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ARTICLE

Polyvinyl Alcohol Modification with Sustainable Ketones

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A series of polyvinyl ketals was synthesized by the condensation of commercially available polyvinyl alcohol (PVA) and biobased ketones, raspberry ketone, zingerone, D-dihydrocarvone, and levulinic acid, as well as acetone, butanone, 3-pentanone, cyclopentanone, cyclohexanone, 3,3,5-trimethylcyclohexanone, along with the aldehyde furfural. Ketalization was confirmed and measured by ^{1}H NMR, ranging from 15.3 to 69.2%. The number average molecular weights of the polyvinyl ketals ranged from 24,400 to 41,100 Da, according to the mass added by ketalization. The glass transition temperature (T_g) of PVA, 75 °C, increased through ketalization, reaching 78°C to 127°C or through acetalization with furfural, reaching 138°C. Kinetic studies of polyvinyl acetone ketal (**PV-A-K**) formation showed the ketalization reaction neared equilibrium (69% ketalization) in 4 hours at 40 °C. During room temperature heterogeneous degradation studies, **PV-A-K** completely hydrolyzed in 1 day at pH = 2 or in 3 months at pH = 5; after 2 years in deionized water or seawater, ketalization diminished from 69% to 66% (3% hydrolysis). At 80 °C over 3 months, **PV-A-K** ketalization diminished to 5% (95% hydrolysis) in deionized water and to 1% (99% hydrolysis) in seawater. These studies suggest that polyvinyl ketals are suitable candidates for water-degradable packaging materials.

Introduction

Currently, about 400 billion kg of plastics are synthesized per year, but only 9% are recycled properly. Shockingly, over 8 billion kg of these plastics are discarded into the oceans annually.[1] Furthermore, most plastics are fossil fuel-based and require centuries to degrade in a landfill or marine environment.[2,3] Various microplastics have been detected worldwide, harming marine habitats.[4] Because of concerns about plastic waste, depletion of fossil fuels, and the effects on animal and human health,[5] an inexpensive, sustainable, and degradable polymer is needed to address these weighty issues.

Polyvinyl alcohol (PVA) is a commercial polymer used in a variety of industrial settings such as transparent packaging, display panel film, medical devices, fibers, and agricultural materials, demanding over 1 billion kg of annual production.[6] PVA is manufactured by polymerization of vinyl acetate, followed by base-catalyzed alcoholysis with ethanol.[7] Although vinyl acetate is currently synthesized from ethylene or acetylene,[8] recent work has demonstrated its sustainable production from bioethanol.[9] Compared to most other synthetic plastics, PVA is more inclined to biodegrade, although only via a limited number of microorganisms.[10,11] PVA has additional attractive attributes, including hydrophilicity, non-toxicity,[12] biocompatibility,[13] and affordability (as low as 1.38 USD per kilogram).[14]

For different applications, PVA's structure has been chemically modified in several ways including crosslinking for hydrogel wound dressings[15] and backbone phosphorylation for flame retardants.[16] An important modification, discovered in the 1920s, is PVA acetalization via condensation with formaldehyde or butyraldehyde, forming polyvinyl formal (PVF) or polyvinyl butyral (PVB).[17,18] PVF, with trade names Formvar® and Vinylec®,[19] is used in electron microscopy support film and wire insulation coatings.[20,21] PVB has the greatest demand in the world market among PVA derivatives, with trade names Butvar®,[22] Butacite®, Winlite®, and Saflex®.[23] PVB is commonly used as the optically-transparent, sound-dampening interlayer of safety glass.[24]

However, a notable drawback of PVF and PVB is their sensitivity to acidic environments, which releases the hydrolysis by-products formaldehyde and butyraldehyde.[25,26] Formaldehyde is water-soluble and fairly toxic to humans,[27] causing nasopharynx cancer and leukaemia. Other health complications from formaldehyde include menstrual disorders and infertility in women.[28,29,30] Consequently, commercial production of PVF is rapidly decreasing. Butyraldehyde can cause irritation to the skin, eyes, and respiratory system and has a slight genotoxicity.[31] Nonetheless, PVB demand is increasing.

A limiting thermal property of commercial PVB is its relatively low glass transition temperature of 62 to 78 °C.[32] This T_g range is suitable for current applications, but higher T_g values are needed to supplant incumbent packaging plastics.[33] T_g is easily reduced by adding plasticizers, thereby increasing a material's flexibility, workability, or distensibility. However, the T_g of PVB cannot be increased with additives,[34] although it would be advantageous to have polyvinyl acetals with higher T_g values, matching those of high-temperature packaging materials such as polystyrene (95 °C).

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To address this goal, our group reported sustainable polyvinyl acetals from bioaromatic aldehydes in 2017.[35] Some naturally occurring aromatic aldehydes are non-toxic or even food grade compounds, such as vanillin. The degree of acetalization ranged from 54 to 75% and the bulky aromatics were shown to markedly increase T_g values up to 157 °C, likely by increasing conformational barriers and pendent group polarity. The general reaction scheme for polyvinyl aromatic acetals is shown in Fig. 1. Beyond polyvinyl acetals, polyvinyl ketals (from ketones) are minimally explored and currently have no commercial presence. In 1987, Nakamura reported a polyvinyl acetone ketal synthesis method[36] and later applied his procedure to a series of aliphatic and aromatic ketones.[37,38] However, critical thermal properties, such as heat stability and glass transition temperature, were not reported.

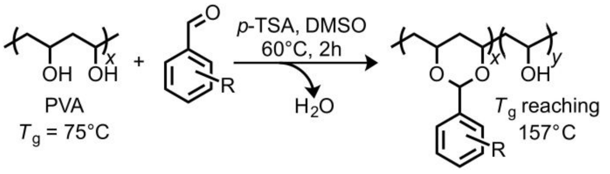


Fig. 1. The acetalization of polyvinyl alcohol (PVA) with bioaromatic aldehydes yields polyvinyl aromatic acetals with degrees of acetalization ranging from 54 to 75% and T_g values ranging from 114 to 157 °C.35

Herein, we describe a series of polyvinyl ketals, synthesized from PVA and ketones under mild conditions. Several ketones are biobased and/or non-toxic. Polymeric thermal properties were controlled and correlated to ketone and polymer structure. Additionally, several examples were formed into optically transparent films. Heterogeneous hydrolysis studies were conducted in aqueous media with varying pH at room temperature and at 80 °C, revealing promising degradation behavior for this class of polymers.

