Thermomechanical properties of poly(vinyl alcohol) prepared at room temperature as a function of degree of hydrolysis and aluminium addition

Benedetto Pizzo [a,*], Fabio Chiozza [b], Fabrizio Bernardini [c]

[a] CNR-IBE, National Research Council of Italy, Institute of Bioeconomy, via Madonna del Piano, 10, Sesto Fiorentino FI, Italy
[b] Vinavil SpA, via Valtellina 63, Milano, Italy
[c] Vinavil SpA, via Toce 7, Villadossola VB, Italy

ARTICLE INFO

ABSTRACT

Poly(vinyl alcohol) (PVOH) is widely used in various industrial applications. However, its water solubility reduces film performance, which is important in PVAc-based wood adhesives. In this sector, $AlCl_3$ is often used as a complexing agent for PVOH. In this work, the effect of heating and aluminium addition on the structure and viscoelastic properties of PVOH with different degrees of hydrolysis (DH), 88%, 92% and 99%, was studied. Products treated with either HCl or acetic acid were also considered. The polymer properties were evaluated by infrared spectroscopy and dynamic mechanical analysis, and the mass loss of the polymers on heating was also evaluated to explain the observed differences. The measurements showed that the peaks of the tanδ curves occurred at slightly lower temperatures as the DH increased, although higher crystallinity was observed at the end of the DMA tests for higher DHs. This is due to the increasing affinity of highly hydrolysed PVOH for water molecules. However, as the temperature increased, the storage modulus was higher for higher DHs due to the better mutual interaction of OH groups that develops during the tests in highly hydrolysed polymers. The addition of aluminium caused a slight increase in Tg, the magnitude of which was inversely proportional to the DH. However, as the temperature increased, the storage modulus decreased more at lower DHs than at higher DHs. This effect was related to a combination of factors: the lower presence of crystallites in products with lower DH and the formation of conjugated polyenes, which was also more pronounced in products with lower DH. Both mechanisms were due to the action of aluminium. Thus, both heat and the addition of aluminium had a determining effect on the properties of PVOH films, although the degree of importance depended on the degree of hydrolysis of the polymer.

1. Introduction

Poly(vinyl alcohol) (PVOH) is a synthetic polymer widely used in various industrial applications such as films and packaging materials [1], fibres [2], hydrogels [3], proton exchange membranes [4], and adhesives [5,6]. This interest is due to its properties such as low gas permeability, high mechanical resistance, water solubility, biocompatibility and easy biodegradability [7].

One of the most interesting applications of PVOH is in water-based wood adhesives, and in particular in polyvinyl acetate (PVAc) latexes, where it acts as a non-ionic stabiliser of the dispersion during the polymerisation phase. In fact, a dispersion prepared with PVOH has many advantages over surfactants, including Newtonian fluidity, wet tackiness, high strength and creep resistance [8]. In this case, in its role

as a protective colloid, PVOH affects not only the colloidal properties but also the characteristics of the formed film. In fact, after film formation, PVOH is uniformly distributed at the boundaries of the PVAc particles [9]. However, due to its water solubility, the use of PVOH reduces film performance in wet conditions [6].

PVOH is usually produced by hydrolysis of PVAc [10]. This hydrolysis reaction involves the substitution of acetate groups in the polymer chain. The progress of the hydrolysis reaction determines the degree of substitution (also called the degree of hydrolysis), which is usually very high for PVOH (typically higher than 85%). Thus, the PVOH chain is composed of vinyl alcohol and vinyl acetate units, i.e. depending on the degree of hydrolysis, PVOH has residual percentages of vinyl acetate units in a chain composed predominantly of vinyl alcohol units. Due to its moderate stereoregularity, PVOH is a partially crystalline polymer.

However, it is intuitive that the hydrolysis conditions can strongly influence most of the physical properties of PVOH. For example, the hydrophilicity of PVOH in aqueous systems depends on the number of hydroxyls, which limits its use in aqueous environments [11]. Several approaches have been used to control the properties of PVOH.

Krumova et al. [12] studied the evolution of mechanical and thermal properties of 98–99% hydrolysed PVOH with increasing degree of crosslinking using hexamethylene diisocyanate in the range of 2 to 74% as a hardener. However, a physical-type interaction with PVOH is a simpler route to follow. Lim et al. [13] considered five different fully hydrolysed (98.0–99.5%) PVOH/boric acid hybrid films prepared by a solution blending method and found that the size and amount of PVOH crystallites decreased with increasing boric acid content, while the crosslinking density of the polymer increased. In the field of PVAc-based wood adhesives, AlCl$_3$ is often used as a complexing agent for PVOH to reduce the availability of hydrophilic groups [14]. This significantly improves the performance of the adhesive in wet conditions [15,16]. AlCl$_3$ was also used as a Lewis acid catalyst immobilised by covalent bonding on cross-linked PVOH microspheres, inducing comparative advantages in terms of stability and loading capacity [17]. It was observed that the addition of aluminium hypophosphite to PVOH (degree of hydrolysis 86.0−90.0%) affected several properties of the polymer (flame retardancy, thermal stability, mechanical properties and transparency). In this case, the degree of crystallinity was reduced while the glass transition temperatures were shifted to higher temperatures [18]. Furthermore, Wang et al. [19] observed that Al^{3+} ions enhanced the molecular interactions between water and the polymer chain and improved the thermal stability of a PVOH (>99% hydrolysed)–gellan gum–aluminium ions composite hydrogel.

However, to the best of our knowledge, a systematic analysis of the effect of heating and the addition of aluminium to PVOH of different degrees of hydrolysis (DH) has not yet been fully investigated. Therefore, the aim of the present work is to investigate how the structure and viscoelastic properties of PVOH films of different grades are affected in these cases. The polymer properties have been evaluated by means of infrared spectroscopy and dynamic mechanical analysis (DMA), also evaluating the mass loss of the polymers upon heating in order to explain the observed differences.

2. Materials and methods

Three commercial polyvinyl alcohols (PVOH) characterised by three different degrees of hydrolysis (88%, 92% and 99%) were used for the present tests (Table 1). They are hereafter referred to as DH88, DH92 and DH99 respectively and were all supplied by Shin-Etsu (Japan). These products were chosen because they had similar viscosity and degree of polymerisation and therefore the same expected polymer properties [20,21]. All the tests were carried out on solid films (see section 2.1) obtained from aqueous solutions with an initial concentration of 27%, studying different combinations:

(a) products used as supplied (series 'as is');
(b) products to which 3% w/w of a 27.6% w/w solution of AlCl$_3$•6H$_2$O was added to the liquid solution of PVOH prior to film preparation (series 'AlCl3'). The measured pH of these solutions was 3;
(c) products to which either a 0.5M solution of HCl or glacial acetic acid was added to obtain the same pH of 3 as measured for the 'AlCl3' preparations (series 'HCl' and 'AcAc', respectively).

The formulations described in point (c) were prepared in such a way as to distinguish the effects due to the presence of Al ions from those due to aluminium-induced acidity (as observed in Series 'AlCl3') at the time of specimen formation.

2.1. Preparation of PVOH specimens and testing procedure

All samples were prepared by pouring the deaerated solutions under vacuum into a 3 mm thick square Teflon mould with an inner side of 80 mm. After casting, the samples were placed in a climatic chamber at 23 $\pm$ 2°C and 50 $\pm$ 5% RH for 3 days. The samples were then cut into strips of 80 mm length and 12 mm width, the thickness of which was not controlled. These strips were kept under standard conditions (23 $\pm$ 2°C and 50 $\pm$ 5% RH) for a further 15 days.

