

Thermal Behavior of Poly(Vinyl Alcohol) Modified with Phosphorous Acid

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Synopsis

The thermal behavior of poly(vinyl alcohol) (PVA) modified with H_3PO_3 has been studied. The effect of phosphorus content in the polymer on the dehydration rate is discussed as well as the temperature-dependent changes in sample weight. It has been shown that the presence of phosphorous acid radicals in PVA causes a lowering in the temperatures of dehydration and pyrolysis and accelerates these processes.

INTRODUCTION

Investigations of thermal behavior of fiber-forming polymers can be conveniently carried out with the aid of thermogravimetry and differential dynamic calorimetry which has already been reflected in the scientific literature.^{1,2} However, few papers deal with poly(vinyl alcohol) (PVA).^{1,3,4}

Gillham and Schwenker¹ have examined thermal properties of PVA of molecular weight 280,000, giving its full characteristics. Duncalf and Dunn³ have carried out a thermogravimetric study of PVA containing a small amount of acetate groups.

In the present paper, results of thermal investigations of PVA modified with phosphorous acid are discussed and interpreted.

EXPERIMENTAL

The examinations were carried out with the aid of a dynamic differential calorimeter DSC.1B and a Perkin-Elmer thermobalance TGS-1.

Samples for DSC were enclosed in containers of aluminum film. All the measurements were carried out under nitrogen flow (about 40 cm³/min) at a heating rate of 16°C/min. Japan-made PVA (alkali hydrolysis) of molecular weight 66,000 was used for the study.

Detailed characteristics of the polymer and the procedure of modification with phosphorous acid were given in the paper published previously.⁵ The control and modified PVA samples used for TGA and DTA were thoroughly purified by extraction with dry acetone under the same conditions for 10 hr. Extracted samples were dried under nitrogen at room temperature and then stored for 48 hr over P_2O_5 in a desiccator.

RESULTS AND DISCUSSION

During examination of the reaction mechanism between PVA and phosphorous acid it has been found⁵ that, besides the main reaction leading to a formation of monoesters, possible crosslinking of macromolecules takes place. Such a finding has been put forward based on the reduced viscosity of solutions of modified polymers. Thermogravimetry and differential thermal analysis have fully confirmed this assumption. It is clear from Figure 1 that, at a temperature of about 300°C, a decrease in the sample weight of untreated PVA (curve 1) occurs, which is a result of dehydration and intra- and intermolecular crosslinking. Above 375°C, a violent fall in the sample weight of PVA is observed, which is due to degradation of

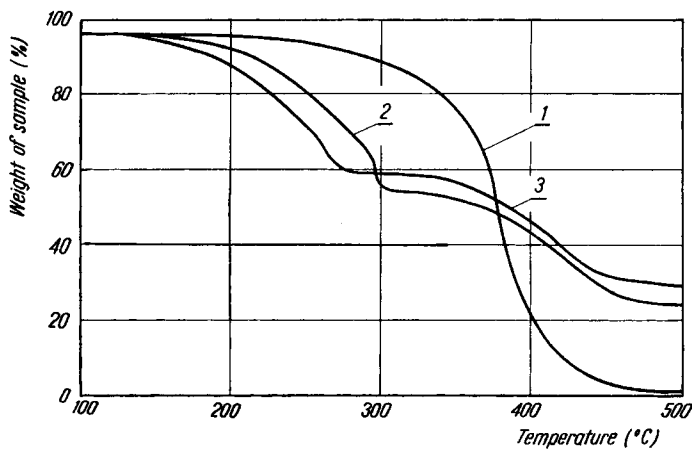


Fig. 1. TGA curves of poly(vinyl alcohol) in nitrogen: (1) no treatment; (2) phosphorus content 1.76%; (3) phosphorus content 5.59%.

