at equilibrium observed in Fig. 4, and once more it indicates a great superiority in values obtained from the hydrogels synthesized with PVA-B (DH=88%) comparatively with those from PVA-A (DH=98%). On the other side, the addition of the polysaccharides to PVAs influenced on the values, mainly for PVA-B, when these are compared to those of the pure main polymer hydrogels, contrary to the results obtained by Varshney (2007) using another PVA type ($\overline{M_w} = 125{,}000\,\mathrm{g\,mol^{-1}}$, DH=88%).

The results of tensile stress at rupture point out a trend of PVA-A hydrogel to diminish from solutions prepared by heating–stirring process in comparison to those prepared by autoclave process. This trend is reverted for its respective binary and ternary blends. In relation to PVA-B, its hydrogel and that of the ternary blend showed a trend to increase from solutions prepared by the autoclave process in comparison to those prepared by the simple heating–stirring process. This tendency is reverted for both hydrogels from the binary blends.

3.4.2. Strain at rupture

All results shown in Table 2 obtained from the hydrogels prepared with two types of PVA and from both dissolution processes of the polymer components strongly show to be probably more influenced by the DH of PVA as observed at swelling results.

The results indicate a great influence of the polysaccharides on the elongation of hydrogels, mainly when both are present in the blend, differently of the stress results (Table 1) with greater values only for PVA-agar blends.

One can observe the following: a trend to diminish the strain at rupture results for the hydrogels of PVA-A and its PVA-A/KC blend from solutions prepared by the autoclave process in comparison to those of the hydrogels obtained from solutions prepared by the simple heating–stirring process. For the hydrogel of PVA-A/agar blend, the values practically kept close, regardless the process utilized in the polymers' dissolution. In the case of the hydrogel of the ternary blend, it showed a trend to increase the values when it is obtained from solutions prepared by the autoclave process.

In relation to PVA-B, there was an abrupt drop of the values for its hydrogel and that of the PVA-B/KC blend (ca. 73% and ca. 40%, respectively) obtained from solutions prepared by the autoclave process if one compares to those from the same solutions prepared by the simple heating–stirring process. For the ternary-blend hydrogel this fact also occurred, but moderately (ca. 9%). On the contrary for the hydrogel of PVA-B/agar blend, whose stress at rupture value slightly increased when obtained from solutions prepared by the autoclave process.

3.4.3. Modulus of elasticity (Young's modulus)

The average results shown in Table 3 suggest a possible influence of the cross-linking density of the hydrogels on their mechanical properties, which can be resumed as: an increase in the cross-linking density for the hydrogels based on the same PVA generally implies a decrease of the elasticity of the polymer system, resulting in an increase of the modulus of elasticity.

For the hydrogels from the solutions of pure PVA-A and blends thereof prepared by autoclave, the values the elasticity modulus were moderately lower than those from hydrogels obtained from

solutions prepared by the heating–stirring process. On the contrary, concerning the hydrogels from PVA-B and its blends – except for PVA-B/agar – such values were higher for the hydrogels from the autoclaved solutions.

4. Conclusions

The results of tests on hydrogels of PVAs as the main polymer and their polysaccharide blends obtained from solutions prepared by the heating–stirring and autoclave processes showed that the dissolution methodology played an important role in the membranes' characteristics, mainly in swelling in water and mechanical properties, depending on type of PVA used.

Interpretation of results from hydrogels based on PVA-polysaccharide blends is not an easy task due to numerous polymer–polymer and polymer-solvent interactions and other factors such as crystallinity, compatibility, etc., which are involved simultaneously.

More experiments on this subject shall be continued by our research group as support for more new results, which most likely should lead us to wide-ranging conclusions.

Acknowledgments

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