The following sequence of measurements was carried out successively on each specimen:

1. Acquisition of IR spectra (see Section 2.2);
2. Measurement of initial mass (before DMA tests), see Section 2.3;
3. Performing the DMA tests (see Section 2.4);
4. Measurement of the mass after the DMA tests;
5. Acquisition of IR spectra on the tested samples.

2.2. ATR-FTIR analysis

FTIR spectra were taken of each sample both before and after the DMA tests. The analysed areas were taken in the protruding parts, outside those included in the stress zones of the DMA clamp. Spectra were recorded using a Bruker Alpha FTIR spectrometer with the following settings: 40 scans per sample; spectral resolution: 4 cm^{-1}, wave number range: 4000 to 400 cm^{-1}, using a diamond single reflection Attenuated Total Reflectance (ATR) device. At least three spectra per sample were recorded directly on the solid film. No additional pre-treatment was performed. Spectra were processed using the OPUS 6.5 software (Bruker Optics). Post spectroscopic manipulations were kept to a minimum: spectra were normalised according to the Min-Max normalisation procedure, performed between 1800 and 800 cm^{-1}. This procedure automatically sets the absorbance unit to 0 at the minimum (in our case at 1800 cm^{-1}) and to 2 at the maximum (in our case at the maximum of the secondary alcohol band, at 1030 cm^{-1}).

2.3. Mass loss tests

Mass loss (ML) tests were performed on each sample subjected to the DMA tests. The sample was weighed immediately before and immediately after the tests on a balance with an accuracy of 0.1 mg. Immediately after the DMA tests, the hot samples were placed in a pre-weighed glass container, sealed with a ground-glass stopper and transferred to the balance. Measurements were taken when the mass stabilised, which was always within 5 seconds. The whole procedure took less than 30 s.

ML was expressed as:

$$ML = \frac{M_{RT} - M_{160°C}}{M_{160°C}} \tag{1}$$

where M_{RT} and $M_{160°C}$ are the masses immediately before (i.e., at room temperature) and immediately after (i.e., at 160°C) the DMA tests,

Table 1
Main characteristics of the analysed products, as obtained from technical data sheets provided by the manufacturer. In the Table, 'n/a' means that the datum was not available.

Name of the commercial product	JP-18	JT-18	JF-17
Brief name	DH88	DH92	DH99
Degree of hydrolysis (mol%)	88.1	92.4	98.5
Viscosity (mPa·s), measured at 20°C on 4% solutions	24.9	30.3	30.4
Degree of polymerisation	ca. 1800	ca. 1800	ca. 1700
pH	5.7	5.7	6.0
Volatiles (%)	3.8	2.5	4.3
Ash (%)	0.3	0.2	0.3
Purity (%)	95.5	96.9	94.9
Sodium acetate (%)	0.64	0.62	n/a

respectively.

2.4. Dynamic Mechanical Analysis (DMA)

DMA tests were performed on a minimum of five samples per series. Prior to testing, samples were stored under vacuum at room temperature (20-23°C) in a desiccator with coloured silica gel moisture indicator for > 50 days. A TA Instruments Q800 machine with a load capacity of 18 N was used for testing, using a dual cantilever clamp, which was calibrated prior to each test session. The loaded area of the specimens was 35 mm in length. The following conditions were used in the tests: oscillation frequency 1 Hz, oscillation amplitude 50 μm. Measurements were made between room temperature (20-23°C) and 160°C, using a temperature ramp of 1.5°C/min.

The DMA tests allowed the variation of both the storage modulus (E') and the loss modulus (E'') with temperature to be measured. Accordingly, the value of tanδ was obtained by the ratio:

$$\tan\delta = \frac{E''}{E'}. \tag{2}$$

As these three parameters are mathematically related, only the values of E' and tanδ are reported in this paper. Changes in tanδ values with temperature are considered to be associated with thermal type transitions or relaxations in polymers. A peak in the tanδ curve associated with changes of one order of magnitude (or more) in the values of E' is considered to represent the glass transition temperature (Tg) of the polymer under consideration.

3. Results

3.1. ATR-FTIR analysis

The comparison of the FTIR spectra of the three products 'as is' shows well the expected difference in composition (Fig. 1). The broad band at 3300 cm^{-1} increased slightly in intensity with increasing DH (Fig. 1a). Major differences were observed in the 500-1800 cm^{-1} region: the band at 1732 cm^{-1} decreased progressively from DH88 to DH92 to DH99, and the band at 1240 cm^{-1} also decreased in the same order. It is also interesting to note the other differences in the spectra: the bands at 1374 and 944 cm^{-1} decreased and those at 1327 and 1141 cm^{-1} increased with increasing DH. Furthermore, the band at 1024 cm^{-1} was clearly visible in DH88, became a shoulder in DH92 and disappeared completely in DH99 (Fig. 1).

The addition of AlCl$_3$ had only a limited effect on the spectra of the products, as can be seen for the representative case of DH99 in Fig. 2. The main difference was related to the enlargement of the broad band centred at 3300 cm^{-1}, which also interested the neighbouring bands at
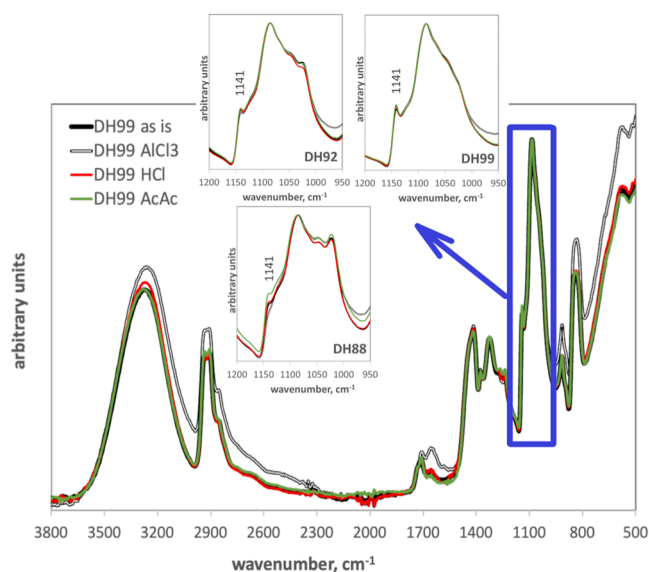

Fig. 2. Spectrum of product DH99 in the various considered combinations: 'as is', added with AlCl$_3$, added with HCl and added with acetic acid. The insets show a detail of the 950 - 1200 cm^{-1} region for the same series and for the three considered degrees of hydrolysis (DH88, DH92 and DH99), where the variation of the band at 1141 cm^{-1} is shown. All spectra were Min-Max normalized in the 800-1800 cm^{-1} range.

2900 cm^{-1}. In addition, a significant lowering of the band at 1141 cm^{-1} was observed for DH88, whereas this occurrence was much less evident for DH92 and DH99 (Fig. 2). It is worth noting that the addition of either HCl or acetic acid did not affect the shape of the spectra (Fig. 2).