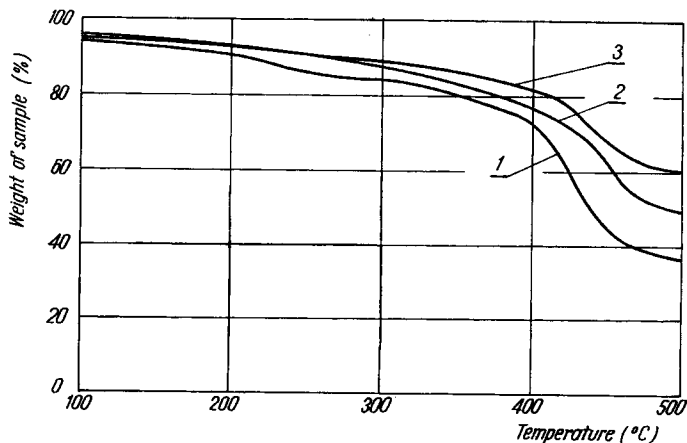


Fig. 2. TGA curves of dehydrated poly(vinyl alcohol) in nitrogen: (1) no treatment; (2) phosphorus content 2.15%; (3) phosphorus content 4.34%.

polymer and evaporation of volatile products. The carbon residue at 500°C amounts to about 3%. A completely different course of changes is observed in thermograms of PVA containing phosphorous acid radicals in side chains (curves 2 and 3). Weight loss of these samples is observed already at a temperature of 150°C. The sections of curves 2 and 3 within the temperature range 150° to 300°C probably characterize dehydration. Phosphorous acid radicals included in the polymer play the part of promoter in this reaction. However, above a temperature of 300°C, pyrolysis takes place leading to the formation of tridimensional structure and volatile products. Under these conditions reactions connected with changes of phosphonic groups may occur.⁶ From the above-discussed curves it appears that with an increase in phosphorous content in the polymer there is a lowering of the dehydration temperature and a decrease in the amount of volatile products of pyrolysis. This may be explained by the fact that phosphorous acid, having reducing properties, is an initiator for the dehydration and pyrolysis, but an inhibitor for the degradation of the polymer retarding the formation of volatile products.

In order to confirm that the sections of curves 2 and 3 within the range 150°–300°C characterize the dehydration, thermogravimetric analysis was carried out on samples of PVA (Fig. 2) previously dehydrated and treated with phosphorous acid. In this case, samples of PVA in the form of fibers were dehydrated according to the procedure described in the literature⁷ and then treated with aqueous solution containing 20% H_3PO_3 and heated for 30 min at 160°C (curve 2) and 220°C (curve 3), respectively.

From the shape of the curves shown in Figure 2 it can be concluded that the temperature range 150°–300°C, and even to 400°C, there are no distinct changes in the polymer samples previously subjected to dehydration. A slight slope of curves 1, 2, and 3 within this range may be due to dehydration resulting from the presence of few OH groups in the samples and due to a slow degradation process which is initiated under these thermal conditions. But over 400°C, there is a clear decrease in the weight of samples, which is connected with the degradation taking place under these conditions. In this case, volatile products of low molecular weight are formed and crosslinking takes place giving a tridimensional structure of the polymer. Thus, by comparison of the shapes of the curves in Figures 1 and 2 and their interpretation, it has been shown that the decrease in weight of PVA samples modified with phosphorous acid (Fig. 1) heated under nitrogen up to 300°C is due to dehydration and, at a temperature of about 400°C, to degradation.

Differential curves of decrease in mass of PVA modified with H_3PO_3 (Fig. 3) show that the dehydration rate is dependent on the phosphorus content in the polymer. The PVA sample containing 5.59% phosphorus undergoes dehydration almost twice as fast as the sample having 1.76% phosphorus. It is also interesting to note the degradation of PVA modified and untreated occurs at the same temperature, about 430°C, but the temperature of dehydration is closely related to the phosphorus content.

