# Polyvinyl alcohol films with different degrees of hydrolysis and polymerization

# Filmes de álcool polivinílico com diferentes graus de hidrólise e polimerização

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# Abstract

The objective of this work was to manufacture biodegradable films based on polyvinyl alcohol (PVA) and also to evaluate the effect of the different degrees of hydrolysis (DH) and degrees of polymerization (DP) of PVA on the properties of these films. Four different types of PVA with DH ranging from 88.0 to 98.4% and DP ranging from 150 to 2000 were used to produce the films by casting, and glycerol was used as plasticizer. Films based on PVA with lower DH (Selvol<sup>TM</sup> 540 and 203) showed higher solubility, water vapor permeability and water sorption capacity, and also were less rigid, and had lower glass transition and melting temperatures when compared to films obtained from higher DH PVA (Selvol<sup>TM</sup> 325 and 107). The DP affected the solubility of the films, the film produced with the higher DP (Selvol<sup>TM</sup> 325 - DP = 1000 – 1500) showed lower solubility value. Films based on PVA with higher DP (Selvol<sup>TM</sup> 540 and 325) showed higher elongation values. Both DH and DP affected PVA films properties, resulting in materials with different possibilities of applications, however, it was observed that however the effect of DH was most important for PVA films properties than DP effect.

Keywords: Biodegradable polymer. Mechanical properties. Thermal properties.

# Resumo

O objetivo deste trabalho foi produzir filmes biodegradáveis à base de álcool polivinílico (PVA) e, também avaliar o efeito dos diferentes graus de hidrólise (DH) e graus de polimerização (DP) do PVA nas propriedades desses filmes. Quatro tipos diferentes de PVA com DH variando de 88,0 a 98,4% e DP variando de 150 a 2000 foram utilizados para produzir os filmes por casting, e o glicerol foi usado como plastificante. Os filmes formulados com PVA com menor DH (Selvol<sup>TM</sup> 540 e 203) apresentaram maior solubilidade, permeabilidade ao vapor de água e capacidade de absorção de água, além de serem menos rígidos e apresentarem menores temperaturas de transição vítrea e de fusão quando comparados aos filmes obtidos com PVA com maior DH (Selvol<sup>TM</sup> 325 e 107). O DP afetou a solubilidade dos filmes, o filme produzido com PVA com maior DP (Selvol<sup>TM</sup> 325 - DP = 1000 – 1500) apresentou menor valor de solubilidade. Os filmes formulados com PVA com maior DP (Selvol<sup>TM</sup> 540 e 325) apresentaram maiores valores de elongação na ruptura. Tanto o DH quanto o DP afetaram as propriedades dos filmes de PVA, resultando em materiais com diferentes possibilidades de aplicação, no entanto, observou-se que o efeito do DH foi mais importante para as propriedades dos filmes de PVA do que o efeito DP.

Palavras-chave: Polímero biodegradável. Propriedades mecânicas. Propriedades térmicas.

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# Introduction

The most employed conventional packaging are obtainbed from synthetic polymers, which are derived from fossil resources, such as polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), polystyrene (PS) e polychlorinated vinyl (PVC). The advantages of using these polymeric materials are countless but the biggest drawback is that they are not biodegradable and are not renewable, thus new alternatives have to be studied to minimize the disposal of these materials in the environment (DEBIAGI *et al.*, 2014; MELLO; MALI, 2014; MERCI; MALI; CARVALHO, 2019; VERCEL-HEZE *et al.*, 2019).

Polyvinyl alcohol (PVA) is a synthetic, non-toxic, biodegradable, biocompatible and promising polymer for the production of biodegradable packaging materials, leaving them as strong as conventional plastics, showing high mechanical strength, adhesion property, high tensile strength and compression, good flexibility, barrier to oxygen, flavors, oils and solvents (ALAVI, 2011; FARIA; VERCELHEZE; MALI, 2012; MORAES *et al.*, 2008; TANG; ALAVI, 2011; WANG *et al.*, 2014). PVA is approved by the US Food and Drugs Administration (FDA) and also by European Medicines Agency (EMA) for human use, and it can be used in food packaging applications (GÓMEZ-ALDAPA *et al.*, 2020).