Experimental

Materials

Polyvinyl alcohol with a reported molecular weight range of 13,000 to 23,000 Da (measured to be M_n = 22,300 Da by GPC in HFIP) and 98% hydrolyzed (Sigma-Aldrich) and polyvinyl alcohol with a reported molecular weight range of 146,000 to 186,000 Da (assumed to have M_n = 166,000 Da, in the middle of this range) and 99+% hydrolyzed (Sigma-Aldrich) were ground before use. Dimethyl sulfoxide (DMSO) ≥99.9% (Sigma-Aldrich), *p*-toluenesulfonic acid monohydrate (*p*-TSA) ≥98% (Sigma-Aldrich), aqueous hydrochloric acid 36.5 to 38% w/w (Fisher), acetone ≥99.5% (Fisher), butanone ≥99% (Fisher), 3-pentanone 99% (Alfa Aesar), cyclopentanone ≥99% (Alfa Aesar), cyclohexanone ≥99% (Alfa Aesar), furfural 99% (Sigma-Aldrich), isophorone 98% (Alfa Aesar), raspberry ketone (Bulk Supplements), zingerone ≥96% (Sigma-Aldrich), D-dihydrocarvone (Fisher, mixture of isomers 97%), L-menthone (Alfa Aesar, mixture of isomers 96%), diacetone alcohol 99%, (±)-camphor ≥95% (Sigma-Aldrich), 3,3,5-trimethylcyclohexanone 97% (Acros Organics), sodium hydroxide 99% (Fisher), anhydrous magnesium sulfate (Fisher), molecular sieves grade 562 (Fisher), tetrahydrofuran ≥99.9% (Fisher, HPLC grade), chloroform ≥99.9% (Fisher), ethanol 95%, ethanol 100% (Decon Labs), and Butvar® B-79 (MuseuM Services Corporation) were purchased and used without further purification. The buffer solution pH 2, buffer solution pH 3 (VWR), and buffer solution pH 5 (Fisher) were purchased and used directly. Seawater was collected from Siesta Key, FL, USA. The NMR solvent, deuterated dimethyl sulfoxide (DMSO-d_6, Cambridge Isotope Laboratories), was stored in a desiccator with activated 4 Å molecular sieves (Sigma-Aldrich).

Polyvinyl Ketal synthesis

A condensation reaction was performed with 14 different ketones (and one aldehyde) and polyvinyl alcohol (PVA, 98% hydrolyzed and M_n = 22,300). The general reaction scheme is shown in Fig. 2. Additionally, acetone was condensed with a higher molecular weight PVA (99+% hydrolyzed and M_n = 166,000). From these condensation reactions, 11 polyvinyl ketals and one polyvinyl acetal were successfully produced. A general synthetic protocol devised for polyvinyl acetone ketal (**PV-A-K**) is described below; other specific methods are provided in the Electronic Supplementary Information (ESI).

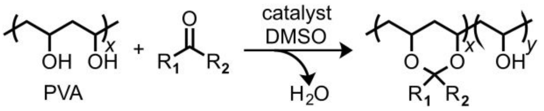


Fig. 2. The general reaction scheme of polyvinyl alcohol ketalization with a ketone (R_1 = alkyl or aryl; R_2 = alkyl or aryl) or acetalization with an aldehyde (R_1 = alkyl or aryl; R_2 = H).

Synthesis of polyvinyl acetone ketal PV-A-K. First, 4.00 g (90.9 mmol) pre-ground PVA, 0.350 g (1.8 mmol) *p*-TSA, 80 mL DMSO, and a stir bar were added to a 500 mL round bottom flask (RBF), which was attached to a condenser. Then, 0.5 g anhydrous magnesium sulfate was wrapped in filter paper and placed at the neck of the condenser. The RBF was lowered into a hot oil bath. At 60°C, PVA and *p*-TSA completely dissolved in the DMSO solvent. Once PVA and *p*-TSA were dissolved, the RBF was charged with 242 mL acetone (3270 mmol, 36 equivalents per PVA hydroxy group) and the temperature was lowered to 40 °C. For 4 hours, the system remained homogeneous. Next, the reaction was cooled and terminated through neutralization with 1 M NaOH. The homogeneous solution was poured into 500 mL deionized (DI) water causing the product to precipitate as a white solid. The polymer was collected, washed with DI water, and then placed on a watch glass in a fume hood to dry overnight, yielding 4.73 g of product. A small piece was cut and dried further via thermogravimetric analysis (TGA) at 100 °C for 20 minutes. 86.5% of the product weight remained after drying with TGA. Assuming a 13.5% water content of the bulk product, the adjusted isolated yield was calculated to be 49.5%. The **PV-A-K** product was suitably pure and not subjected to subsequent purification. For some polymers, a purification procedure was necessary to remove minor peaks in the ^{1}H NMR spectrum and this protocol is described below for polyvinyl 3,3,5-trimethylcyclohexanone ketal **PV-TM-K**. ^{1}H NMR analysis was conducted for **PV-A-K**. ^{1}H NMR (DMSO-d_6) δ ppm 4.15-4.7 (-O**H**, m, 1.00 H), 3.5-4.15 (-C**H**OR, m, 3.25 H) and 0.8-1.9 (-CH$_2$-, -CH$_3$, m, 13.77 H). The peak at 1.9-2.0 ppm is attributed to the unhydrolyzed acetate methyl group. Additionally, the small peak at 4.9-5.2 ppm is attributed to the main-chain methine proton proximal to the unhydrolyzed acetate group. ^{13}C NMR δ ppm 169.8, 107.0, 99.6, 97.8, 67.9, 65.6, 64.8, 63.3, 62.9, 45.0, 44.5, 43.8, 41.76, 39.5, 38.8, 37.2, 30.3, 30.2, 26.0, 24.6, 21.0, and 19.9. The small peaks at 21.0, 67.9, and 169.8 ppm are attributed to methine, methyl, and carbonyl carbons associated with the unhydrolyzed acetate group.

Purification of PV-TM-K. First, 0.243 g of crude **PV-TM-K** was removed from 3.113 g of crude product and then dissolved in 5 mL DMSO. Once dissolved, the DMSO solution was poured into 20 mL of DI water causing the white, pure product to precipitate. Solids were collected and dried overnight; 0.152 g of **PV-TM-K** were obtained.

Characterization

All NMR samples were prepared in DMSO-d_6 and spectra were recorded on a Bruker 600 MHz or Inova 500 MHz spectrometer. The analysis included 1D experiments such as proton and carbon nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR), and 2D experiments including gradient Heteronuclear Single Quantum Correlation (*g*HSQC), gradient Heteronuclear Multiple-Bond Correlation (*g*HMBC), and COrrelated SpectroscopY (COSY). Because of the short transverse relaxation time T_2 of PVA and polyvinyl ketals, ^{1}H NMR signals displayed broad peaks. Therefore, the peaks were reported in ranges in parts per million (ppm).

Thermal properties were measured by thermogravimetric analysis (TGA, Q5000, TA Instruments) and differential scanning calorimetry (DSC, Q1000, TA Instruments). The thermal stability was assessed by TGA using a 2-10 mg sample heated from 25 to 600 °C with a gradient of 20 °C min^{-1} under a nitrogen flow rate of 25 mL/min. The decomposition temperature T_{95} was the temperature at which 5% of the mass was lost. The glass transition temperature (T_g) was measured by DSC. 2-10 mg samples were sealed in an aluminium pan. The measurement program was set to a heat and cool cycle with a gradient of 10 °C min^{-1} under a helium flow rate of 25 mL/min. The temperature range was typically from 20 to 220 °C.