The acquisition of the spectra after the DMA tests allowed the effect of heat supply (in addition to limited stress) on the products to be assessed. In films of the 'as is' series (Fig. 3a), the main change was the appearance or more intense vibration of the band at 1141 cm^{-1} for the three DHs considered (Fig. 3a). The same occurrence was observed in the 'HCl' and 'AcAc' series. On the other hand, when AlCl$_3$ was added to the product, exposure to heat induced: a) the narrowing of the band centred at 3300 cm^{-1}, which had broadened after the addition of AlCl$_3$ in the absence of heat (Fig. 3b); b) the appearance of a band at 1580 cm^{-1} (Fig. 3c). This band was not present in the 'AlCl3' series (Fig. 2) nor in the 'as is' series exposed to heat (Fig. 3a), and is therefore due to the simultaneous presence of aluminium and heat. Furthermore, unlike the 'as is' series, the band at 1141 cm^{-1} did not appear in any of the DHs and, on the contrary, the small shoulder initially visible in DH92 disappeared completely (Fig. 3c).
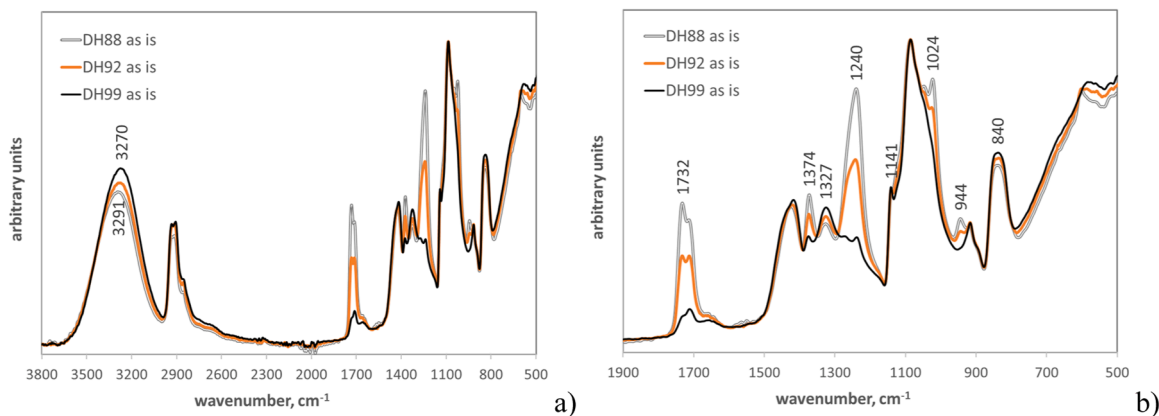

Fig. 1. Spectra of products of the series 'as is'. Comparison between the three considered degrees of hydrolysis. In (b), the range 500-1900 cm^{-1} is detailed. Spectra were Min-Max normalized in the range 800-1800 cm^{-1}.
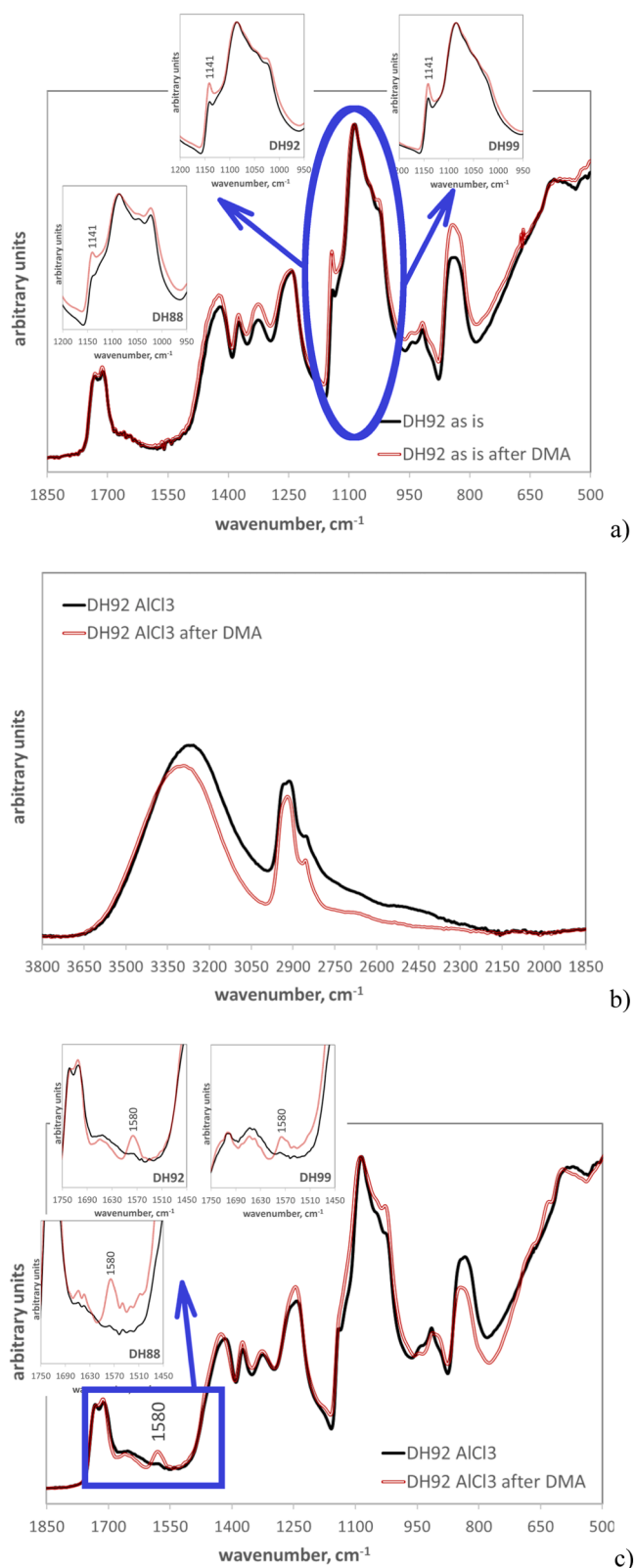
Fig. 3. Comparison among the spectra of product DH92 as is (a) and after the addition of AlCl₃ (b,c) before and after the execution of DMA tests. The insets show a detail of the range 950 and 1200 cm⁻¹ (a) and 1450-1750 cm⁻¹ (c) for the same series and for the three considered degrees of hydrolysis. All spectra were Min-Max normalized in the 800-1800 cm⁻¹ range.

3.2. Mass loss tests

Measurements of the mass loss of the samples showed very similar values for the different series considered, with the notable exception of the series supplemented with AlCl₃, which lost significantly more mass during the tests (Table 2). This loss is inversely proportional to the degree of hydrolysis (the higher it is, the lower the mass loss).

3.3. Dynamic Mechanical Analysis (DMA)

DMA tests of the series 'as is' showed interesting differences between the three degrees of hydrolysis (Fig. 4). Each product showed a large thermal transition in the 20-90°C range (Fig. 4b). Considering that these transitions are also associated with a dramatic decrease in storage modules (Fig. 4a), they can be considered as glass transitions. In particular, the glass transition temperature (Tg) is usually taken as the peak of the tanδ curves. These values were 50.2°C, 48.9°C and 45.9°C for DH88, DH92 and DH99, respectively (Fig. 4b). Therefore, there was a trend towards a slightly lower Tg and a decrease in the viscous part, represented by the lower values of tanδ, with an increasing degree of hydrolysis among the three products. An opposite trend was observed in the values of E' at temperatures higher than the corresponding Tg, that is, in the rubbery state: while below Tg, E' was similar among the three DHs (Fig. 4a), above Tg, DH99 was stiffer than DH92, which in turn was stiffer than DH88 (Fig. 4a).