In an industrial scale, PVA is obtained by partial or complete hydrolysis of polyvinyl acetate to remove acetate groups, and partially hydrolyzed grades contain residual acetate groups (TANG; ALAVI, 2011). Considering the DH, the PVA are classified as partially hydrolyzed (above 88%) or highly hydrolyzed (98-99%), and considering the DP the PVA are classified as very low viscosity (viscosity = 3 - 4 cP; DP = 150 - 300), low viscosity (viscosity = 5 - 6 cP; DP = 350 - 650), medium viscosity (viscosity = 22 - 30 cP; DP = 1000 - 1500) and high viscosity (viscosity = 45 - 72 cP; DP = 1600 - 2200) (MARIA *et al.*, 2008; TABOADA *et al.*, 2008; TANG; ALAVI, 2011).

The casting technique is widely used for the production of biodegradable materials, where the polymer is dissolved in a solvent to obtain the filmogenic solution, and this solution is placed on a support to evaporate the solvent. Some parameters must be controlled, as the thickness which can influence the mechanical properties and water vapor permeability of the obtained films (SOBRAL *et al.*, 2001; GALDEANO *et al.*, 2013; MALI; GROSS-MANN; YAMASHITA, 2010). Many authors have studied the properties of the PVA film produced by casting and blended with starch (FARIA; VERCELHEZE; MALI, 2012), gellan (SUDHAMANI; PRASAD; SANKAR, 2003) or gelatin (MARIA *et al.*, 2008; MORAES *et al.*, 2008; TABOADA *et al.*, 2008), and in some papers (MARIA *et al.*, 2008; MORAES *et al.*, 2008; TABOADA *et al.*, 2008) it was studied the influence of the degree of hydrolysis concerning the properties of these films, but the influence of the degree of polymerization on the properties of the pure PVA films have not been studied.

The objective of this work was to manufacture biodegradable films based on polyvinyl alcohol (PVA) and also to evaluate the effect of the different degrees of hydrolysis (DH) and degrees of polymerization (DP) of PVA on the properties of these films. These films may be an alternative to reduce solid waste on the environment and the dependence on use of conventional plastic polymers.

# Material and methods

#### Materials

Polyvinyl alcohols with different degrees of hydrolysis (DH) and polymerization (DP) used in this work were obtained from Sekisui Specialty Chemicals America (Dallas – TX - USA). Four types were used: Selvol<sup>TM</sup> 203 (DH=88.1%, DP = 150 – 300), Selvol<sup>TM</sup> 540 (DH = 88.0%, DP = 1600 – 2000), Selvol<sup>TM</sup> 107 (DH = 98.3% DP = 350 – 650) and Selvol<sup>TM</sup> 325 (DH = 98.4%, DP = 1000 – 1500). Glycerol, used as plasticizer, technical grade, was purchased from Dinâmica Ltda (São Paulo – SP - Brazil).

## Preparation of biodegradable films

The films were produced by casting preparing a filmogenic solution by mixing an aqueous solution 2% (w/v) of each PVA with glycerol (0.25 g glycerol / g PVA). PVA solutions and glycerol were manually homogenized, and the solutions were homogenized with constant manual stirring at 95 °C  $\pm$  5 °C for 30 min, and each solution was then sonicated for 10 min at room temperature to remove air bubbles.

The filmogenic solutions were poured over glass plates (0.35 g filmogenic /  $cm^2$  solution), which were dried in an oven with air circulation and renovation at 30 °C / 24 h to obtain the films. After drying, the films were manually removed from the plates and conditioned on a relative

humidity (RH) of 58% in B.O.D. containing saturated sodium bromide at 25  $^{\circ}$ C for further characterization.

## Characterization of the films

#### Thickness and water solubility

The thickness of the films was determined using a digital micrometer Digimess IP 54 (Brazil) with a resolution of 1 micrometer. For each formulation was performed an arithmetic average of 3 values of 6 samples.

The water solubility of the films was defined as the dry matter content that was solubilized after 24 h of immersion in water at 25 °C. Analyses were performed in triplicate as described by Gontard, Guilbert and Cuq (1992).

