

Modification of Poly(vinyl alcohol) Polymers by Aliphatic Carboxylic Acids via Reactive Blending

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ABSTRACT: The modification of poly(vinyl alcohol) with a series of long-chain aliphatic carboxylic acids via reactive blending was studied. The method involves the reaction in the melt of polymer hydroxyl groups with carboxylic acids using a laboratory scale reactor, a medium-scale Brabender rheomixer, and a large-scale twin-screw extruder. The presence of the long aliphatic chains acted as lubricants during reactive processing. The reactivity was generally low, and increased with decreasing chain length of the acids. All modified polymers displayed lower temperature thermal transitions and improved thermal stabilities compared to the parent polymer. Thermogravimetry established that polymers incorporating short chain residues were more thermally stable than their long-chain analogs. The polymer obtained in the twin-screw extruder showed a higher degree of incorporation with improved thermal stability compared to the polymers obtained in the laboratory mixer or the rheomixer. Intermediate degree of incorporation and thermal stability was exhibited by the polymers obtained in the rheomixer. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1885–1890, 1998

Key words: poly(vinyl alcohol); reactive blending; aliphatic acids; thermogravimetry

INTRODUCTION

The excellent gas barrier ability of poly(vinyl alcohol) (PVOH)^{1–3} and its nontoxicity are characteristic properties for this polymer. These properties are, however, counterbalanced by the poor thermal stability⁴ of the polymer, which renders melt processing difficult. For this purpose, many efforts have been made to improve processability and strength of poly(vinyl alcohol)^{5–11} without affecting the desirable low gas permeability.

Recently, we have found¹² that the interaction of PVOH, in the molten phase, with a series of epoxides results in the preparation of modified polymers that displayed improved thermal stability compared to the parent polymer. The experi-

ments were performed under conditions that resembled reactive extrusion. Conversion of PVOH to acetate, to improve its processability and mechanical behavior, is commonplace in this area. This is achieved by the action of acetic acid, acetic anhydride, or acetyl chloride in solution.¹³

In the present study a series of aliphatic carboxylic acids were used to modify, in the melt, a commercial PVOH grade, for improving its thermal stability and melt processability. The reactions were performed in a previously employed laboratory scale reactor,¹² a rheomixer and a twin-screw semiindustrial extruder. The acids employed are inexpensive, commercially available solids or high-boiling liquids being therefore suitable for reactions occurring at high temperatures. Modification of the polymer properties is discussed in terms of the chain length of the acids and the mixing equipment employed. NMR spectroscopy elucidated the structure of the modified polymers. The thermal properties of the polymers

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were characterized by differential scanning calorimetry and thermogravimetry.

EXPERIMENTAL

Materials

A commercial grade of partially hydrolyzed poly(vinyl alcohol), Mowiol M8-88 supplied by Hoechst was used for the modification reactions. The copolymer, of molecular weight 67,000 g/mol was 87.7% hydrolyzed and used as supplied. The acids employed in the modification reactions were of high purity (>99%) being used without further purification. The polymer and carboxylic acids were dried in a vacuum oven at 80 and 25°C, respectively, for several hours.

Reactive Blending

Modification reactions were carried in a laboratory-scale custom-made reactor described elsewhere,¹² in a Brabender rheomixer and also in a corotating twin-screw extruder. Thus, a mixture containing dry PVOH and carboxylic acid (8–10 g) was charged in the reactor and blended at 190°C with a mixing speed of 100 rpm for 8 min. A Brabender rheomixer equipped with a Plasticorder PL 2000-6 and a mixer head type W50E with three heating zones was employed for medium scale reactions (50–60 g). Finally, a 30-mm diameter corotating intermeshing twin-screw extruder (Maris Spa) with L/D = 50 was used for a large scale reaction. The modified polymers were purified by dissolution in water at 70–80°C and reprecipitation by acetone. The polymers obtained were finely ground and dried under vacuum at 80°C for at least 12 h.