When aluminium was added to the polymers, their viscoelastic behaviour changed (Fig. 5). In Fig. 5 the series added with acetic acid is not shown for better clarity of the figures, as the behaviour was similar to 'HCl'. For all three products, the presence of aluminium induced a slight increase in Tg, the magnitude of which was inversely proportional to the degree of hydrolysis. The difference measured was +5°C, +4.4°C and +2.5°C for DH88, DH92 and DH99, respectively (Fig. 5). The presence of Al also induced the appearance of a relaxation at approx. 30°C, the height of which was clearly visible in the tanδ curve for DH88 and became progressively less important for DH92 and DH99 (Fig. 5). The introduction of both hydrochloric and acetic acids had an opposite effect on the Tg, which decreased by an amount proportional to the DH: the difference with the Tg of the polymers was 0.3°C, 1.3°C and 3.9°C for DH88, DH92 and DH99, respectively, when HCl was added (Fig. 5).

After the glass transition (temperatures > 70°C) something happened to the polymers, depending on their degree of hydrolysis. More specifically, in the 'AlCl3' series the tanδ values of DH88 were always higher than those of the other two series ('as is' and 'HCl'), and the same was true for DH92, although to a lesser extent (Fig. 5b,d,f). These increases in tanδ were due to the corresponding decreases in E' in the same temperature range (Fig. 5a,c,e) rather than increases in E", which instead remained quite similar for the different series (not shown).

4. Discussion

4.1. Series 'as is'

The broad band at 3300 cm⁻¹ is due to the stretching of O–H from intra- and intermolecular hydrogen bonds by hydroxyls in alcohols

Table 2
Average mass loss of the considered series, as assessed after DMA tests. The number after the symbol '±' represents the standard deviation of data.

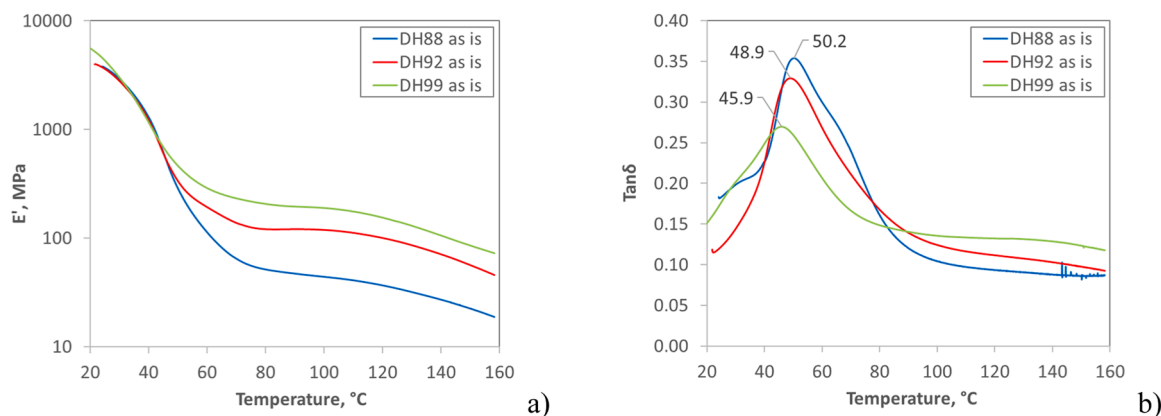| Product	JP-18	JT-18	JF-17
Brief name	DH88	DH92	DH99
Series 'as is', %	4.4 ± 0.6	4.2 ± 0.4	4.0 ± 0.5
Series 'HCl', %	3.7 ± 0.8	4.1 ± 0.6	4.2 ± 0.9
Series 'AcAc', %	3.7 ± 0.6	4.0 ± 0.8	3.9 ± 0.8
Series 'AlCl3', %	11.8 ± 0.8	9.1 ± 0.8	6.7 ± 1.7

Fig. 4. Comparison among Storage modules (a) and tanδ curves (b) of the three considered degrees of hydrolysis of series 'as is'.

(Table 3). This broad band slightly increased in intensity with increasing DH due to the progressively higher amount of OH groups in more hydrolysed polymers. The band at 1732 cm^{-1} progressively decreased from DH88 to DH92 to DH99 (Fig. 1) because this band is due to ester groups, which are proportionally less abundant in highly hydrolysed products such as DH99 (Table 3). For the same reason, the band at 1240 cm^{-1} attributed to the C–O–C bond between the acetate group and the PVOH backbone also decreased in the same order (in fact, acetate groups are more abundant in products with a lower degree of hydrolysis, such as DH88).

It is also interesting to note the other differences in the spectra, namely the bands at 1374, 1024 and 944 cm^{-1}, which decreased, and those at 1327 and 1141 cm^{-1}, which increased with increasing DH (Fig. 1). The band at 1141 cm^{-1} can be attributed to the stretching of C–O and C–C bonds and is indicative of the degree of crystallinity of PVOH [22]. Thus, its increase indicates that highly hydrolysed PVOH has greater crystallinity than less hydrolysed polymer. This phenomenon is well known and is related to the more ordered structure of the highest DH polymers, whereas the presence of acetate groups in the chains limits the possibility of close contact between chain segments [23]. The band at 1327 cm^{-1} is attributed to C–OH bending associated with C–H wagging vibrations (see group 1 in Fig. 6). Therefore, its vibration is proportionally more intense in the polymer with a higher degree of hydrolysis, richer in hydroxyls. The band at 1374 cm^{-1} is associated with the symmetric deformation of aliphatic C–H and, considering that it decreases with increasing DH, it must be due to the –CH$_3$ group in the ester moiety (group 2 in Fig. 6).

In contrast, the assignment of the other bands mentioned is more problematic. These bands are rarely described in the literature on PVOH. In general, the band at 944 cm^{-1} is attributed to O–H deformation, for example in carboxylic acids [24], while the band at 1024 cm^{-1} is usually attributed to C–O stretching coupled to C–C vibrations [25] and has been related to C–O stretching in primary alcohols [26]. In the present case, however, their origin must be different. In fact, PVOH is primarily a secondary alcohol, and no FTIR detectable acids are expected to be present in PVOH. On the other hand, the band at 946 cm^{-1} has also been attributed to deformational vibrations of C–H [27], and it has been previously reported that the C–H out-of-plane vibration in vinyl-bound products shifts from 990 cm^{-1} for alkenes to lower wavenumbers of the order of about 945 cm^{-1} for vinyl esters [28]. Furthermore, the band at 1024 cm^{-1} can also be attributed to the vibration of the CH$_3$ group [29,30]. Therefore, it seems reasonable to suggest that these two bands (944 and 1024 cm^{-1}) are related to the ester group in the acetate moiety, in a context where the bond attribution can only be approximate due to the strong coupling between C–H, C–O and C–C vibrational modes, as in this case (Table 3). Indeed, a similar assignment to ours has been proposed for poly(vinyl acetate) [31,32].

