Polymer Bulletin 58, 489–494 (2007)
DOI 10.1007/s00289-006-0685-1

Polymer Bulletin

Conductivity studies of poly (vinyl alcohol)-iodine complex membrane

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Received: 28 May 2006 / Revised version: 6 September 2006 / Accepted: 20 September 2006
Published online: 29 September 2006 – © Springer-Verlag 2006

Summary

The conductivities of polymers like poly (vinyl alcohol) (PVA) and its iodine complex membranes are reported here. PVA-iodine complex membrane was prepared by dipping PVA film into an I_2–KI solution. The formation of the complex membrane was confirmed by IR spectra. Conductivities were determined from 30 to 300°C with a frequency ranges from 42Hz to 500 KHz in solid state. It was observed that iodine is known to act as a catalyst for dehydration of PVA. A possible mechanism for the dehydration of PVA catalyzed by iodine is also explained.

Introduction

Like amylose, PVA gives a characteristic blue colour with iodine. Imai and Matsumoto [1] found that the colouring ability of PVA was sensitive to the preparative conditions used for the parent poly (vinyl acetate). Although this ability was also affected by various structural factors such as the chain length of the polymer and the presence of foreign monomer units in the PVA chain. The blue PVA-iodine complex was first found by German scholars as early as 1927. Since then the colour reaction of PVA with iodine in solution has attracted positive attention. With regard to amylose-iodine, the formation of a polyiodide complex inside the helical chain of amylose was first proposed by Freudenberg. A similar coloration mechanism was also proposed for the blue-colored aqueous solution of PVA-iodine by Zwick and Tebelev [2, 3]. Zwick thought that the polyiodide ions may be formed in the host of helical PVA molecules, whereas Tebelev insisted that it is formed in the voids of the molecular aggregates of PVA. Regarding the PVA-iodine complex, Yokota and Kimura [4-7] proposed a discrete structure of the chromophoric polyiodine species and the mechanism of its formation. It is known that the colour reaction of PVA with iodine in solution is thermally reversible, like amylose with iodine. Sahio and Tanaka [8] explained that heating the PVA-iodine membrane caused a two-stage colour change. At first, the blue of the complex membrane turned yellow and subsequently changed to deep brown. They suggested that iodine or HI which is formed as intermediate during the thermal reaction is act as a catalyst for dehydration of PVA. But they could not point out which of them was the exact catalyst.

The conductivity studies of PVA-iodine complex membrane is not reported in literature. Here, in this paper an attempt is made to prepare PVA-iodine complex membrane and to characterize the same by IR, TGA and conductivity studies and compared with PVA membrane.

Experimental

Materials

Poly vinyl alcohol, white crystalline form (BDH reagent grade; viscosity average molecular weight of 75,000; contained 1% of residual vinyl acetate) was used without further purification, Iodine (BDH reagent grade), Potassium iodide (BDH reagent grade) and Potassium sulfate were used without further purification.

Preparation of PVA-I_2 Complex membrane

On a silica plate (0.9x 5.0 cm) 0.25 ml of an aqueous solution of PVA (2 wt %) was spread and dried under atmospheric pressure and followed by vacuum to a thin film (thickness about 10 μm). The plate was dipped into 20 ml of an I_2 (1.25×10^{-3} M)-KI (7.5×10^{-3}M) solution saturated with potassium sulphate for over night at 20°C. Here potassium sulphate was used to increase the common ion effect of K^+ for reducing sublimation of I_2 from the I_2-KI solution. The resulting PVA-I_2 membrane was dried over $CaCl_2$.

Physical measurement

The IR of the PVA and PVA-I_2 membrane were recorded in the region between 4000cm^{-1} and 600cm^{-1} with a Bruker, Vector22 FTIR using thin film of the polymers. The bulk electrical conductivity of these compounds was evaluated from the complex impedance-admittance plots recorded at different temperatures using a HIOKI 3532-50, frequency response analyzer. The plots were recorded in the frequency range from 50 Hz to 500 kHz keeping the signal amplitude of 20 mV. The geometry of the cell for the measurement of conductivity was Pt|polymer film|Pt, where platinum plate was used as electrodes. The experiment was carried out under a relative humidity of 57% [9]. TGA and DTA were performed using Perkin-Elmer thermal analyzer in nitrogen at a heating rate of 10°C/min using 5±1 mg samples.