Characterization

Proton NMR spectra of the polymers were obtained at 60°C employing a Bruker AC 250 spectrometer operating at 250 MHz. Sample concentrations were approximately 8–10% w/v in perdeuterated dimethyl sulfoxide solutions that was also used as an internal locking agent.

Solution viscosity measurements were carried out in a Cannon-Ubbelohde viscometer at 30°C in water. The polymers were hydrolyzed with 12.5 N NaOH solution before they were subjected to viscosity measurements according to a standard procedure.¹⁴

For Differential Scanning Calorimetry (DSC) measurements a TA Instruments DSC 10 unit was employed coupled with a 2100 Controller. The samples in powder form were heated under nitrogen from 0 to 230°C at a rate of 15°C/min.

Thermogravimetric analysis (TGA) measurements were performed with a TA Instruments, model 2050 TGA analyzer using a thermal procedure that simulates the thermal conditions in the extruder and specifically: (1) heating to 220°C at a rate of 50°C/min, and (2) isothermal heating run for 15 min. Both the balance chamber and the oven were being purged with nitrogen throughout the course of the thermal experiments.

RESULTS AND DISCUSSION

Synthesis

The esterification reaction is affected by the varying chain length of the acids because of steric and compatibility reasons. Chain length, therefore, determines the incorporation of the acids into the polymer backbone. Caproic acid, the least lipophilic in the series, is expected to react faster in contrast to stearic acid, which is the most lipophilic and should be the least reactive. In these esterification experiments the reaction is only thermally induced in contrast to conventional esterifications in solution that are acid catalyzed. For reactions in the laboratory mixer a relatively high concentration of the carboxylic acid (5 mol %) was employed, while in the two other reactors smaller amounts were used because mixing was found to be more efficient. To avoid decomposition of the polymeric materials several experiments were performed before deciding on the temperature and duration of esterifications. The experimental conditions are summarized in Table I. At temperatures above 270°C and 10-min duration of the reactions, some decomposition of the material was detected and degradation products were observed with NMR. For the experiments performed under the chosen reaction conditions, solution viscosity measurements of the modified and virgin PVOH polymers resulted in limiting viscosities that are almost identical. This implies that the molecular weights remain unchanged after the modification reaction.

The reaction proceeds via a condensation mechanism through which water formed is taken off with the subsequent formation of the ester linkage. The reaction scheme is shown below.

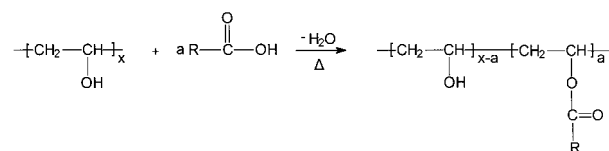
Table I Reaction Conditions Pertaining in the Reactive Blending of PVOH with Aliphatic Acids in the Melt at 190°C

Reaction Product	Aliphatic Acid	Amount Used (mol %)	Reactor Type	Reaction Time (min)	Appearance of End Product
PVOH	—		Mixer	8	Light yellow
P6	Caproic (C6)	5.0	Mixer	8	Off-white
P8	Caprylic (C8)	5.0	Mixer	8	Off-white
P10	Capric (C10)	5.0	Mixer	8	Off-white
P12	Lauric (C12)	5.0	Mixer	8	White
P14	Myristic (C14)	5.0	Mixer	8	White
P16	Palmitic (C16)	5.0	Mixer	8	White
P18	Stearic (C18)	5.0	Mixer	8	White
P18B	Stearic (C18)	1.0	Brabender	8	Off-white
P18Ba	Stearic (C18)	1.0	Brabender	4	Off-white
P18Bb	Stearic (C18)	1.5	Brabender	8	Off-white
P18TS	Stearic (C18)	1.0	Twin Screw	10	Off-white

The advantageous use of the aliphatic carboxylic acids was first shown during the reactive mixing process. Carboxylic acids act as lubricants preventing the adhesion of PVOH on the walls of the reactor a problem that is usually encountered.^{12,15} They also seem to protect the heat-sensitive polymer, by postponing the signs of thermal decomposition observed by the rapid darkening of the parent PVOH. As a consequence, the duration of mixing can be prolonged and the process results to modified polymers displaying white color. As expected, the same behavior was encountered in the rheomixer and the twin-screw extruder. In contrast, when zinc stearate was added to Mowiol 8–88 it started decomposing following a 10-min reaction.