After the DMA tests, the band at 1141 cm^{-1} appeared in the 'as is'

series (Fig. 3a), demonstrating the formation of new crystallites in PVOH. The increase in crystallinity in PVOH due to heating is due to annealing effects [33,34]. In our case, however, this event showed that the conditions used in the DMA test were mild enough to allow PVOH to crystallise upon heating. At the same time, the DMA measurements showed that the peaks of the tanδ curves occurred at slightly lower temperatures as the DH increased (Fig. 4b). This is counterintuitive, as it is usually assumed that Tg increases in more crystalline polymers [34]. However, it is known that the glass transition in polymers is dependent on the presence of plasticisers, the effect of which is to reduce of the measured Tg. This means that in polymers containing plasticisers, the glass transition occurs at lower temperatures than in the same pure polymers. PVOH are highly hydrophilic polymers and moisture can act as a plasticiser for this class of macromolecules [35]. In our case, the decrease in Tg observed with the degree of hydrolysis is related to an increasingly greater affinity for water molecules in highly hydrolysed PVOH, since in the latter the acetate ester groups are replaced by hydroxyls, which are hydrophilic. In fact, at temperatures as low as 50°C, and thus below Tg, water molecules are still present in the polymer chains because the moisture content is so strongly absorbed in the polymers that it could not be completely removed by vacuum treatment at room temperature [36]. Thus, the effect of moisture on Tg is most evident in DH99, which contains the largest amount of OH groups; therefore, the lower value of the tanδ peak in DH99 compared to DH92 and DH88 is related to the same phenomenon. However, the adsorbed moisture is quickly released on heating and dehydration during the DMA tests is confirmed by FTIR analysis as a decrease in the band at 3300 cm^{-1}. Already at 70°C it is apparent from Fig. 4a that the storage modulus of DH99 is higher than that of DH92, which in turn is significantly higher than that of DH88. This is due to the better mutual interaction that characterises DH99, where the OH groups are highly polar and are able (once the water molecules have been removed) to form strong inter- and intra-molecular hydrogen bonds that make the polymer chains stiffer. Thus, in DH99 the transition starts earlier than in DH92 and DH88 (lower Tg values), but with a simultaneous advance in moisture loss, the mechanical properties are maintained better than in the other grades. This mechanism confirms the results obtained by FTIR analysis of an increase in crystallinity after DMA, which is most pronounced in DH99.

These effects become progressively less important as the number of OH groups is reduced, as in the case of polymers with a lower degree of hydrolysis (DH92 and DH88). In these cases, the presence of ester groups prevents the good mutual interaction between the PVOH chains, thus reducing the mechanical properties. The presence of a similar mechanism is also confirmed in the FTIR spectra, where a higher crystallinity is associated with DH99 compared to DH92 and DH88.
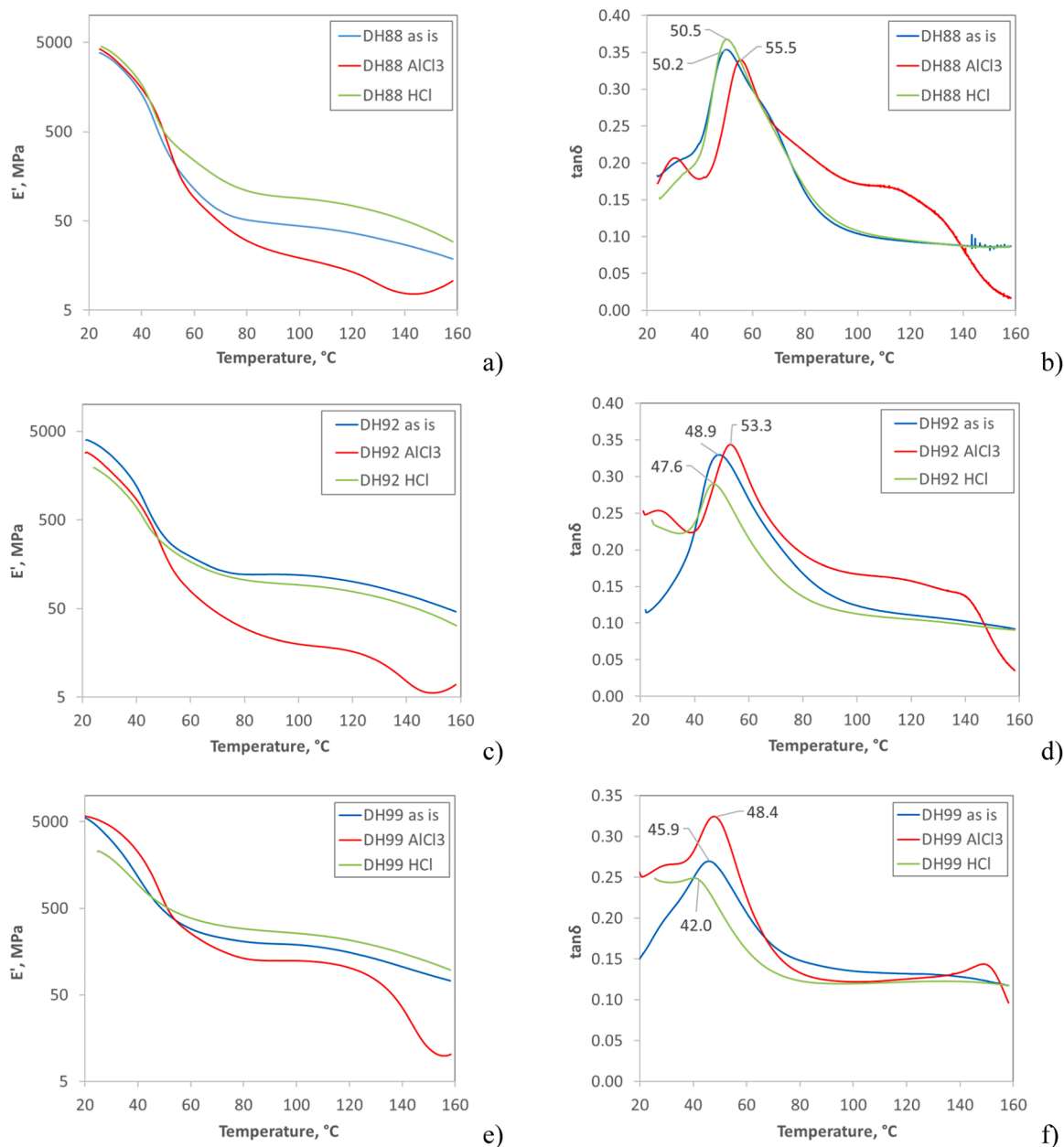
Fig. 5. Comparison among Storage modules (a, c, e) and tanδ curves (b, d, f) of the three considered degrees of hydrolysis for the series not modified ('as is') and added with either aluminium chloride (series 'AlCl3') or hydrochloric acid (series 'HCl'). The series added with acetic acid was not shown because its behaviour was similar to 'HCl'.

Table 3
Band assignment of the groups of interest for the considered polyvinyl alcohols with different degrees of hydrolysis.