#### Water vapor permeability (WVP)

WVP was determined in appropriate diffusion cells (ASTM, 2000) using three different relative humidity (RH) gradients (0 – 33%, 33 – 64%, 64 – 90%). The salt solutions (33% - magnesium chloride, 64% - sodium nitrate and 90% - barium chloride) were prepared and held at 25 °C. The films were fixed into the openings of cells containing a salt solution that provided a lower relative humidity (0, 33 or 64%, depending on the case) and placed in a hermetic chamber containing a salt solution that provided a higher relative humidity (33, 64 or 90%, depending on the case). The chamber with the diffusion cells was kept at 25 °C, and weight gain was recorded and plotted as a function of time. The slope of each line was calculated by linear regression ( $r^2 > 0.99$ ), and the water vapour transmission rate (WVTR) was calculated from the slope of the straight line (g/s) divided by the transport area  $(m^2)$ . WVP  $(g.Pa^{-1}.s^{-1}.m^{-1})$  was calculated as WVP = [WVTR/S  $(R_1 - R_2)$ .D], where S is the saturation vapour pressure of water (Pa) at the given temperature (25  $^{\circ}$ C), R<sub>1</sub> is the RH inside the desiccator, R2 is the RH inside the permeation cell, and D is the thickness of the film (m). All tests were conducted in triplicate.

#### Moisture sorption isotherms

Samples were finely cut and pre-dried for 15 days in a desiccator containing anhydrous calcium chloride. Thereafter, the dried samples were placed individually in a generator equipment isotherms AquaSorp (Decagon Devices, USA) operating by method for dynamic dew point isotherm. A quantity of 0.500 to 0.800 g of each sample was placed into the specific compartment. An initial desorption cycle was programmed to reach to the minimum water activity to the top of the adsorption test. Scanning the adsorption cycle was held in the range 0.15 to 0.85 water activity under 25 °C. After adsorption, a new desorption cycle was performed to determine the dry sample weight, used in the calculation of the equilibrium moisture content of the samples. The GAB (Guggenheim-Anderson-de-Boer) model (BIZOT, 1984) was used on the Sorptrack 1:14 software (Decagon Devices, USA), and can be expressed as follows:

$$M = \frac{m_0.C.Ka_w(1 - K.a_w(1 - C))}{(1 - K.a_w)},$$
 (1)

where *M* is the moisture (g / 100 g of solids or g / g solids), *K* and *C* are GAB constants,  $m_0$  is the monolayer value and have the same unit of *M*.  $a_w$  is the water activity in moisture *M*. All tests were performed in triplicate.

### Mechanical properties

The mechanical properties were determined in a texturometer Stable Micro Systems (model TA-XT Plus, England) according on ASTM method D-882-02 (2002), with modifications. Samples (100 x 25 mm) were conditioned (58% and 85% RH) for 48 h at 25 °C in separate desiccators containing different saturated salt solutions (58% - sodium bromide and 85% - potassium chloride). Seven samples from each formulation were placed in the tensile grips. The initial distance between the grips was 50 mm and the crosshead speed was set at 0.8 mm/s. The maximum tensile strength (MPa), elongation at break (%) and Young's or elasticity modulus (MPa) were assessed.

#### Scanning electron microscopy (SEM)

The micrographs of the surface and the fracture of the samples were performed in a scanning electron microscope (SEM) FEI Quanta 200 (Oregon, USA). The samples were dried in an oven with air circulation and renovation at 40 °C for 12 h, and then, they were manually fractured with liquid nitrogen, fixed on aluminum supports and coated with a gold film under vacuum. The samples were analyzed using an accelerator voltage 30 kV.

#### Differential scanning calorimetry (DSC)

The analysis of differential scanning calorimetry (DSC) was performed on a Shimadzu DSC 60 calorimeter. The samples were dried in an oven with air circulation and renovation at 40  $^{\circ}$ C for 12 h and maintained in

a desiccator containing anhydrous calcium chloride for 15 d. Around 0.3 g of the sample were placed in platinum containers equipment, and were heated to -30 °C a 250 °C at a heating rate of 5 °C/ min in a helium atmosphere. Two scans were carried out on each sample. The glass transition temperature (Tg) was calculated as the inflection point of the base line and the melting temperature (Tm) such as endothermic peak in the thermogram flow curve.