¹H-NMR Characterization of Polymers

NMR spectroscopy has been applied extensively to poly(vinyl alcohol) polymers and copolymers characterization^{16–21} primarily for the study of their microstructure and determination of structural irregularities and molar fractions of the various components. Therefore, the main resonances of PVOH polymers have been assigned and it was,

**Scheme 1**

therefore, convenient to assign the new minor peaks due to the introduction of the aliphatic chains.

The NMR spectra obtained from all modified polymers were neat in accordance with the starting copolymer. The only additional peaks present in the spectra of the modified polymers were the upfield resonances at about 0.85 ppm and 1.25 ppm assigned to the methyl and methylene protons, respectively, of the aliphatic pendant chain. The NMR assignments are shown in Table II,

Table II ¹H-NMR Chemical Shifts of Side-Chain Peaks and Calculated Incorporation into the Polymer Backbone

Reaction Product	Chemical Shift, δ (ppm) ^a		Incorporation ^b (mol %)
	CH ₃ —	—CH ₂ —	
PVOH	—	—	—
P6	0.85 (t)	1.25 (s, b)	0.23
P8	0.86 (t)	1.25 (s, b)	0.17
P10	0.86 (t)	1.27 (s, b)	0.10
P12	0.87 (t)	1.26 (s)	0.10
P14	0.86 (t)	1.26 (s)	0.07
P16	0.86 (t)	1.26 (s)	0.07
P18	0.86 (t)	1.25 (s)	0.07
P18B	0.87 (t)	1.26 (s)	0.11
P18Ba	0.87 (t)	1.26 (s)	0.10
P18Bb	0.87 (t)	1.26 (s)	0.12
P18TS	0.86 (t)	1.24 (s)	0.12

^a t, triplet; s, singlet; b, broad.

^b Calculated from CH₃— peak.

along with the calculated incorporation of the side chain attached to the backbone. The latter was determined from the integral values of the side-chain methyl protons with respect to the integral value of the methyl protons of the acetate residue that is present in 12.7% on the copolymer composition. It is seen that the incorporation is generally low for all aliphatic acids used under the experimental conditions employed. For this reason the experiments were performed at least three times and found to be reproducible within $\pm 6\%$. The extent of incorporation, as expected, shows an increasing trend as the chain of the aliphatic acid becomes shorter. Caproic acid is, therefore, incorporated in larger amounts (0.23 mol %), while myristic, palmitic, and stearic acid-modified polymers exhibit the lowest incorporations (0.07%). Carboxylic acids with C8, C10, and C12 alkyl chains show intermediate reactivity. This trend is consistent with the expected reactivities of the acids due to steric and compatibility reasons.

It is of interest to note that the polymers modified in the rheomixer (e.g. P18B) and the twin-screw extruder (P18TS) using stearic acid display higher incorporations (0.12 and 0.11 mol %, respectively) compared to the corresponding polymer that was produced in the laboratory reactor (P18). The fact that they also display higher incorporations than P10, P12, P14, and P16, may, therefore, be attributed to the geometry of the reactor type with the concomitant changes occurring in the shear and mixing conditions pertaining in these reactors. The three products obtained using the rheomixer show practically the same incorporation (Table II), indicating that significant changes employed in the reaction duration or added amount of the acid do not affect the esterification reaction.