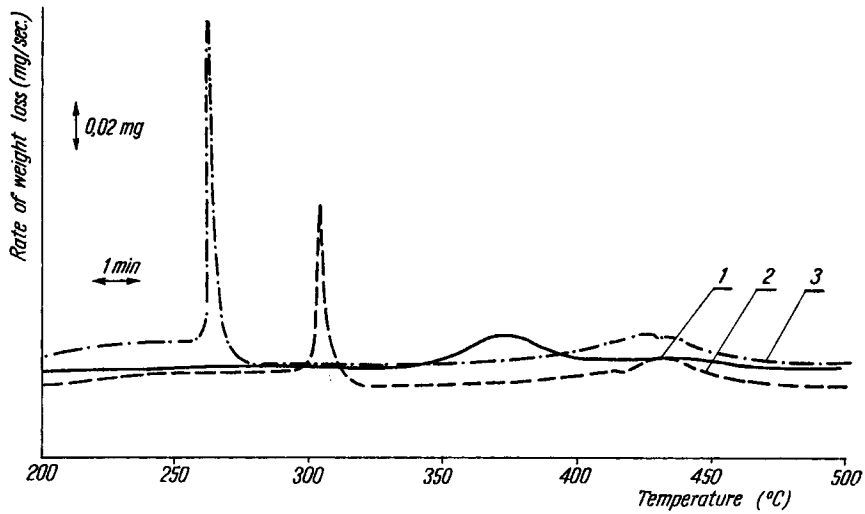


Fig. 3. Rate of weight loss of poly(vinyl alcohol) in nitrogen; (1) no treatment; (2) phosphorus content 1.76%; (3) phosphorus content 5.59%.

Dehydration of untreated PVA occurs at a relatively low rate in the range of 350°–385°C, with the maximum rate at 372°C. In the case of modified PVA containing 1.76% phosphorus, the maximum of dehydration rate is at 304°C, and that for the polymer having 5.59% phosphorus is at 266°C. It may be concluded that phosphonic groups introduced into PVA increase the rate of dehydration and decrease its temperature.

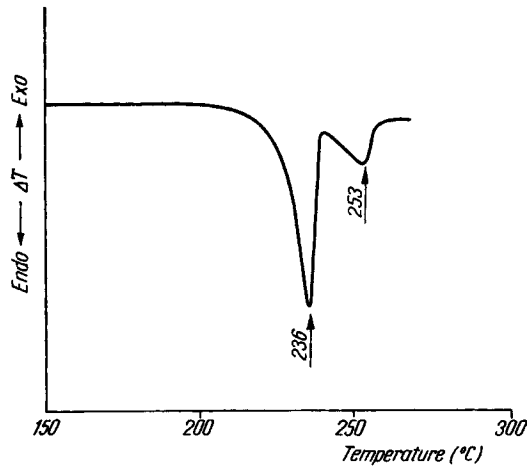


Fig. 4. DTA curves of original poly(vinyl alcohol) in nitrogen. DSC measurement were carried out at sensitivities $R = 8$.

Endothermal effects of PVA used for modification having maxima at 236°C and 253°C are shown in Figure 4. The first band probably corresponds to the recrystallization of polymer and the second, to melting of crystalline regions. Such an assumption is confirmed by the fact that the samples of polymer under investigation heated under experimental condi-

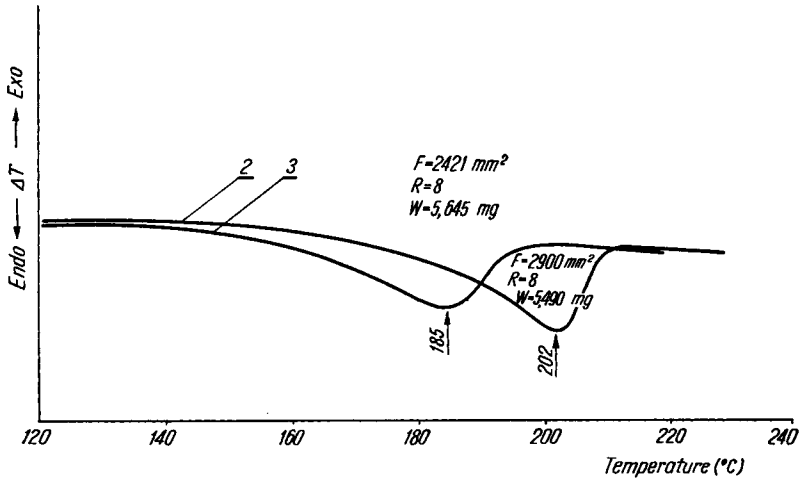


Fig. 5. DTA curves of poly(vinyl alcohol) with phosphorous acid, in nitrogen. DSC measurement were carried out at sensitivities R-8. (2) phosphorus content 1.76%, weight of sample (W) 5490 mg, area of endothermal effect (F) 2900 mm²; (3) phosphorus content 5.59%, weight of sample (W) 5645 mg, area of endothermal effect (F) 2421 mm².