Band (cm^{-1})	Band assignments
3300	O–H stretching due to hydroxyls in alcohols
1732	C=O in ester groups
1580	conjugated C=C stretching in polyenes (appears after heating in presence of Al)
1374	symmetric deformation of aliphatic C–H in the –CH$_3$ group of the ester moiety
1327	C–OH bending associated with C–H wagging vibrations
1240	C–O–C bond between the acetic group and the PVOH skeleton
1141	stretching of C–O and C–C bonds, indicative of the degree of crystallinity of PVOH
1024	C–O stretching coupled with C–C vibrations
944	vibration of C–H associated with C–O and C–C bonds

4.2. The other series

The addition of AlCl$_3$ affected the band at 1141 cm^{-1} in the IR spectra, with an effect inversely proportional to the DH (Fig. 2). This implies that the presence of Al tends to hinder the formation of crystallites in PVOH, similar to what happens with boric acid [13]. The effect of Al is more pronounced in cases, such as DH88, where the presence of acetate groups is already an obstacle to crystallisation. In addition, the presence of aluminium induced a slight increase in Tg, the unit of which is inverse to DH (Fig. 5), while below Tg this relaxation only slightly affected the E' of the polymer (Fig. 5). To explain this occurrence, it should be remembered that the FTIR analysis showed that Al did not modify the chemical bonds within the polymers (Fig. 3). In principle, however, a physical coordination between Al and PVOH could be hypothesised. The mechanical properties of polymers with linear chains are due to a combination of factors: a) the covalent bonds in the linear
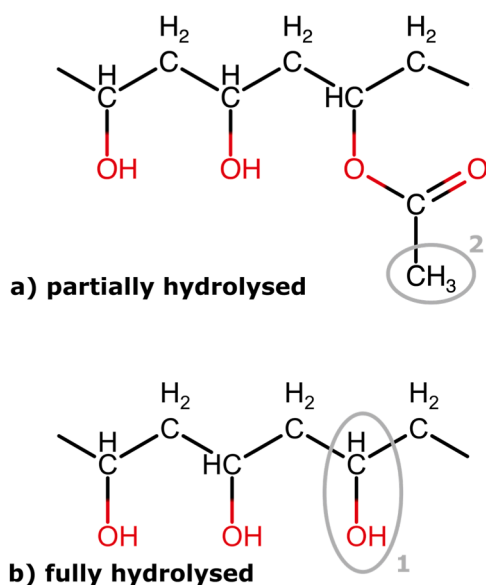
Fig. 6. Main chemical structure of partially hydrolysed (a) and fully hydrolysed (b) polyvinyl alcohol. The groups circled and numbered are commented on in the text.

chain; b) the chain entanglement density; c) the lateral contact points between chain segments, e.g. due to physical cross-linking [20]. Thus, the possible coordination between Al and PVOH should have a positive effect on b) and/or c). However, considering that E' was not significantly affected by Al, an explanation other than coordination between Al and PVOH must be considered. In particular, it can be suggested that aluminium is able to coordinate water molecules without reacting with them [14]. This is actually equivalent to sequestering some of the same water molecules that act as plasticisers for the polymer, slightly increasing its glass transition temperature. This also means that the structures formed with Al are external to the polymer structure and therefore do not affect the mechanical properties of the polymer.

The FTIR spectra also showed that the same structures disappeared after the DMA tests (and therefore on heating), and that the unit of signal decrease was inverse to DH (Fig. 2 and Fig. 3). It can therefore be speculated that the relaxations observed at temperatures lower than Tg (around 30°C) are related to the destruction of these Al-water structures. The fact that this relaxation is more noticeable in DH88 can be related to the fact that in DH88 there are more water molecules available to form structures with Al, since in the initial stages of setting (i.e., drying from the liquid state) DH99, which has the highest amount of hydrophilic OH groups in the chain, attracts water molecules more intensely. In contrast, DH88, which has the highest amount of ester groups, has a lower affinity for water molecules and therefore the Al ions have a lower amount of competing groups to create interactions with water. DH92 appears to be intermediate between the other two polymers.

Tests carried out in the presence of either HCl or CH3COOH showed a decrease in Tg values proportional to DH compared to the 'as is' series (Fig. 5). This can be attributed to the lower degree of interaction between polymer chains induced by the presence of acids, which reduces inter- and intra-molecular hydrogen bonding. Indeed, it has previously been shown [37] that the addition of HCl to PVOH hydrogels reduces the melting point from 200°C to between 164°C and 170°C. The effect of HCl is obviously more pronounced at higher DHs. Thus, despite the increased acidity in AlCl$_3$ added polymers, the effect of the presence of aluminium counteracts this effect and indeed its coordinating ability increases the polymer Tg (Fig. 5).

At temperatures > 70°C, higher tanδ values were observed for the polymers depending on their degree of hydrolysis. This was most evident for the 'AlCl3' series of DH88 (Fig. 5b,d,f), and was associated

with a decrease in E' values in the same temperature range (Fig. 5a,c,e). This behaviour can be attributed to the absence or reduced extent of crystallisation, which was hindered in the presence of Al for the lowest DH, as mentioned above, whereas the crystallisation ability was less affected by Al in DH99 (Fig. 3a). However, based on the FTIR spectra, a mechanism overlapping and complementing the previous one can also be suggested. Indeed, the FTIR spectra obtained after the DMA tests showed the appearance of a band at 1580 cm^{-1}, more intense in DH88 and progressively less intense in DH92 and DH99 (Fig. 3c). It was previously shown that thermal treatment at the very high temperature of 150-170°C induces in PVOH the elimination of OH groups as water and various gases (including acetic acid). This elimination reaction generates C=C and forms a polyene structure in the polymer chain at the end of the first stage of degradation [18,38,39]. In our case, these polyenes should be conjugated in order to absorb at such low wavenumbers [40, 41]. The band at 1580 cm^{-1} also appeared after exposing the polymers to a temperature of 120°C, lower than the final temperature to which the polymers were subjected during the DMA tests (160°C) (not shown). This indicates that the aforementioned degradation mechanism occurred at not very high temperatures, lower than those expected for the thermal degradation of PVOH. This is due to the catalytic activity of acidity induced by the presence of Al, similar to what happens with other polymers [42–44]. The fact that this catalytic activity was not observed in either the 'HCl' or 'AcAc' series is due to the fact that in both cases the concentration of these acids was limited, although it was sufficient to reach the same pH level as in the 'AlCl3' series. Moreover, these acids tend to evaporate, unlike Al, which is more persistent. Indeed, Gavrilov et al. [39] observed this catalytic activity when air was continuously blown through a solution of concentrated hydrochloric acid and a column containing a drying agent. The formation of polyenes is proportionally less abundant in polymers with higher DH, as these are richer in crystalline phases that are less subject to this mechanism [38]. In addition, the same mechanism induces moisture loss, as apparent from Fig. 7. Thus, the progressive increase in mass loss after the DMA tests observed in the polymers analysed (Table 2) confirms the evidence obtained from the FTIR spectra and the DMA tests of an increasingly more abundant degradation of the polymers with lower DH.

The weakening effect of aluminium was apparently more important at higher temperatures. This may explain the sudden increase in E' values (with the associated decrease in tanδ) at T > 140°C (Fig. 5), due to an effect similar to strain hardening.