# Statistical analysis

The data were analyzed using the Statistica 7.0 software (Statsoft, Oklahoma), with the analysis of variance (ANOVA) and Tukey's test evaluated at a 5% significance level.

## **Results and discussion**

#### Thickness and water solubility

The results of thickness and solubility of the films are shown in Table 1, and it can be observed that there was no significat difference ( $p \le 0.05$ ) between the thicknesses of the films produced with different types of PVA, and the results ranged from 0.151 to 0.159 mm (Table 1). Since the thickness is a parameter that influences the properties of the films it is important to control its uniformity. According to Sobral *et al.* (2001), in films produced by casting, the thickness control depends largely on the viscosity and solids content of the filmogenic solution.

**Table 1 –** Thickness and water solubility of polyvinyl alcohol films<sup>*a*</sup>.

Samples <sup>b</sup>	Thickness (mm)	Water solubility (%)
Selvol <sup>™</sup> 540	$0.159^a~(\pm~0.021)$	$100.00^{a}~(\pm~0)$
Selvol <sup>™</sup> 203	$0.151^a~(\pm~0.020)$	$100.00^{a}~(\pm~0)$
Selvol <sup>™</sup> 325	$0.154^{a}~(\pm~0.013)$	$32.84^{c} (\pm 5.2)$
Selvol <sup>™</sup> 107	$0.152^a~(\pm~0.018)$	$61.74^{b} (\pm 10.4)$

<sup>*a*</sup> Results express in mean ( $\pm$  standard deviation). Different letters in the same column indicate significant differences ( $p \le 0.05$ ) according to the Tukey's test.

<sup>b</sup> Selvol<sup>™</sup> 540 (DH = 88.0%, DP = 1600 − 2000). Selvol<sup>™</sup> 203 (DH = 88.1%, DP = 150 − 300). Selvol<sup>™</sup> 325 (DH = 98.4 %, DP = 1000 − 1500). Selvol<sup>™</sup> 107 (DH = 98.3%, DP = 350 − 650).

Source: The authors.

Regarding to the water solubility, it can be observed that DH significantly affected the solubility of the films, as well as the DP (Table 1). Films produced with lower DH (Selvol<sup>TM</sup> 540 and 203 with  $\sim 88\%$  DH) were more soluble than those produced with SELVOL<sup>TM</sup> 325 and 107, which have higher DH (~ 98% DH). Moraes *et al.* (2008) observed the same trend in films based on gelatin and PVA with different DH. According to Jang and Lee (2003), the increase of DH of PVA decreases its solubility in water because the largest number of free hydroxyl groups increases the number of interactions (hydrogen bonds) carried out between the polymer chains, leaving less free hydroxyls to interact with the water.

Tang and Alavi (2011) reported that the increased in DH results in polymers more crystalline, and thus, less soluble, possibly due to increased free hydroxyls able to interact between them through hydrogen bonding, resulting in more organized regions (crystal) with lower solubility, while partially hydrolyzed grades PVA, such as Selvol<sup>™</sup> 540 and Selvol<sup>™</sup> 203 contain residual acetate groups, which decreases the number of interactions between hydroxyl groups, reducing the overall degree of crystallinity and resulted in more soluble materials.

#### Water vapor permeability (WVP)

The water vapor permeability (WVP) of films measured in different relative humidity gradients are shown in Table 2. The WVP was significantly lower in films produced with Selvol<sup>™</sup> 325 and 107 (~ 98% DH) than films produced with Selvol<sup>™</sup> 540 and 203 (~ 88% DH) for gradient 0 - 33% RH and 33 - 64% RH, while for the largest gradient in the range of RH, the Selvol<sup>™</sup> 325 showed the lowest value (Table 2). It can be noticed a tendency of the films produced with the PVAs lower degree have higher WVP, and such data that are consistent with water solubility results (Table 1), since the permeation process depends on the solubility of the material (MALI et al., 2005). According Jang and Lee (2003), the increase of DH of PVA increases its resistance to water, which indicates that a decrease of DH increase its hydrophilicity and hygroscopicity, as observed in this study. The DP not significantly affect the WVP values of the samples (Table 2).