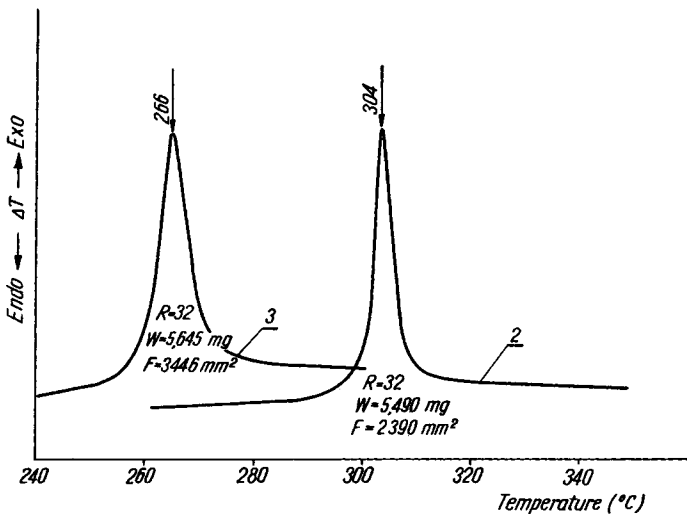


Fig. 6. DTA curves of poly(vinyl alcohol) modified with phosphorous acid, in nitrogen. DSC measurement were carried out at sensitivities R-32 ($R = 8 \times 4$): (2) content 1.76%, weight of sample (W) 5490 mg, area of exothermal effect (F) 2390 mm². (3) phosphorus content 5.59%, weight of sample (W) 5645 mg, area of exothermal effect (F) 3446 mm².

tions to a temperature of 265°C changed their color from white to weak orange. It means that at this temperature there is no dehydration which would cause the formation of a large number of chromophoric groups in the polymer and connected with a loss of weight. The change in polymer mass is not observed before the temperature exceeds 350°C (Fig. 1, curve 1). The divergence of these results and those given in the literature¹ is probably due to different structure and chemical composition of samples used for investigations.

The magnitude of endothermal effects of PVA modified with H_3PO_3 (Fig. 5) depends on the phosphorus content in the polymer. Melting of crystalline regions in PVA containing 1.76% phosphorus (curve 2) occurs with a greater endothermal effect than in the case of the polymer having 5.59% phosphorus. This fact is in agreement with many experimental findings which show that the increase in the degree of modification of polymer causes a decrease in the crystallization degree and lowering of the melting point of the polymer. In our case, this was fully confirmed, since the melting temperatures of crystalline regions of modified PVA are 202°C and 185°C, respectively, while for the untreated PVA the melting point is 253°C.

Exothermal effects in modified PVA (Fig. 6) with a maximum at 266°C for the sample containing 5.59% phosphorus and at 304°C for that containing 1.76% phosphorus correspond to the activated dehydration process and concomitant chemical reactions. The samples heated to about 10°C above the mentioned temperatures become completely black. This would confirm that a considerable amount of chromophoric groups is formed in these samples due to dehydration. The samples were of a pale-orange color at the temperature below the exothermal effect. It should be also mentioned that the increase in the phosphorus content in the polymer causes an increase in the exothermal effect of the discussed process. The process occurs both inside and between macromolecules resulting in the formation of a tridimensional structure.

The exothermic effect is attributed to dehydration of PVA modified with phosphorous acid, in spite of the fact that conventional dehydration processes in compounds of low molecular weight⁸ and polymers² are accompanied by an endothermic effect.

The exothermic effect taking place during dehydration of PVA modified with phosphorous acid results in thermal reactions at the given temperature, mainly of activated dehydration and intra- and intermolecular cross-linking of phosphorous acid radicals bounded to macromolecules of the polymer.

The results shown in the present paper and those previously reported⁵ confirm the assumption that phosphorous acid radicals in modified PVA play a part of activator for the dehydration process leading to crosslinking of the polymer.

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