Differential Scanning Calorimetry

The thermal transitions of the parent²² and modified polymers are shown in Table III. Due to thermal instability of PVOH the thermal parameters were obtained on the first heating run. Inspecting the DSC thermograms it becomes evident that the modified polymers retain the semicrystallinity of the parent polymer. Results summarized in Table III reveal a decreasing trend in the melting points of modified resins. This is mainly a function of the incorporation of side chain on the backbone and also dependent on the length of the side chain. Significant decrease in melting points are exhib-

ited by polymers P6 and P8 modified by the short aliphatic chains with the highest incorporation. For P10 to P18, the low incorporation is partially counterbalanced by the increasing chain length. Thus, their melting points are higher than P6 and P8, although they are still about 3° lower than the parent polymer.

The melting of polymer P18TS, modified in the extruder is at 199.4°C i.e., 2° higher than the T_m of parent PVOH and, interestingly, about 5° higher than that of P18. The differentiation of the polymer properties may be attributed to reactive processing that took place in equipments with different construction characteristics. P18TS was reactive blended in the twin-screw extruder, which provides a thorough mixing and differentiated shearing profile compared to laboratory reactors. It seems that a better distribution of the side chain residues along the polymer backbone occurs, permitting in this case a better packing of the modified polymer chains. An analogous trend is encountered with polymers produced in the rheomixer. For instance, polymer P18B shows a melting transition at 195.2°C, which is higher than the T_m of P18, although it contains almost a double amount of stearic residues.

The glass transition temperatures show more or less similar behavior to the melting transitions. T_g 's of the modified polymers are appreciably lower than the T_g of the parent polymer with the exception of P18TS. The latter shows the highest T_g among modified polymers just as it displays the highest T_m . In this case the explanation that has been provided for T_m may also be given for glass transition temperatures.

Thermogravimetric Analysis

The thermal stability behavior is known to be the most crucial property for melt processing of poly-(vinyl alcohol) based polymers.⁴ Specifically, when melt processing of PVOH is attempted, decomposition of the polymers results and, consequently, the products cannot be used further. It should, therefore, be desirable that polymer modification provides (a) improved melt processability, and (b) an end product with improved thermal stability.

The thermal curves obtained by thermogravimetry are shown as a function of time in Figure 1. The time period between 3.5 and 18.5 min represents an isothermal heating period of 15 min at 220°C. Examination of the curves in Figure 1 suggests that modified polymers exhibit improved

Table III Thermal Transitions of Modified PVOH Polymers as Determined by DSC

Modified Polymers	Glass Transition, T_g (°C)	Melting Point, T_m (°C)	Enthalpy of Melting, ΔH (J/g)
PVOH	69.5	197.4	36.2
P6	62.6	192.2	39.9
P8	60.5	192.6	42.7
P10	61.5	194.1	40.6
P12	61.8	195.0	44.3
P14	61.9	193.7	44.7
P16	62.6	193.2	43.3
P18	61.5	194.2	42.9
P18B	62.1	195.2	37.2
P18TS	63.6	199.4	41.5

thermal stability having weight loss, for the least stable material (P18 or P16) about 1% of their initial weight compared to the untreated PVOH with a weight loss of about 2.5%.

There is a trend among polymers modified in the laboratory mixer according to which those incorporating the longer aliphatic chains display inferior thermal stability compared to polymers bearing shorter ones. Specifically P18, P16, and P14 polymers exhibit better thermal stability compared to PVOH, due to the long side chains. However, with respect to the rest of the modified polymers (P12, P10, P8, P6, P18TS, and P18B) they exhibit inferior thermal stability probably because of the extremely small molar content of incorporation (0.07 mol %). Polymers P12 and P6

exhibit intermediate behavior as far as their thermal stability is concerned. Polymer P6 modified by the short hexyl residue is present in relatively larger quantity than every other polymer (0.23 mol %), and it seems that the greater number of alkyl residues compensates for its short length. Finally, polymers P8 and P10 have identical TGA profiles and exhibit the most satisfactory behavior towards thermal degradation. This may be attributed to a favorable combination of the side chain lengths and molar percentage of incorporation.