Gel permeation chromatography (GPC) was performed using an Agilent Technologies 1260 Infinity Series liquid chromatography system with an internal differential refractive index detector, and two Waters Styragel HR-5E columns (7.8 mm i.d., 300 mm length, guard column 7.8 mm i.d., 25 mm length) at a flow rate of 1.0 mL/min, using narrow molecular weight polystyrene standards and THF as the solvent. Additional GPC analysis was performed with the same kind of instrument equipped with one Agilent HFIPgel guard column (PL HFIPgel Guard, 50 x 4.6 mm, 9 µm) and two Agilent HFIPgel HPLC columns (PL1514-5900HFIP, 4.6 × 250 mm, 9 µm). Experiments were conducted at 40°C using a 20 mM solution of sodium trifluoroacetate (CF$_3$COONa) dissolved in HPLC grade hexafluoroisopropanol (HFIP) as the mobile phase at a flow rate of 0.300 mL/min. Column calibration was performed with narrow-dispersity poly(methyl methacrylate) (PMMA) standards.

Kinetic studies

For the kinetic study, 3.00 g (68.2 mmol) pre-ground PVA, 0.230 g (1.2 mmol) *p*-TSA, 60 mL DMSO, and a stir bar were added to a 500 mL three-neck RBF. This was then heated to 60 °C in a hot oil bath to dissolve the PVA and *p*-TSA. One neck of the RBF was attached to a condenser containing a MgSO$_4$ bag as a drying agent, while the other two necks were sealed by rubber septa. Once the PVA and *p*-TSA were dissolved, the system was cooled to 40 °C and then charged with 180 mL acetone, ensuring the system remained homogeneous. At initial 15-minute intervals (T = 15, 30, 45, 60, 75, 90, 105, 120, 135, 150, 165, and 180 minutes) and increasing intervals thereafter (T = 240, 360, 480, and 1440 minutes), 10 mL aliquots were removed by syringe and then neutralized with 0.1 mL 1 M aqueous NaOH. Precipitation from these aliquots was encouraged by adding 30 mL ethyl acetate for those taken at T = 15 and 30 minutes and DI water for the remaining aliquots. The products were isolated by filtration and placed on watch glasses in a fume hood for overnight drying. The ketalization degree was then determined by ^{1}H NMR in DMSO-d_6.

Hydrolysis experiments

Two hydrolysis studies were performed: a long-term (room temperature) hydrolysis study and an accelerated (heated) hydrolysis study.

Room temperature hydrolysis study. 10 mL of pH 2, 3, and 5 aqueous buffers, DI water, and seawater were placed into five different 20 mL glass vials, along with 10 mg of **PV-A-K**. The vials were capped and placed on an orbital shaker set to 100 rpm at room temperature. At certain time intervals (T = 3 hours, 24 hours, 1 week, 2 weeks, 1 month, 2 months, 3 months, 6 months, 1 year, and two years), photographs were taken, aliquots were neutralized by 1 M aqueous NaOH, and the isolated polymers were analyzed by ^{1}H NMR (see the ESI).

Heated hydrolysis study. 10 mg **PV-A-K** samples were placed into two 20 mL glass vials charged with 10 mL DI water and seawater, respectively. The glass vials were capped and heated to 80 °C. At certain time intervals (T = 1 week, 1 month, and 3 months), photographs were taken, aliquots were neutralized by 1 M aqueous NaOH, and the isolated polymers were analyzed by ^{1}H NMR (see the ESI).

Film Preparation

First, 0.2 g **PV-A-K** were dissolved in 1.5 mL 75% aqueous ethanol inside a sealed glass vial at 60 °C. Once dissolved, the **PV-A-K** solution was pipetted and transferred onto a watch glass, which was placed in a fume hood overnight for solvent evaporation. The next day, the **PV-A-K** film was peeled away via spatula and photographs were taken. Films of **PV-TM-K**, **PV-CH-K**, **PV-LA-K**, **PV-RK-K**, and commercial Butvar® were prepared similarly, but with chloroform instead of 75% ethanol. Additionally, a PVA film was made with this method, but with a dissolution temperature of 80 °C in deionized water.

Results and discussion

Ketones and bioketones employed

Fig. 3 describes ten bioketones, four fossil fuel-based ketones, and one bioaldehyde investigated for attachment to polyvinyl alcohol (PVA). The model ketone for this experiment was acetone, most of which is produced commercially through the cumene process.[39] However, a sustainable production of acetone (**A**) has been demonstrated through bacteriological sugar fermentation.[40] Diacetone alcohol (**DA**)[41] and isophorone (**IP**)[42] are prepared from acetone using base catalysis. The hydrogenation of isophorone yields 3,3,5-trimethylcyclohexanone (**TM**).[43] L-menthone (**MT**) is produced through distillation of peppermint essential oil.[44] Raspberry ketone (**RK**) and zingerone (**ZG**) have low natural abundance but can be prepared through aldol condensation of 4-hydroxybenzaldehyde or vanillin with acetone and subsequent hydrogenation.[45,46] D-dihydrocarvone (**DC**) can be made via enantioselective reduction of the oil extracted from caraway seeds.[47] A complex reaction of sugars in an acidic aqueous environment yields levulinic acid (**LA**)[48] and furfural (**F**), the sole aldehyde used in these experiments.[49] Camphor (**CF**) has been derived from the camphor laurel tree, but present commercial production is from α-pinene.[50] The four fossil fuel ketones, butanone (**B**), 3-pentanone (**P**), cyclopentanone (**CP**), and cyclohexanone (**CH**), are aliphatic ketones commonly used as industrial solvents.[51]

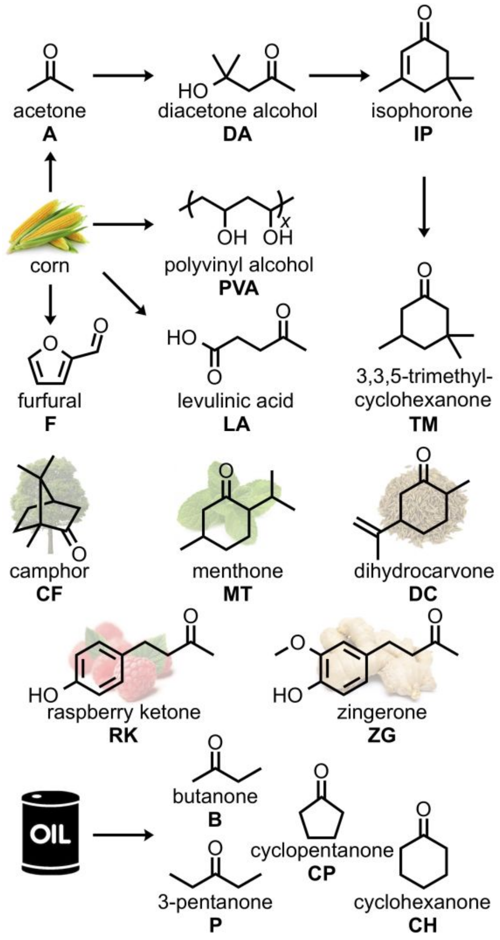


Fig. 3. The sources of 14 ketones and one aldehyde investigated for attachment to polyvinyl alcohol (PVA). **A**, **DA**, **IP**, **LA**, **TM**, **CF**, **MT**, **DC**, **RK**, and **ZG** are biobased or potentially biobased, while **B**, **P**, **CP**, and **CH** are prepared from fossil fuels. **F** is a biobased aldehyde.