Results and Discussion

Figure 1 shows the IR spectrum of the complex membrane at room temperature and after heating at various temperatures. Before heating, the band at 3300cm^{-1} and 1100cm^{-1} are due to the [ν(OH)] and [ν(C-O)] groups [10] respectively which are disappeared almost completely and instead new bands are appeared after heating at 300°C. It is also observed from IR spectrum (Figure 1 c) that the process is started at around 200°C. The shoulder at 3005cm^{-1} can be assigned to [ν(=CH)], the bands at 960 and 750 cm^{-1}, to [δ(C-H)] of trans and cis-double bonds respectively. Similarly the bands at 1735 and 1600cm^{-1} can be assigned to unsaturated carbonyl groups and conjugated double bonds respectively.

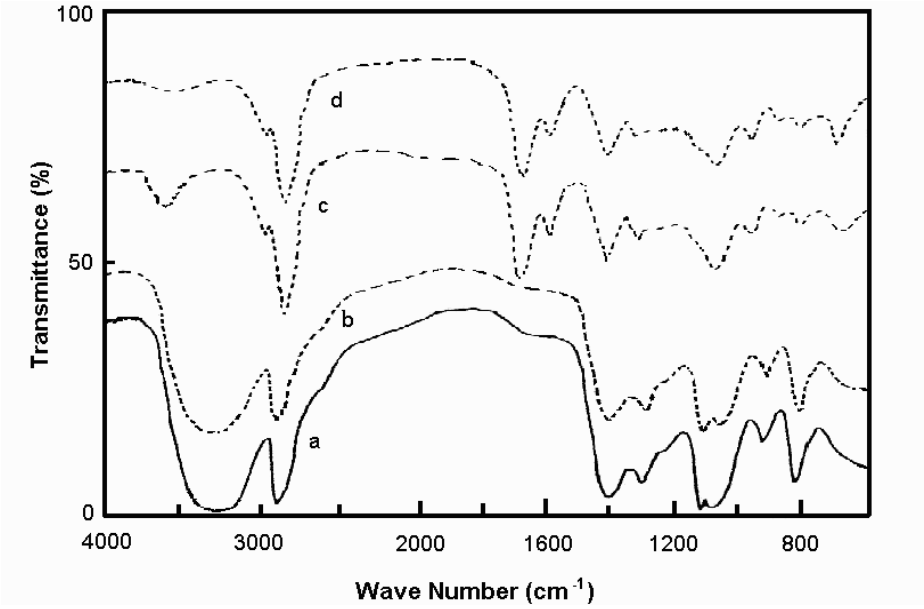
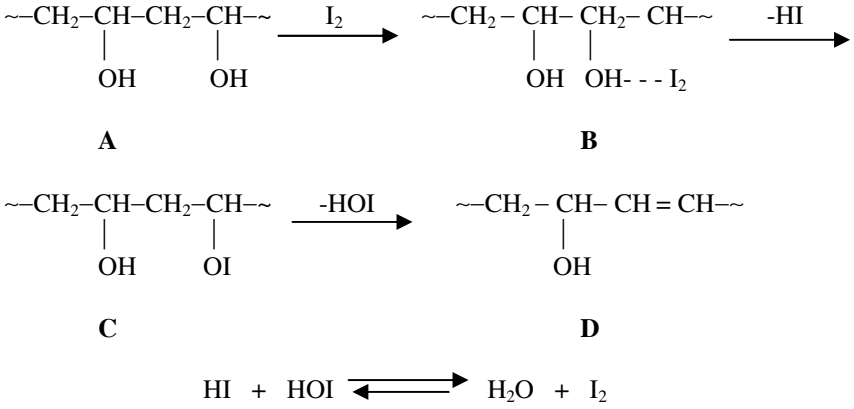


Figure 1. IR Spectrum of PVA-I_2 membrane: a. before heating, b. after heating 100°C, c. after heating 200°C, d. after heating 300°C (in thin film).