WVP values were significantly lower in the lower gradient of  $\Delta$ RH (0 – 33%), and increased between 8 and 23 times in the larger gradients  $\Delta$ RH (33 – 64% and 64 – 90%), with no significant difference in these conditions (Table 2). A similar trend was observed by other authors who report that although the values of the three relative humidity gradients ( $\Delta$ RH) are similar, with the increase of the absolute RH values there was and increased WVP (SANTOS *et al.*, 2014).

**Table 2 –** Water vapor permeability as a function of relative humidity gradient  $(\Delta RH)^a$ .

Samples <sup>b</sup>	Water vapor permeability (g/m.s.Pa) x 10 <sup>10</sup>		
	$\Delta RH (0 - 33\%)$	ΔRH (33-64%)	$\Delta RH (64 - 90\%)$
Selvol <sup>™</sup> 540	$0.413^{a,B} (\pm 0.012)$	$4.270^{a,A} (\pm 0.444)$	$3.522^{a,A} (\pm 0.143)$
Selvol <sup>™</sup> 203	$0.212^{a,b,B}~(\pm~0.077)$	$3.574^{a,b,A}~(\pm 0.425)$	$3.436^{a,b,A}~(\pm 0.205)$
Selvol <sup>™</sup> 325	$0.114^{b,B}~(\pm 0.104)$	$2.157^{b,A}~(\pm 0.118)$	$2.647^{b,A}~(\pm~0.248)$
Selvol <sup>™</sup> 107	$0.129^{b,B}~(\pm~0.009)$	$2.403^{b,A}~(\pm~0.441)$	$3.032^{a,b,A}~(\pm 0.240)$

<sup>*a*</sup> Means with different small letters in the same column are different at the 0.05 level in Tukey's test. Means with different capital letters in the same line are different at the 0.05 level in Tukey's test.

<sup>b</sup> Selvol<sup>TM</sup> 540 (DH = 88.0%, DP = 1600 - 2000).

Selvol<sup>TM</sup> 203 (DH = 88.1%, DP = 150 - 300).

Selvol<sup>TM</sup> 325 (DH = 98.4%, DP = 1000 - 1500).

Selvol<sup>TM</sup> 107 (DH = 98.3% DP = 350 - 650).

Source: The authors.

#### Moisture sorption isotherms

The experimental data of the sorption isotherms of films are shown in Figure 1. It was observed that the samples produced with Selvol<sup>TM</sup> 540 and 203, with lower DH ( $\sim 88\%$ ), showed the highest moisture gains as a function of the water activity variation in the whole range of studied water activity, confirming the trend of PVA samples with lower DH have higher hydrophilicity and hygroscopicity (JANG; LEE, 2003).

**Figure 1 –** Water sorption isotherms of PVAs films plasticized with glycerol.



Source: The authors.

Table 3 shows the parameters calculated from GAB model, which was efficient to describe the sorption isotherms of different PVA samples ( $R^2 > 0.98$ ). Selvol<sup>TM</sup> 325 and 107 films had the lowest monolayer values, 6.25 and 6.47 g water/100 g solids, respectively, while Selvol<sup>TM</sup> 203 and 540 showed the highest values, 8.62 and 8.60 g water/100 g solids, respectively.

Table 3 – GAB<sup>a</sup> model parameters of PVA films.

Samples <sup>b</sup>	С	K	M <sub>o</sub> (g/100 g)
Selvol <sup>™</sup> 540	1.76	0.99	8.60
Selvol <sup>™</sup> 203	1.50	0.96	8.62
Selvol <sup>™</sup> 325	1.51	0.99	6.25
Selvol <sup>™</sup> 107	0.86	1.01	6.47

<sup>*a*</sup> where *M*, equation (1), is the equilibrium moisture content at a water activity  $(a_w)$ ,  $m_0$  is the monolayer value (g water/100g solids) and *C* and *K* are the constants.  $R^2$  of all models > 0.98.