Ketalization optimization

Catalysts *p*-TSA and HCl. In a prior report, *p*-TSA was employed as an acid catalyst for PVA acetalization/ketalization with several aldehydes and ketones.[52] Presently, *p*-TSA proved effective for ketalization with acetone, butanone, 3-pentanone, cyclopentanone, cyclohexanone, raspberry ketone, zingerone, levulinic acid, and furfural (Table 1, Entries 1–8, 11). However, for D-dihydrocarvone, 3,3,5-trimethylcyclohexanone, isophorone, camphor, and L-menthone, ketalization was not observed with normal or increased doses of *p*-TSA (Table 1, Entries 9, 10, 12–15). An alternative catalyst, HCl, proved to be an effective catalyst for PVA ketalization with D-dihydrocarvone and 3,3,5-trimethylcyclohexanone (Table 1, Entries 9, 10). Perhaps the greater acidity of HCl vs. *p*-TSA results in a greater concentration of activated ketone and hence, a faster ketalization reaction.

Stoichiometry. Differences in ketalization degrees were explored by varying the ketone equivalents employed vs. –OH groups of PVA. Higher ketone equivalents generally led to higher degrees of ketalization, likely because of mass action (Le Chatelier's principle). For example, increasing acetone equivalents of 5, 25, 30, and 36 led to ketalization degrees of 43.5, 60.8, 63.1, and 69.2%, respectively (see Table S2).

Drying agents. To achieve high degrees of ketalization, drying agents were applied to either the starting materials and/or during the reaction to remove water. Prior to the experiment, molecular sieves were placed in DMSO overnight to capture residual water. As described in the experimental section, $MgSO_4$ was situated near the reflux condenser to scavenge evolved water and drive the ketalization forward. This drying agent was shown to improve the ketalization degree by about 4% for **PV-A-K** (see Table S3); therefore, it was adopted as part of the standard ketalization protocol.

Kinetic studies

In a prior study, the kinetics of PVA ketalization with acetone were analyzed by chemical functionalization with iodoform.[36] Herein, the kinetic analysis was performed by ^1H NMR with a greater density of data points over time. The reaction was conducted at 40 °C with *p*-TSA catalyst and an [acetone]:[PVA-OH] ratio of 30:1. Aliquots were extracted periodically and the ketalization degree was determined by integration of PVA hydroxy vs. backbone methine ^1H NMR resonances. As shown by Fig. 4 (and Table S4), ketalization to 53.1% was rapid within the first hour, neared equilibrium in about four hours (67.4%), and attained a final value of 68.2% after 24 hours.

Ketalization of PVA

Table 1 compiles reaction and polymer characterization data, including: the fourteen ketones and one aldehyde reacted with PVA; catalyst; isolated yield; ketalization degree; polymer glass transition temperature (T_g); polymer decomposition temperature for 5% mass loss (T_{95}); and number average molecular weight, M_n, assuming no PVA chain scission and an increase of polymer mass corresponding to the degree of ketalization determined by ^{1}H NMR.

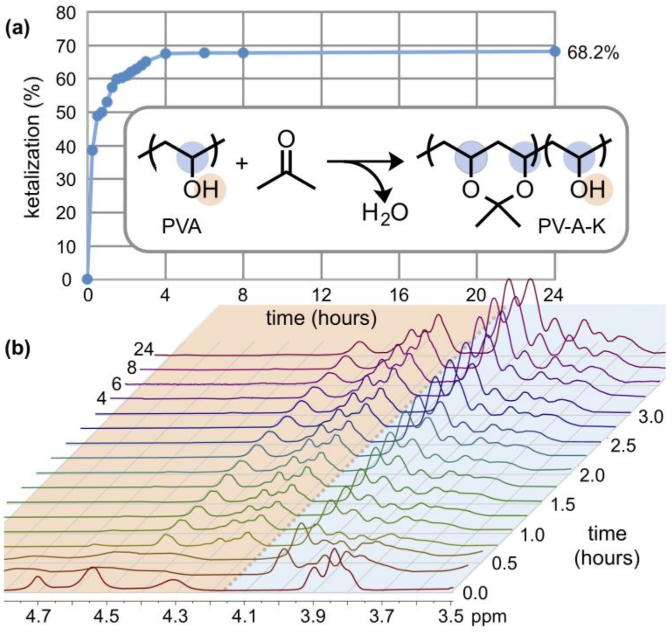


Fig. 4. The kinetic study of PVA ketalization with acetone at 40 °C measured by ^{1}H NMR: (a) **PV-A-K** ketalization degree versus time over 24 hours; (b) ^{1}H NMR spectra cascade for the hydroxy region (4.15–5.00 ppm; orange) vs. the methine region (3.50–4.15 ppm; blue) every 0.25 hours for the first 3 hours, followed by 4, 6, 8, and 24 hours.

As the kinetic study suggested, the ketalization with acetone essentially reached equilibrium after 4 hours at 40 °C and the change was thereafter miniscule. Hence, the ketalization reaction times were 24 hours or less. To ensure homogeneity for even the least soluble ketones (**LA**, **DC**, and **TM**), a uniform ketalization temperature of 60 °C was selected. Higher temperatures, such as 100 °C, led to unexpected side reactions giving yellowish products (see Table S5). Furthermore, ketalization was found to be lower at higher temperatures since the reaction is an exothermic process.[53] This was demonstrated by the reaction of PVA with 3-pentanone: the ketalization degree was 21.9% at 40°C, but only 13.8% at 100 °C.

The ketalization reactions were terminated by neutralizing the acid catalyst, *p*-TSA or HCl, with 1 M aqueous sodium hydroxide solution. The ketal functional groups present are stable to water under these basic conditions. A purification process was generally necessary since the crude product contained precipitated polymer, unreacted ketone, and catalyst. These impurities significantly impact the thermal properties of the ketalized polymer, rendering the purification process of high importance.