5. Conclusion

The aim of the present work was to study the structure and viscoelastic properties of PVOH of different DHs when heated and when aluminium was added to the formulations. The comparative tests allowed full interpretation of the differences found in the IR spectra of the PVOH polymers, with band assignments rarely found in the literature related to PVOH. DMA measurements showed that the peaks of the tanδ curves occurred at slightly lower temperatures with increasing DH, although higher crystallinity was observed at the end of the DMA tests for higher DHs. Although this may seem counterintuitive, as Tg is usually expected to increase in more crystalline polymers, this behaviour can be related to the increasingly higher affinity of highly hydrolysed PVOH for water molecules in a matrix where moisture has not been fully released during the setting from the wet phase. It should be noted that
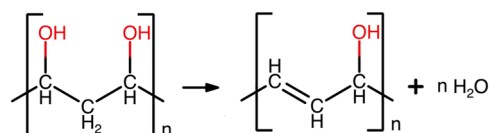

Fig. 7. Proposed mechanism of polyenes formation in PVOH polymers at high temperatures and in presence of aluminium.

this is a common situation in practical cases such as wood adhesives. However, as the temperature gradually increased, the storage modulus was higher at higher DHs due to the better mutual interaction of OH groups in highly hydrolysed polymers. This led to the formation of new crystallites as the temperature increased during the tests. The addition of aluminium ions changed this picture.

In fact, at low temperatures, aluminium partially dehydrates the polymer, but retains the water molecules (which do not disappear) in structures so unstable that they break as soon as they are heated. Instead, at room temperature, simple drying is not enough to overcome this interaction energy. It can therefore be speculated that the relaxations observed at temperatures lower than Tg (around 30°C) are related to the destruction of these Al-water structures. Therefore, at lower temperatures, the presence of aluminium induced a slight increase in Tg, the unit of which is inversely related to DH. However, as the temperature increased, the usual decrease in storage modulus normally observed in polymers was dependent on DH, being higher for DH88 compared to DH92 and then to DH99. This effect was related to a combination of factors: the lower presence of crystallites in products with lower DH, since aluminium tends to inhibit their formation especially in products with low DH, and the formation of conjugated polyenes, whose formation was clear in the FTIR spectra and that was more pronounced in products with lower DH. The same mechanism induced an additional dehydration in the polymer chain with a consequent higher mass loss, which was indeed observed after DMA tests.

All the results reported confirmed the determining effect of temperature and the presence of aluminium as an acid catalyst on the properties of PVOH films, although the importance of these two factors is strongly dependent on the degree of hydrolysis of the polymer.

Funding

Acknowledgements

CRediT authorship contribution statement

Benedetto Pizzo: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Fabio Chiozza:** Writing – review & editing, Visualization, Resources, Funding acquisition, Conceptualization. **Fabrizio Bernardini:** Writing – review & editing, Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

References

[1] A.A. Oun, G.H. Shin, J.W. Rhim, J.T. Kim, Recent advances in polyvinyl alcohol-based composite films and their applications in food packaging, Food Packag. Shelf Life 34 (2022) 100991, https://doi.org/10.1016/j.fpsl.2022.100991.

[2] X. Hong, Y. Xu, L. Zou, Y.V. Li, J. He, J. Zhao, The effect of degree of polymerization on the structure and properties of polyvinyl alcohol fibers with high strength and high modulus, J. Appl. Polym. Sci. 138 (2021) 49971, https://doi.org/10.1002/app.49971.

[3] H. Adelnia, R. Ensandoost, S. Shebbrin Moonshi, J.N. Gavgani, E.I. Vasafi, H.T. Ta, Freeze/thawed polyvinyl alcohol hydrogels: Present, past and future, Eur. Polym. J. 164 (2022) 110974, https://doi.org/10.1016/j.eurpolymj.2021.110974.

[4] D.U. Imaan, F.Q. Mir, B. Ahmad, Proton exchange membrane based on poly (vinyl alcohol) as support and alpha alumina as filler and its performance in direct methanol fuel cell, J. Environ. Chem. Eng. 9 (2021) 106119, https://doi.org/10.1016/j.jece.2021.106119.

[5] F. Chiozza, I. Santoni, B. Pizzo, Discoloration of poly(vinyl acetate) (PVAc) gluelines in wood assemblies, Polym. Degrad. Stab. 157 (2018) 90–99, https://doi.org/10.1016/j.polymdegradstab.2018.10.003.

[6] F. Chiozza, F. Toniolo, B. Pizzo, Effects of radio frequency and heat on wood bonding with a poly(vinyl acetate) dispersion adhesive, J. Appl. Polym. Sci. 129 (2013) 1157–1169, https://doi.org/10.1002/app.38805.

[7] P.F. Vera Garcia, L.A. Guerrero Dimas, J.J. Cedillo Portillo, O.A. Martínez Anguiano, A. Sáenz Galindo, R.I. Narro Cespedes, P. Acuña Vazquez, A. Castañeda Facio, PVA Blends and Nanocomposites, Properties and Applications: A Review, in: F. Avalos Belmontes, F.J. González, M.Á. López-Manchado (Eds.), Green-Based Nanocomposite Mater. Appl., Springer International Publishing, Cham, 2023, pp. 191–206, https://doi.org/10.1007/978-3-031-18428-4_10.

[8] M. Nakamae, K. Yuki, T. Sato, H. Maruyama, Preparation of polymer emulsions using a poly(vinyl alcohol) as protective colloid, Colloids Surf. Physicochem. Eng. Asp. 153 (1999) 367–372, https://doi.org/10.1016/S0927-7757(98)00458-0.

[9] J.L. Keddie, Fundamentals of latex film formation: processes and properties, Springer, Dordrecht; New York, 2010.

[10] H.R. Hedayati, M. Khorasani, M. Ahmadi, N. Ballard, Preparation of well-defined Poly(Vinyl alcohol) by hydrolysis of Poly(Vinyl acetate) synthesized by RAFT suspension polymerization, Polymer 246 (2022) 124674, https://doi.org/10.1016/j.polymer.2022.124674.

[11] T. Uragami, K. Okazaki, H. Matsugi, T. Miyata, Structure and Permeation Characteristics of an Aqueous Ethanol Solution of Organic–Inorganic Hybrid Membranes Composed of Poly(vinyl alcohol) and Tetraethoxysilane, Macromolecules 35 (2002) 9156–9163, https://doi.org/10.1021/ma020850u.

[12] M. Krumova, D. López, R. Benavente, C. Mijangos, J.M. Pereña, Effect of crosslinking on the mechanical and thermal properties of poly(vinyl alcohol), Polymer 41 (2000) 9265–9272, https://doi.org/10.1016/S0032-3861(00)00287-1.

[13] M. Lim, H. Kwon, D. Kim, J. Seo, H. Han, S.B. Khan, Highly-enhanced water resistant and oxygen barrier properties of cross-linked poly(vinyl alcohol) hybrid films for packaging applications, Prog. Org. Coat. 85 (2015) 68–75, https://doi.org/10.1016/j.porgcoat.2015.03.005.

[14] A. Salvini, L.M. Saija, S. Finocchiaro, G. Gianni, C. Giannelli, G. Tondi, A new methodology in the study of PVAc-based adhesive formulations, J. Appl. Polym. Sci. 114 (2009) 3841–3854, https://doi.org/10.1002/app.31032.

[15] P.A. Steward, J. Hearn, M.C. Wilkinson, An overview of polymer latex film formation and properties, Adv. Colloid Interface Sci. 86 (2000) 195–267, https://doi.org/10.1016/S0001-8686(99)00037-8.

[16] F. Chiozza, B. Pizzo, Innovation in poly(vinyl acetate) water resistant D3 glues used in wood industry, Int. J. Adhes. Adhes. 70 (2016) 102–109, https://doi.org/10.1016/j.ijadhadh.2016.06.003.

[17] Z. Wang, B. Gao, Preparation, structure, and catalytic activity of aluminum chloride immobilized on cross-linked polyvinyl alcohol microspheres, J. Mol. Catal. Chem. 330 (2010) 35–40, https://doi.org/10.1016/j.molcata.2010.06.028.