<sup>b</sup> Selvol<sup>™</sup> 540 (DH = 88.0%, DP = 1600 - 2000).
Selvol<sup>™</sup> 203 (DH = 88.1%, DP = 150 - 300).
Selvol<sup>™</sup> 325 (DH = 98.4%, DP = 1000 - 1500).
Selvol<sup>™</sup> 107 (DH = 98.3%, DP = 350 - 650).

Source: The authors.

The monolayer value indicates the maximum amount of water that can be adsorbed in a single layer per gram of dry matter of the material, and is related to the hygroscopicity and hydrophilicity of the material (MALI *et al.*, 2005; SHIRAI *et al.*, 2013), so the higher DH of PVA films resulted in less hydrophilic films. It was not possible to establish a relationship between the DP and the value of the monolayer of PVA samples studied in this work.

### Mechanical properties

Tensile strenght of PVA films ranged from 3.99 to 10.51 MPa, and the produced with Selvol<sup>™</sup> 540, 325 and 107 showed the higher results, which were not significant different when compared (Table 4).

Tensile strength indicates the resistance of the material at the point of rupture during the tensile test (OLIVATO *et al.*, 2013), and in this work was not possible to establish a relationship between tensile strength and the DH or DP of PVA.

Table 4 – Results of mechanical properties. tensile strength (TS). elongation at break (E) and young modulus (YM)<sup>a</sup>

Samples <sup>b</sup>	TS (MPa)	E (%)	YM (MPa)
Selvol <sup>™</sup> 540	10.51 <sup>a</sup> (± 2.81)	$262.25^a (\pm 65.33)$	$7.79^c (\pm 1.78)$
Selvol <sup>™</sup> 203	$3.99^b~(\pm 0.80)$	96.61 <sup>d</sup> (± 31.3)	$7.56^c~(\pm~0.77)$
Selvol <sup>™</sup> 325	$10.05^a~(\pm~1.40)$	$198.08^{a.b} \ (\pm 52.44)$	$15.29^b \ (\pm \ 1.00)$
Selvol <sup>™</sup> 107	$10.23^a~(\pm~2.24)$	$163.29^{b.c} (\pm 54.51)$	$21.58^a$ (± 2.24)

<sup>*a*</sup> Results express in mean ( $\pm$  standard deviation).

Different letters in the same column indicate significant differences ( $p \le 0.05$ ) according to the Tukey's test.

<sup>b</sup> Selvol<sup>TM</sup> 540 (DH = 88.0%, DP = 1600 - 2000).

Selvol<sup>TM</sup> 203 (DH = 88.1%, DP = 150 - 300).

Selvol<sup>TM</sup> 325 (DH =98.4 %, DP = 1000 - 1500).

Selvol<sup>TM</sup> 107 (DH = 98.3%, DP = 350 - 650).

Source: The authors.

Silva *et al.* (2008) produced gelatin-based films with five types of PVA (DH ranging from 88 to 99.7%) and observed that the film with the highest tensile strength was produced with PVA with DH of 91.8% (82.3 MPa).

Analyzing the results of elongation at break (Table 4), it was observed that the films produced with Selvol<sup>™</sup> 540 and 325 (higher DP) showed the highest elongation values, 262.25 % and 198.08 %, respectively, and this could be related to their larger chain size and higher viscosity, resulting in more flexible and deformable materials.

It was observed (Table 4) that films based on PVA with higher DH (Selvol<sup>™</sup> 325 and 107) showed higher stiffness (Young's modulus) than those based on PVA with lower DH (Selvol<sup>™</sup> 540 and 203). The increased in DH results in polymers more crystalline due to increased free hydroxyls able to interact between them through hydrogen bonding, resulting in more organized regions (crystal) (TANG; ALAVI, 2011), resulting in materials with higher Young's modulus.

#### Scanning electron microscopy (SEM)

The SEM micrographs of the surface of the films are shown in Figure 2. It can be observed that all films showed continuous and smooth surface, without imperfections or roughness, without pores or fissures. According Galdeano *et al.* (2013), a homogenously matrix is a good indicative of structural integrity of the film, which contributes to obtain good mechanical properties.