The number average molecular weight (M_n) and dispersity ($Đ$) of **PV-A-K**, polyvinyl cyclopentanone ketal (**PV-CP-K**) and polyvinyl cyclohexanone ketal (**PV-CH-A**) were determined by gel permeation chromatography (GPC) since they were soluble in tetrahydrofuran (Table 1, Entries 1, 7, and 8). These polyvinyl ketal molecular weights ranged from 27,400 to 31,900, higher than the 22,300 value measured for PVA itself (by GPC in HFIP)—as expected since mass is added by ketalization. Dispersities ranged from $Đ$ = 1.88 to 2.32 and were near that of PVA, $Đ$ = 2.05. The other polyvinyl ketals had low solubility in THF and were unsuitable for this GPC analysis. Instead, polyvinyl ketal M_n was calculated from the M_n of PVA (22,300), augmented by the ketalization degree for each polymer, according to the following equation:

$$M_n = \left\{ \frac{\left[FW\text{vinyl alcohol} + \frac{1}{2}FW\text{ketone} - \frac{1}{2}FW\text{water}\right] \times \text{ketal\%}}{(FW\text{vinyl alcohol})} + (1 - \text{ketal\%}) \right\} \times (M_n \text{ of PVA})$$

Polymer characterization by NMR

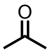
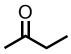
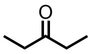
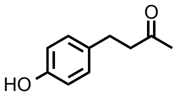
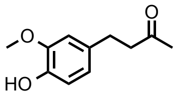
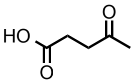
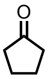
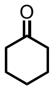
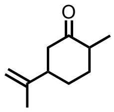
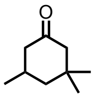
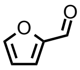
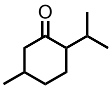
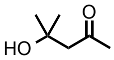
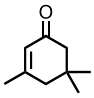
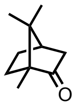
NMR was employed to investigate the structures of polyvinyl ketals and **PV-A-K** was chosen as the primary model. Since the **PV-A-K** ^{1}H NMR peaks overlapped significantly, ^{13}C and 2D NMR helped to elucidate the ^{1}H NMR assignment. The ^{13}C NMR spectra showed multiple peaks for **PV-A-K** because of main-chain tacticity and diastereotopic methyl groups. The resonances near 98 ppm were assigned to ketal carbons and confirmed ketalization.[54] ^{1}H-^{13}C gHSQC and gHMBC correlated protons and carbons, while ^{1}H-^{1}H COSY provided detailed proton coupling information. Thus, all peaks could be assigned in the ^{1}H NMR spectra, allowing ketalization quantification by comparing the integration values of the unreacted PVA hydroxy hydrogens (-CH(O**H**), 4.15–4.7 ppm) and the methine hydrogens of the main-chain (-C**H**(OR), 3.50–4.15 ppm). The unfunctionalized PVA –[CH$_2$CHOH]– repeat unit has one hydroxy hydrogen and one methine hydrogen. Two PVA repeat units can lose two hydroxy hydrogens to form a cyclic ketal by reacting with one ketone. Hence, the ketalization degree equates to {[-C**H**(OR)] – [-CH(O**H**)]} / [-C**H**(OR)], generally. Ketalization degrees with zingernone (Table 1, Entry 5) and levulinic acid (Table 1, Entry 6) were calculated with alternative methods because of overlapping ^{1}H NMR peaks (see the ESI). Note that esterification of levulinic acid was not detected under these conditions; esterification of PVA typically employs basic catalysts, [55] or more reactive reagents, such as acid anhydrides[56] or acid halides.[57] For polyvinyl furfural acetal (Table 1, Entry 11), the acetalization degree equates to 4 times the quotient [acetal–**H**]/[total –**CH**$_2$–].[35]

Degree of ketalization

For irreversible ketalization, the maximum ketalization degree of PVA is 86.5%;[58] the remaining 13.5% would be stranded hydroxy groups lacking an adjacent partner for ketalization. However, this reaction is reversible and the limit of 86.5% can be exceeded, as demonstrated in commercial PVF with 90% acetalization and PVB (Butvar® B-76 and B-79) with 88% acetalization.[59,60]

Herein, the ketalization of PVA ranged from 15.3 to 69.2%, and there were three major factors that controlled this value: the extent of by-product water removal; the stoichiometric ratio of ketone:PVA; and steric hindrance. First, since the ketalization reaction is reversible, the presence of water as a by-product suppresses the ketalization. Second, an excess of ketone to PVA should push the equilibrium to the product side, increasing the degree of ketalization. This effect was demonstrated for the aldehyde furfural; increasing the [furfural]:[PVA-OH] ratio from 2:1 to 10:1 increased the acetalization degree from 67.7 to 83.2% (see Table S2). Third, bulky ketones suppress the thermodynamic

Table 1. Ketalization (acetalization) of polyvinyl alcohol (PVA) with fourteen ketones (and one aldehyde).[a] Characterization data are provided for the corresponding polyvinyl ketals (and acetal, Entry 11).

Entry	Ketone (Aldehyde)	Catalyst	Yield (%)	Ketalization (%)[b]	T_g (°C)[c]	T_{95} (°C)[d]	Calculated M_n (Da)[e] (M_n, $Đ$ by GPC)
0 **PVA**	none/commercial	-	-	0	75	231	22,300 (22,300, $Đ$ = 2.05)[f]
1 **PV-A-K**		*p*-TSA	49.5	69.2	100	314	29,300 (27,400, $Đ$ = 1.90)[g]
2 **PV-B-K**		*p*-TSA	49.3	54.8	84	293	29,800
3 **PV-P-K**		*p*-TSA	37.9	21.9	78	273	26,100
4 **PV-RK-K**		*p*-TSA	62.3	41.5	109	290	37,700
5 **PV-ZG-K**		*p*-TSA	46.2	39.0	60	260	39,700
6 **PV-LA-K**		*p*-TSA	12.8	15.3	80	205	26,100
7 **PV-CP-K**		*p*-TSA	42.9	62.7	106	298	32,800 (31,900, $Đ$ = 2.32)[g]
8 **PV-CH-K**		*p*-TSA	60.8	62.4	101	304	35,400 (30,200, $Đ$ = 1.88)[g]
9 **PV-DC-K**		HCl	38.7	55.2	107	273	41,100
10 **PV-TM-K**		HCl	62.4	51.7	127	258	38,300
11 **PV-F-A**		*p*-TSA	66.1	83.2	138	314	38,800
12 **PV-MT-K**		HCl or *p*-TSA	NR	none	-	-	-
13 **PV-DA-K**		HCl or *p*-TSA	NR	none	-	-	-
14 **PV-IP-K**		HCl or *p*-TSA	NR	none	-	-	-
15 **PV-CF-K**		HCl or *p*-TSA	NR	none	-	-	-
16 **PVA***	none/commercial	-	-	0	70	218	166,000[h]
17 **PV-A-K***		*p*-TSA	70.6	68.1	105	260	217,500

[a] Reactions conducted with 2 mol% *p*-TSA in dimethyl sulfoxide at 40 or 60 °C for 4–24 hours with [ketone]/[PVA-OH] ranging from 2 to 36, aiming for a substantial ketone excess without inducing polymer precipitation. [b] Determined by ^{1}H NMR. [c] Determined by DSC. [d] Temperature reported upon 5% mass loss by TGA under nitrogen. [e] *Calculated* number average molecular weight (M_n) from initial M_n = 22,300 for PVA (or 166,000 for Entry 17), augmented by % ketalization. [f] M_n and dispersity ($Đ$) obtained by GPC in hexafluoroisopropanol (HFIP) at 40 °C versus PMMA standards.