[18] B. Yuan, C. Bao, Y. Guo, L. Song, K.M. Liew, Y. Hu, Preparation and Characterization of Flame-Retardant Aluminum Hypophosphite/Poly(Vinyl Alcohol) Composite, Ind. Eng. Chem. Res. 51 (2012) 14065–14075, https://doi.org/10.1021/ie301650f.

[19] F. Wang, Y. Wen, T. Bai, Thermal behavior of polyvinyl alcohol–gellan gum–Al3+ composite hydrogels with improved network structure and mechanical property, J. Therm. Anal. Calorim. 127 (2017) 2447–2457, https://doi.org/10.1007/s10973-016-5757-3.

[20] J.E. Mark, Physical Properties of Polymers Handbook, 2nd Edition, Springer-Verlag, New York, NY, 2007.

[21] K. Balani, V. Verma, A. Agarwal, R. Narayan, Physical, Thermal, and Mechanical Properties of Polymers, in: Biosurfaces Mater. Sci. Eng. Perspect., 1st ed., Wiley, 2014 https://doi.org/10.1002/9781118950623.

[22] D.I. Bower, W.F. Maddams, The vibrational spectroscopy of polymers, Cambridge University Press, Cambridge [Cambridgeshire] ; New York, 1992, 1st pbk. ed.

[23] M. Hdidar, S. Chouikhi, A. Fattoum, M. Arous, Effect of hydrolysis degree and mass molecular weight on the structure and properties of PVA films, Ionics 23 (2017) 3125–3135, https://doi.org/10.1007/s11581-017-2103-0.

[24] M.R. Derrick, D.C. Stulik, J.M. Landry, Infrared spectroscopy in conservation science, Getty Conservation Institute, Los Angeles, 1999.

[25] N. Bensemra, H. Tran Van, A. Guyot, M. Gay, L. Carette, Thermal dehydrochlorination and stabilization of poly(vinylchloride) in solution: Part IV—Synergistic effects of β-diketone compounds and metal soap stabilizers, Polym. Degrad. Stab. 24 (1989) 89–111, https://doi.org/10.1016/0141-3910(89)90105-5.

[26] C.M. Popescu, M.C. Popescu, G. Singurel, C. Vasile, D.S. Argyropoulos, S. Willfor, Spectral Characterization of Eucalyptus Wood, Appl. Spectrosc. 61 (2007) 1168–1177, https://doi.org/10.1366/000370207782597076.

[27] E. Bubev, A. Georgiev, M. Machkova, ATR-FTIR spectroscopy study of the photodegradation protective properties of BP-4 and 4HBP in polyvinyl acetate thin

films, J. Mol. Struct. 1118 (2016) 184–193, https://doi.org/10.1016/j.molstruc.2016.04.013.

[28] G.E. McManis, L.E. Gast, IR spectra of long chain vinyl derivatives, J. Am. Oil Chem. Soc. 48 (1971) 668–673, https://doi.org/10.1007/BF02638515.

[29] H. Houjeij, Experimental study on the Capture/Desorption of gaseous iodine (I2, CH3I) on environmental aerosols, Université de Bordeaux, 2020.

[30] V. Koleva, Vibrational Behavior of Calcium Hydrogen Triacetate Monohydrate, CaH(CH3COO)3 H2O, Croat. Chem. Acta 78 (2005) 581–591.

[31] S. Wei, V. Pintus, M. Schreiner, Photochemical degradation study of polyvinyl acetate paints used in artworks by Py–GC/MS, J. Anal. Appl. Pyrolysis 97 (2012) 158–163, https://doi.org/10.1016/j.jaap.2012.05.004.

[32] S. França De Sá, C. Viana, J.L. Ferreira, Tracing Poly(Vinyl Acetate) Emulsions by Infrared and Raman Spectroscopies: Identification of Spectral Markers, Polymers 13 (2021) 3609, https://doi.org/10.3390/polym13213609.

[33] H.E. Assender, A.H. Windle, Crystallinity in poly(vinyl alcohol). 1. An X-ray diffraction study of atactic PVOH, Polymer 39 (1998) 4295–4302, https://doi.org/10.1016/S0032-3861(97)10296-8.

[34] M.L. Cerrada, R. Benavente, E. Pérez, J.M. Pereña, The effect of annealing on the structure and relaxation processes of vinyl alcohol–ethylene copolymers, J. Polym. Sci. Part B Polym. Phys. 39 (2001) 1–12, https://doi.org/10.1002/1099-0488(20010101)39:1<1::AID-POLB10>3.0.CO;2-4.

[35] Å. Nyflött, Ç. Meriçer, M. Minelli, E. Moons, L. Järnström, M. Lestelius, M. G. Baschetti, The influence of moisture content on the polymer structure of polyvinyl alcohol in dispersion barrier coatings and its effect on the mass transport of oxygen, J. Coat. Technol. Res. 14 (2017) 1345–1355, https://doi.org/10.1007/s11998-017-9937-2.

[36] R.R. Khasbiullin, Yu.V. Kostina, T.F. Petrova, G.N. Bondarenko, A.E. Chalykh, V. F. Chuvaev, V.K. Gerasimov, Residual water in polyvinyl alcohol, Polym. Sci. Ser. A 56 (2014) 569–578, https://doi.org/10.1134/S0965545×14050095.

[37] M.J.D. Nugent, A. Hanley, P.T. Tomkins, C.L. Higginbotham, Investigation of a novel freeze-thaw process for the production of drug delivery hydrogels, J. Mater. Sci. Mater. Med. 16 (2005) 1149–1158, https://doi.org/10.1007/s10856-005-4722-7.

[38] B.J. Holland, J.N. Hay, The thermal degradation of poly(vinyl alcohol), Polymer 42 (2001) 6775–6783, https://doi.org/10.1016/S0032-3861(01)00166-5.

[39] M.Z. Gavrilov, R.N. Sviridova, I.N. Ermolenko, Spectroscopic investigation of the thermal conversion of catalytically dehydrated polyvinyl alcohol, J. Appl. Spectrosc. 44 (1986) 272–275.

[40] B. Stuart, Infrared spectroscopy: fundamentals and applications, J. Wiley, Chichester, West Sussex, England ; Hoboken, NJ, 2004.

[41] B.D. Mistry, A Handbook of spectroscopic data chemistry (UV, IR, PMR, 13CNMR and mass spectroscopy), 1st ed, Oxford Book Co., Jaipur, 2009.

[42] J. Yu, L. Sun, C. Ma, Y. Qiao, H. Yao, Thermal degradation of PVC: A review, Waste Manag 48 (2016) 300–314, https://doi.org/10.1016/j.wasman.2015.11.041.

[43] A.F. Halasa, J.M. Massie, R.J. Ceresa, The Chemical Modification of Polymers, Sci. Technol. Rubber (2013) 517–546, https://doi.org/10.1016/B978-0-12-394584-6.00011-X.

[44] C. Hoffendahl, G. Fontaine, S. Duquesne, F. Taschner, M. Mezger, S. Bourbigot, The fire retardant mechanism of ethylene vinyl acetate elastomer (EVM) containing aluminium trihydroxide and melamine phosphate, RSC Adv 4 (2014) 20185–20199, https://doi.org/10.1039/C4RA01111B.