#### Differential scanning calorimetry (DSC)

Figure 3 presents the DSC thermograms of the PVA films and Table 5 shows the thermal properties obtained

**Figure 2** – SEM micrographs of surfaces of PVA films: (a) Selvol<sup>TM</sup> 540, (b) Selvol<sup>TM</sup> 203, (c) Selvol<sup>TM</sup> 325 and (d) Selvol<sup>TM</sup> 107.



Source: The authors.

from DSC curves. The glass transition temperatures (Tg) of Selvol<sup>™</sup> 325 and 107 (higher DH) films were higher than Selvol<sup>™</sup> 540 and 203 (lower DH) films (Table 5). Glass transition temperature (Tg) is an important parameter in determining the mechanical properties of amorphous and semicrystalline materials, when submitted to a temperature above their Tg, the materials are in the elastomeric state and below Tg they are in the glassy state. The chains have increased mobility in the elastomeric state, and the physical and mechanical properties are strongly affected (OLIVATO et al., 2013; SHIRAI et al., 2013). Films based on PVA with higher DH presented more interactions between its polymer chains, resulting in lower molecular mobility and higher Tg values, as observed in Table 5. Moraes et al. (2008) produced films based on gelatin and PVA with different DH and they observed that Tg of these

films ranged from 28.5 to 33.7  $^{\circ}\mathrm{C}$  and Tm ranged from 125.6 to 145.0  $^{\circ}\mathrm{C}.$ 





Source: The authors.

Melting temperatures (Tm) of Selvol<sup>™</sup> 325 and 107 (higher DH) films were also higher than those of Selvol<sup>™</sup> 540 and 203 (Table 5) films, which can be explained by greater number of interactions between polymer chains, resulting in films with a higher Tm. Tg and Tm were not affected by the DP of PVA.

**Table 5 –** Glass transition (Tg) and melting (Tm) temperatures of PVA films.

	Samples <sup>a</sup>	Tg (°C)	$Tm(^{\circ}C)$	
	Selvol <sup>™</sup> 540	32.70	167.20	
	Selvol <sup>™</sup> 203	31.00	165.70	
	Selvol <sup>™</sup> 325	49.20	213.95	
	Selvol <sup>™</sup> 107	49.42	213.33	
а	Selvol <sup>™</sup> 540 (DH	= 88.0 %, I	DP = 1600 - 2	2000).
	Selvol <sup>™</sup> 203 (DH	= 88.1 %, D	$\mathbf{P} = 150 - 30$	0).
	Selvol <sup>™</sup> 325 (DH	= 98.4 %, D	P = 1000 - 1	500).
	Selvol <sup>™</sup> 107 (DH	= 98.3 %, D	P = 350 - 65	0).

Source: The authors.

# Conclusion

Biodegradable films based on PVA presented good processability and the obtained results indicated that the effect of different DH were more important for properties of films than the effect of DP. Films based on PVA with lower DH (Selvol<sup>™</sup> 540 and 203) showed higher water solubility, higher water vapor permeability and higher water sorption capacity compared to films produced with PVA with higher DH (Selvol<sup>™</sup> 325 and 107). The micrographs of films showed continuous and smooth surfaces, without imperfections, pores or fissures, independent of DH or DP. The thermal properties of films were affected by DH of PVA, films with higher DH (Selvol<sup>™</sup> 325 and 107) had higher glass transition and melting temperatures. The DP affected the solubility of the films produced with PVA with higher DP, Selvol<sup>™</sup> 325 (DP = 1000 – 1500) showed lower solubility values, and films based on PVA with higher DP (Selvol<sup>™</sup> 540 and 325) showed higher elongation values. Considering the variation in the PVA films properties, the different PVA types can be used for different purposes. Films based on PVA with higher DH (Selvol<sup>™</sup> 325 and 107) showed the higher water resistance and lower water sorption capacity, and they could be used in food packaging to prevent food deterioration caused by water. Films based on PVA with lower DH (Selvol<sup>™</sup> 540 and 203) were more soluble in water, and could be used when higher solubilities were required.

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