[g]M_n and dispersity (*Đ*) obtained by GPC in THF versus polystyrene standards. [h]Assumed here as the midpoint of the range 146,000–186,000 reported by the manufacturer.

favorability of ketalization because of increased steric demand compared to small ketones. The importance of sterics is demonstrated by the ketalization degrees measured for acetone, butanone, and 3-pentanone, as they compete for finite space along the PVA polymer chain. The smallest ketone, acetone, managed a ketalization degree of 69.2%, whereas this value decreased to 54.8% for butanone (Table 1, Entry 2) and was only 21.9% for 3-pentanone (Table 1, Entry 3). Note that this result of 21.9% ketalization for 3-pentanone employed only 5 equivalents of ketone. For direct comparison, 5 equivalents of acetone still resulted in a greater ketalization of 43.5%—further confirming that the smaller acetone is better sterically accommodated by the PVA polymer. Cyclopentanone (Table 1, Entry 7) and cyclohexanone (Table 1, Entry 8) have similar sterics and similar ketalization degrees of 62.7 and 62.4%, respectively. Dihydrocarvone (Table 1, Entry 9) and trimethylcyclohexanone (Table 1, Entry 10) are bulkier analogues of cyclohexanone and thus, have somewhat smaller ketalization degrees of 55.2% and 51.7%, respectively. While raspberry ketone (Table 1, Entry 4) and zingerone (Table 1, Entry 5) possess a large, aromatic group, they still are methyl-ketones and thus achieve moderate ketalization degrees of 41.5 and 39.0%, respectively. Menthone (Table 1, Entry 12), although electronically similar to cyclohexanone or dihydrocarvone, has great steric encumbrance that altogether precluded its attachment to PVA. Other bulky ketones, diacetone alcohol, isophorone, and camphor (Table 1, Entries 13–15) also failed to react with PVA under the present conditions. While isophorone (Table 1, Entry 14)[61] and camphor (Table 1, Entry 15)[62] can be ketalized with the primary/primary diol ethylene glycol, the sterics are more congested with PVA since it presents as a secondary/secondary diol. Additionally, the conjugation of isophorone and the tendency of diacetone alcohol (Table 1, Entry 13) to become conjugated via dehydration seemed to deter their attachment to PVA.[63] In line with this steric discrimination argument, the aldehyde furfural (Table 1, Entry 11) showed an acetalization degree (83.2%) greater than all of the ketalization degrees. Ketalization with levulinic acid (Table 1, Entry 6) was only 15.3%. This low value might result from interference by the acid functionality, since a much higher ketalization (33%) was achieved with the analogous ester, methyl levulinate.

Thermal properties

Fully hydrolyzed PVA is a semi-crystalline polymer with a melting temperature reaching 230 °C,[64] which is above its initial degradation temperature (T_{95} = 220 °C).[65] Residual acetyl groups in PVA diminish crystallinity[66] and thus, its glass transition temperature (T_g) can be a critical thermal property for application assessment.[33] The T_g value is affected by several factors, including molecular structure, molecular weight, and additives. The commercial PVA studied herein has M_n = 22,300 Da and a T_g value of 75 °C. Attachment of ketones or aldehydes to PVA by a cyclizing ketalization/acetalization reaction generates six-membered rings as part of the polymer main-chain. The decreased conformational mobility rigidifies the polymer chains and thereby increases the T_g. Sterically bulky groups on the ketal/acetal ring can further inhibit conformational mobility and further increase T_g. Accordingly, ketalization of PVA boosts its T_g of 75 °C to 78—127 °C, as illustrated in Fig. 5. No melting temperatures for these polymers were detected by DSC. Hence, the presumed processing temperatures of these polyvinyl ketals are above their T_g values, which range from 78 to 127 °C—still well below the T_{95} degradation values, which range from 205 to 314 °C. Note that ketalization apparently improves thermal stability since T_{95} values (228, 238, 277, 314 °C) increase with increasing ketalization for **PV-A-K** (60.8, 63.1, 65.0, and 69.2%). Presumably the polyvinyl ketals and PVA share similar thermal degradation pathways via pendent OH groups,65 but these pathways become less available as the degree of ketalization increases.

The T_g values can be correlated to the polyvinyl ketal structures. Among those derived from linear and aliphatic ketones, **A**, **B**, and **P**, **PV-A-K** showed the highest T_g of 100 °C. This can be attributed to its high degree of ketalization (69.2%), along with its compact methyl groups, which result in less free volume versus ethyl groups. The T_g values of **PV-B-K** (84 °C) and **PV-P-K** (78 °C) still exceed that of PVA. The polymers **PV-LA-K** and **PV-P-K** shared a similar T_g value near 80 °C probably because of similar low degrees of ketalization (15.3 and 21.9%) and similar free volume considerations. The polymer derived from **RK** exhibited a T_g of 109 °C, somewhat higher than that of **PV-A-K**. Interchain interactions are probably enhanced because of hydrogen bonding and aromatic polarity.[67] Despite the similarity of zingerone (**ZG**) and raspberry ketone (**RK**), the former conferred the lowest T_g of this study at 60 °C. The methoxy group of **ZG** either increased the free volume available, diminished hydrogen bonding between chains, or both.

For polyvinyl ketals derived from cyclic ketones, **PV-CP-K** and **PV-CH-K** displayed similar ketalization degrees and comparable T_g values of 106 and 101 °C, respectively, because **CP** and **CH** are similar in volume and steric demand. Their T_g values were higher than the polymers from **B** and **P** because their cyclic pendent groups generate less free volume than acyclic analogues. Polyvinyl D-dihydrocarvone ketal (**PV-DC-K**) and polyvinyl 3,3,5-trimethylcyclohexanone ketal (**PV-TM-K**) showed T_g values of 107 and 127°C, respectively. **PV-DC-A** exhibited a lower T_g probably because its conformationally flexible methylethenyl group induces more free volume than gem-methyl groups. The polymer from polyvinyl furfural acetal (**PV-F-A**) displayed a remarkably high T_g value of 138 °C. Probable reasons for this are its very high degree of acetalization (83.2%), conformational inflexibility, and aromatic polarity.[35] A previous report of **PV-F-A** attained a much lower degree of acetalization (57%) and offered no T_g value.[68]