A possible mechanism for the dehydration of PVA catalyzed by iodine [11] is



The conductivity curves of PVA and PVA-I_2 complex membrane are presented in Figure 2. From the curve it is observed that the conductance of complex membrane abnormally increases from 150°C to 170°C and becomes stable at 180°C. Conductivity of the complex membrane again abruptly falls from 200°C to 240°C and almost stable at 250°C. So, it may be predicted that at 180°C and 250°C there must be formation of new compounds C and D of the complex membrane. Due to the loss of HI molecule from the complex membrane, its conductance attains the maximum value. But as soon as it is converted to polyene (D) by the loss of HOI molecule, it shows minimum conductance. It is found that iodine alone is less soluble and less reactive in aqueous PVA solution whereas HI is more soluble and more reactive in the

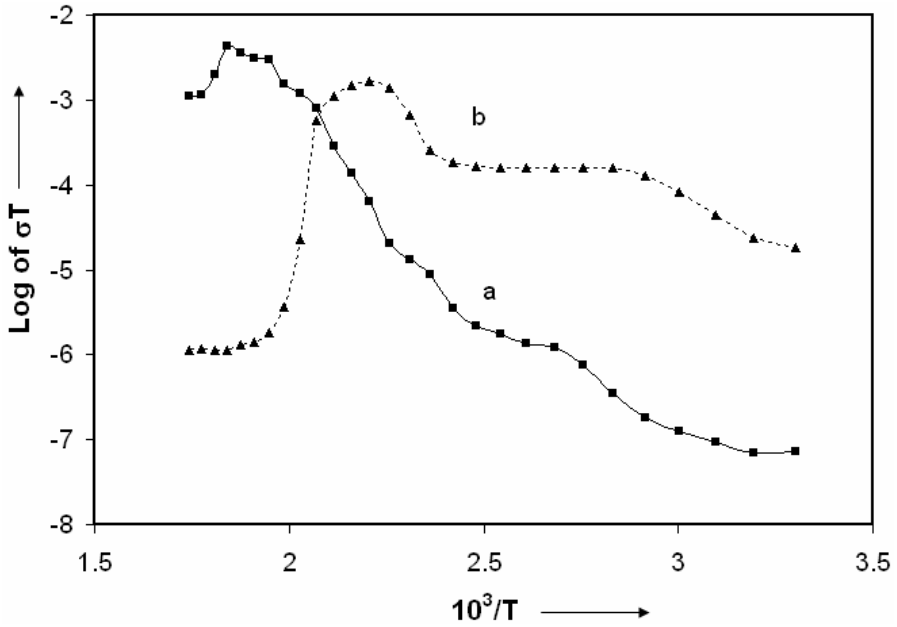


Figure 2. Log of σT vs. 1/T plot for: a. PVA, b. PVA-I_2 membrane.

same PVA solution. Again, conductance of state 'C' is higher then state 'D'. So, it can be explained that I_2 molecule act as a dehydrating catalyst and HI act as a promoter in the dehydrating process. Further, the impedance vs temperature curve of PVA and PVA-I_2 membrane at 50Hz (Figure 3) also support the above findings. A slight