Polymers P18TS and P18B have been modified with stearic acid in a twin-screw extruder and a rheomixer, respectively, and their thermal stabilities are shown in Figure 2 along with the P18 profile in order to examine the effect of mixing and shearing effect of the equipment. P18TS has the best overall stability, having lost only about

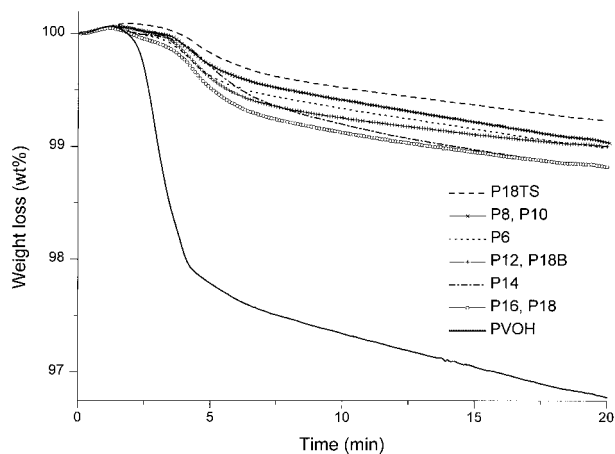


Figure 1 TGA curves of aliphatic acid-modified PVOH polymers and parent polymer. Two thermal regions are shown: (a) 0–3.5 min, heating from 40 to 220°C at 50°C/min; (b) 3.5–18.5 min, isothermal heating at 220°C for 15 min.

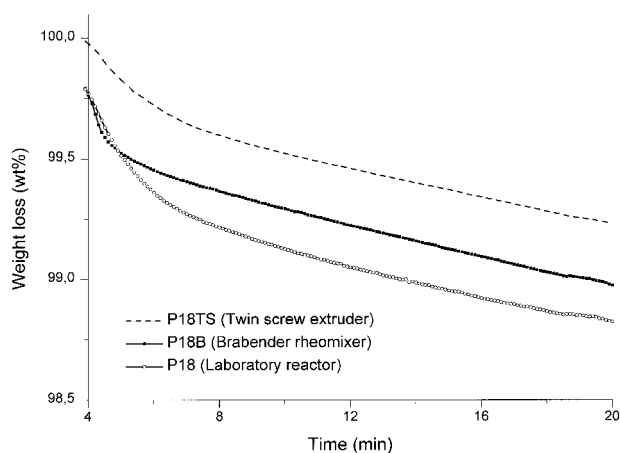


Figure 2 TGA curves of PVOH polymers modified with stearic acid in three different mixing equipments. Same thermal profile as in Figure 1.

0.5% of its initial weight, while P18B, although less stable than P18TS, has better thermal stability compared to P18. This behavior may be attributed to more efficient mixing achieved in the extruder and the rheomixer compared to the laboratory mixer, and the higher incorporation of side chains achieved thereof. It has to be noted that three polymer batches prepared in the rheomixer using different reaction conditions (Table II) have the same thermal stability behavior.

It is well known that the hydroxyl groups of PVOH participate and initiate, in fact, thermal degradation processes. On the other hand, hydroxyl groups are very important for the excellent barrier properties. The length of side chain, the percentage of molar incorporation of alkyl chains, and their appropriate placement on the polymer backbone are affecting thermal stability towards this end. Our experiments have shown that low levels of incorporation of aliphatic residues that are unlikely to significantly affect barrier properties reduce thermal degradation rendering PVOH melt processable.

CONCLUSION

Reactive blending of poly(vinyl alcohol) with aliphatic acids in a laboratory scale reactor resulted in modified polymers with improved processability, appearance, and thermal stability compared to the parent polymer. These improved properties were obtained with limited incorporations of the acids in the polymer backbone with a concomitant low decrease of the temperature of thermal transitions of the polymers compared to the parent polymer. Furthermore, reactive blending of PVOH with stearic acid in a Brabender rheomixer and a semiindustrial twin-screw extruder produced polymers (P18B, P18TS) with higher incorporation exhibiting improved thermal stability properties.

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