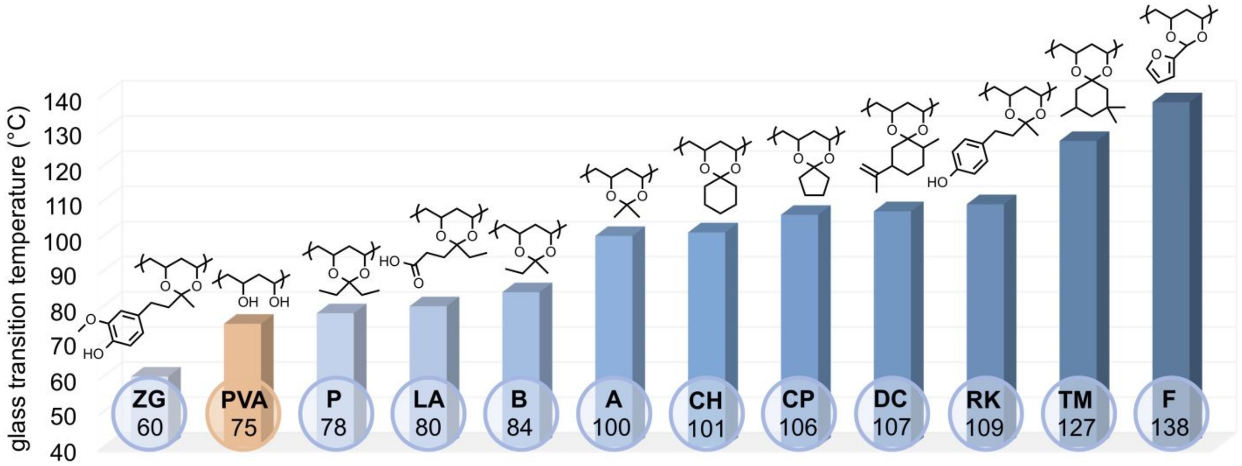


Fig. 5. The glass transition temperature (T_g) of PVA was boosted from 75 °C to values ranging from 78 to 127 °C by ketalization (or to 138 °C by acetalization) with ketones (or an aldehyde, yielding **PV-F-A**).

By increasing the [acetone]/[PVA-OH] reaction quotient from 5 to 25 to 30 to 36, four different **PV-A-K** polymers with increasing ketalization degrees were synthesized: 43.5, 60.8, 63.1, and 69.2% (see Table S2). An additional **PV-A-K** polymer prepared with [acetone]/[PVA-OH] = 36, but without a drying agent, showed a comparatively lower ketalization degree of 65.0% (Table S3, Entry 18 of the ESI). For these four **PV-A-K** polymers, the measured T_g values were proportional (although not linearly) to the % ketalization: 83, 91, 96, and 100 °C, respectively. This correlation is best attributed to loss of main-chain conformational flexibility; a greater degree of ketalization introduces more rings per polymer chain, decreasing conformational freedom, and boosting T_g. The same qualitative response was observed for **PV-F-A** and **PV-RK-K**: increasing the acetalization of **PV-F-A** from 67.7 to 83.2% increased the T_g from 134°C to 138°C; increasing the ketalization of **PV-RK-K** from 35.9 to 41.5 % increased the T_g from 94°C to 109°C. In short, modified PVAs made from the same ketone or aldehyde exhibit T_g values proportional to their degree of ketalization or acetalization (see Figure S1).

Effect of PVA molecular weight on polyvinyl ketal properties

Commercially available PVA is characterized by molecular weight and extent of hydrolysis (as it originates with polyvinyl acetate). Entries 1–15 of Table 1 employ PVA with a reported molecular weight of 13,000–23,000 Da and a measured M_n of 22,300 Da. To investigate the effect of molecular weight on ketalization degree and thermal properties, a notably higher molecular weight PVA, reportedly 146,000 to 186,000 Da, was purchased and ketalized with acetone via the same protocol. The high and low M_n **PV-A-K** polymers displayed similar ketalizations of 68.1% and 69.2%, respectively. Molecular weight augmented the T_g value slightly, with the T_g of high M_n **PV-A-K** registering at 105 °C, about 5 °C higher than that of the low M_n **PV-A-K**. One interpretation of this difference is that the lower M_n material has a higher concentration of chain ends and therefore more free volume—in line with the Flory–Fox equation.[69]

Heterogeneous hydrolysis studies

Heterogeneous hydrolysis studies were conducted at room temperature (20°C) with **PV-A-K** having 69.2% ketalization. 10 mg pieces were cut from a large **PV-A-K** sample and placed in aqueous buffers with pH = 2, 3, and 5, as well as deionized (DI) water, and seawater. The polymers in pH = 2 and pH = 3 buffer dissolved in 3 hours and 24 hours, respectively. ^{1}H NMR confirmed that the ketal functional groups were almost completely hydrolyzed at these low pH levels (1.0 and 2.0% residual ketalization, Fig. 6). The **PV-A-K** samples at pH = 5, in DI water, and seawater remained visibly unchanged over 24 hours and the ketalization degree remained essentially unaltered, as measured by ^{1}H NMR (Fig. 6). By visual inspection, the pH = 5 sample swelled, became transparent, and then dissolved over the course of 3 months, whereupon ^{1}H NMR analysis indicated complete hydrolysis. Expectedly, more acidic conditions cause faster polyvinyl ketal hydrolysis, as shown by the observed dissolution and measured extent of hydrolysis.

Over two years in deionized water or seawater, the **PV-A-K** ketalization dropped from 69.2% to 66.2% or 65.9%, respectively (Fig. 7a). This amounts to about 3% hydrolysis for this long-term experiment. Visually, these polymers remained unchanged in both seawater and deionized water. Although longer experiments are necessary to fully assess its environmental hydrolysis behavior, **PV-A-K** is seemingly ingestion-friendly since the stomach pH of mammals, fish, reptiles, and birds is low enough (pH ~ 2.5) to fully hydrolyze this polymer into innocuous, water-soluble PVA and acetone in a matter of hours.[70]

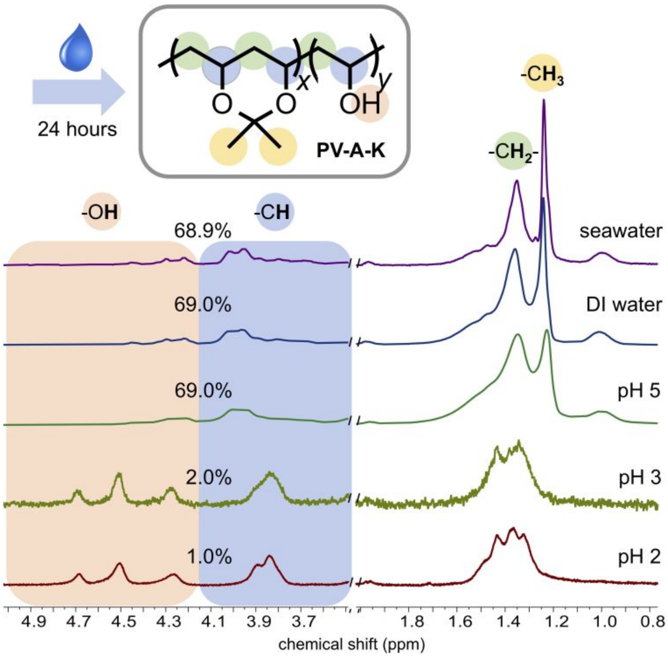
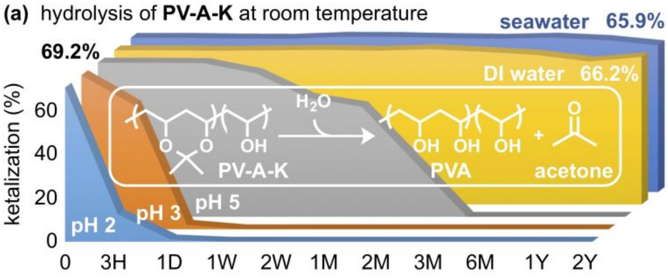