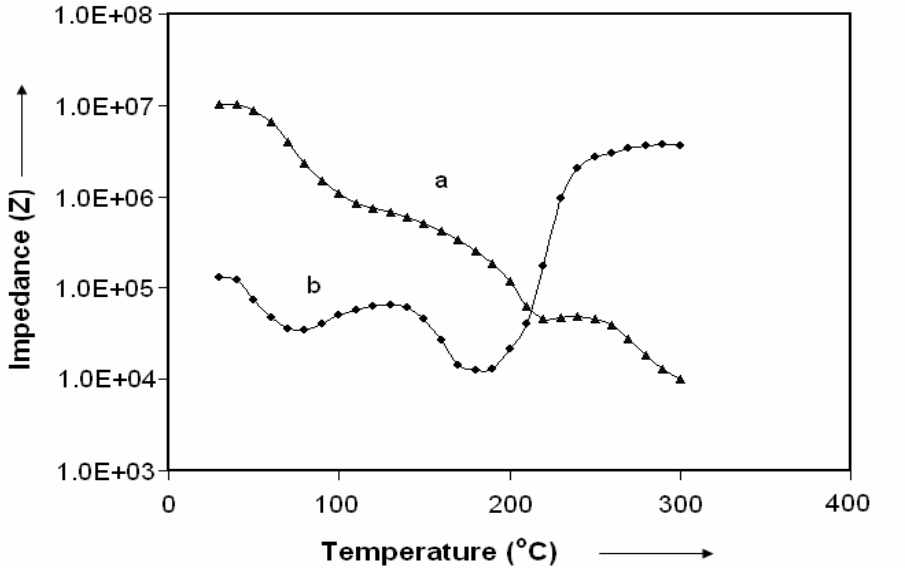


Figure 3. Impedance vs. Temperature curve at 50Hz for: a. PVA, b. PVA-I_2 membrane.

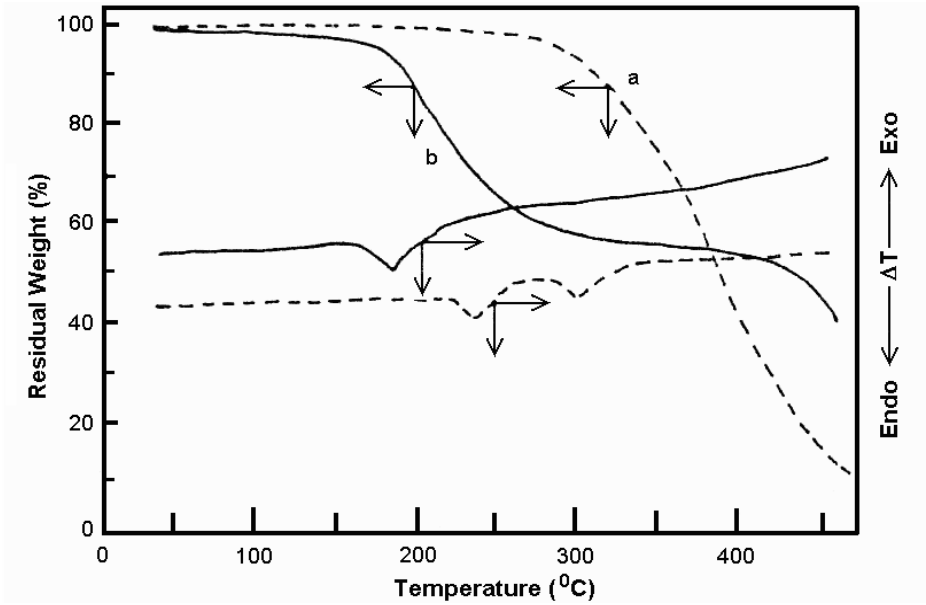


Figure 4. TGA and DTA curves of: a. PVA, b. PVA-I_2 membrane under nitrogen at a heating rate of 10°C/min.

decrease of the impedance from 70°C may include the sublimance of some amount of iodine contain in the complex membrane.

The TGA and DTA curves (Figure 4) of PVA and its complex membrane also support this explanation. From the curves it is observed that the decomposition of PVA film begins at about 230°C due to the removal of H_2O from neighbouring pairs of hydroxyl groups [12] of the PVA. The second stage decomposition begins at about 300°C due to the removal of CO, CO_2, hydrocarbons etc. [13] from the PVA film. The thermo gravimetric behaviour of the complex membrane is quite different from that of the PVA film.

There is a weight loss of 0.9 % up to about 180°C due to the sublimation of some amount of iodine contained in the complex membrane. The exact decomposition of the complex membrane begins at around 180°C, which is considerably lower than that for the PVA film. This observation and conductivity data support the formation of a single complex of PVA-I_2. The steep weight loss up to about 250°C indicates the dehydration of the complex membrane.

Acknowledgement. Authors are thankful to DST, GoI for financial assistance in the form of project No.SR/S1/PC-20/2003.

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