Fig. 6. Hydrolysis study of **PV-A-K** at room temperature with 69.2% initial ketalization. Over 24 hours, **PV-A-K** in pH = 5 aqueous buffer, deionized water, or seawater exhibited no hydrolysis. Hydrolysis was significant in more acidic aqueous media with residual ketalization of 1.0 or 2.0 % for pH = 2 or 3, respectively.

(a) hydrolysis of **PV-A-K** at room temperature



(b) hydrolysis of **PV-A-K** at 80°C

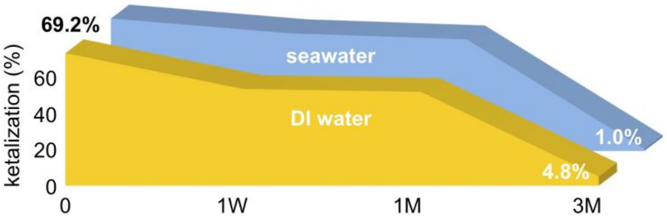


Fig. 7. Hydrolysis study of **PV-A-K** with 69.2% initial ketalization at room temperature (a) and at 80 °C (b). At room temperature, acidic conditions effected full hydrolysis in 6 months or less; over two years, ketalization dropped to 66.2% in deionized water and to 65.9% in seawater. At 80 °C over 3 months, ketalization diminished to 4.8% in deionized water and to 1.0% in seawater.

An accelerated hydrolysis study of **PV-A-K** was performed at 80 °C in seawater and in deionized water (Fig. 7b). In one week, both samples appeared to swell at this elevated temperature. In one month, the samples began to physically disintegrate. In three months, the samples completely dissolved. The ketalization degree dropped from 69.2% to 4.8% in deionized water—a somewhat slower hydrolysis vs. seawater, where ketalization dropped to 1.0%. This is opposite the prediction based on pH, which concludes that ketals should be more stable in seawater (pH range of 7.5 to 8.5) because it is slightly more basic than deionized water (pH ~ 7).[71] Perhaps the dissolved salts in seawater behave as weak catalysts for ketal hydrolysis. These elevated temperature results are quite encouraging because they suggest that **PV-A-K** could hydrolyze over the course years or decades in various land or marine environments—especially those that are warm or somewhat acidic.[72]

Films

Commercial polyvinyl alcohol (PVA), polyvinyl butyral (PVB), and polyvinyl formal (PVF) are commonly employed as films. PVA film is normally cast from water because of its high hydrophilicity; however, the polyvinyl ketals described herein are comparatively hydrophobic. Therefore, films were cast from 75% aqueous ethanol or chloroform with polymers built from acetone (**A**), raspberry ketone (**RK**), trimethylcyclohexanone (**TM**), cyclohexanone (**CH**), and levulinic acid (**LA**). Photographs of these polyvinyl ketal films indicate an optical transparency comparable to that of commercial PVA and PVB, which were also cast into films for comparison (Fig. 8). Note that some polyvinyl ketal polymers required purification before film preparation; otherwise, the resulting films were cloudy or even opaque. Interestingly, the **PV-A-K** film showed elastic hysteresis while maintaining transparency.

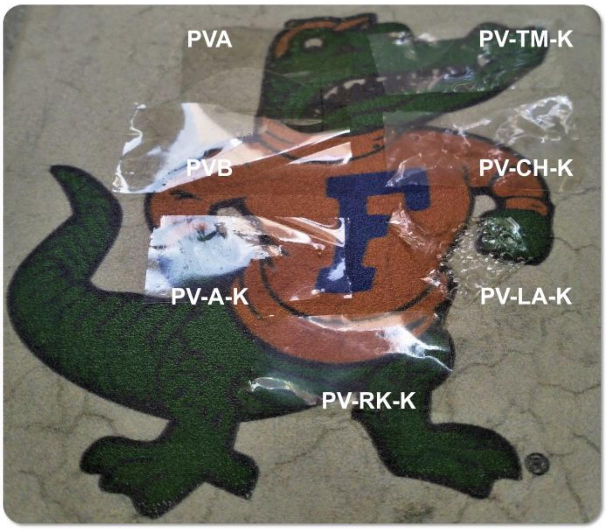


Fig. 8. Films from **PV-A-K**, **PV-RK-K**, **PV-TM-K**, **PV-CH-K**, and **PV-LA-K** exhibit optical transparency comparable to that of films from commercial polyvinyl alcohol (PVA) and polyvinyl butyral (PVB).

Conclusions

Polyvinyl alcohol (PVA) is a non-persistent, conditionally biodegradable polymer, but it is water soluble and has a relatively low glass transition temperature (T_g).[73] This study demonstrated its ketalization with a variety of ketones with the primary goal of transforming PVA into a useful packaging plastic. The ketalization protocols were designed to be environmentally benign and economical by employing biobased and/or sustainable ketones and avoiding toxic reagents, heavy metal catalysts, and extreme reaction conditions. Upon ketalization, the T_g of the PVA was increased from 75 °C to values ranging from 78 to 127 °C—substantially exceeding the T_g value of incumbent packaging plastics like polyethylene terephthalate (PET, 72 °C) and polystyrene (PS, 95 °C). Moreover, this important thermal property was shown to be tuneable and proportional to the degree of ketalization, which ranged from 15.3 to 69.2%. Several of the polyvinyl ketone ketals were solvent-cast into thin films. This process was straightforward and afforded rather optically transparent materials.

Polyvinyl acetone ketal (**PV-A-K**) has great commercial prospects because its T_g of 100 °C essentially matches that of polystyrene (PS) and it is built from inexpensive starting materials, PVA and acetone. It was subjected to a variety of degradation experiments, which showed that **PV-A-K** hydrolyzes readily in acidic media back into benign PVA and acetone. Over two years at room temperature, hydrolysis reached about 3% in deionized water or seawater, but was nearly complete in three months when heated to 80 °C in these same media. This high-temperature simulation suggests that **PV-A-K** and perhaps some of the other polyvinyl ketone ketals prepared could hydrolyze in just years or decades under typical aquatic conditions—thereby avoiding the environmental persistence of today's common packaging plastics.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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