Evaluation of Crystallinity in Poly (Vinyl Alcohol) and Its Oxidation Products by X-Ray Diffraction*

S D WADEKAR†, H U MEHTA, A K KULSHRESHTHA‡ & N E DWELTZ
Ahmedabad Textile Industry's Research Association, Ahmedabad 380015

&

J J TRIVEDI
M G Science Institute, Ahmedabad 380009

Received 14 May 1982; accepted 24 July 1982

An X-ray method for evaluating the degree of crystallinity in poly(vinyl alcohol) is described. The method has been used for the characterization of oxidized PVA samples. The results of X-ray characterization of PVA polymers are in conformity with their infrared spectroscopic evaluation.

Polyvinyl alcohol (PVA) has assumed increasing technological significance on account of its role in textile finish formulations¹ and use as a sizing agent² for multicomponent yarns. Most of the studies carried out on the physico-chemical characterization of PVA relate to its hydrogen-bonding characteristics, solubility, stereoregularity and crystallinity. It is known that the stereoregularity of PVA chains does not lead to higher crystallinity in the product³. The physical properties of PVA, such as solubility in water, are likely to be influenced by its degree of crystallinity (DC). Estimates of DC in PVA are generally made using the infrared spectroscopy⁴, as no suitable X-ray method seems to have been reported in literature.

The present study was aimed at the development of an X-ray diffraction technique for the estimation of PVA polymer crystallinity and the application of this technique for the characterization of oxidized PVA samples, which have been fractionated from solution and represent the aggregates of insoluble high molecular weight residues. Since the principles of various X-ray methods for crystallinity evaluation are well-known, a particular procedure can be adapted for obtaining the relative crystallinities of PVA samples. We have chosen the correlation method⁵, which provides a numerical comparison of an unknown sample with the most crystalline and most amorphous extremes (standards) that can be physically obtained for the polymer species in a laboratory. The correlation method has been used widely for the estimation of DC in a variety of polymers and fibres⁶,⁷, copolymers⁸ and phase mixtures⁹. Some of the pioneering work, leading to the success of this method, was carried out earlier by Radhakrishnan and co-workers⁹—¹¹ at ATIRA. Since the procedures for the collection of polymer X-ray data and computation of DC have already been standardized in the laboratories of ATIRA, the problem of estimating DC in various PVA samples reduces to that of developing the appropriate crystalline and amorphous standards for this particular polymer.

Materials and Methods

Out of the six commercially available samples, ALCOTEX - 1017 (fully hydrolyzed grade) and PVA - 057 (partially hydrolyzed grade, containing 17% acetyl groups) were selected for X-ray analysis.

Hypochlorite oxidation¹²,¹³ of PVA—ALCOTEX - 1017 was oxidized at room temperature and at neutral pH (buffered with NaHCO₃), using 310 m moles of available chlorine per PVA monomer unit as oxidant concentration, for various durations (15 - 1440 min). The oxidized products were treated with dilute acetic acid, stirred to remove the residual chlorine and finally treated with sodium thiosulphate solution. Distilled alcohol was then added to the reaction mixture subjected to constant agitation. As a result, the polymer got precipitated and was allowed to settle down. The precipitates were filtered through a sintered
funnel and washed successively with acidic alcohol-water (80:20) mixture, alcohol-water (80:20) mixture and absolute alcohol, to remove the low molecular weight polymer fractions. They were then dried under vacuum and weighed. Unconsumed available chlorine was estimated with respect to reaction period. From this, the available chlorine consumed per PVA unit was calculated as a function of reaction period.

Infrared measurements of polymer tacticity—Density ratio \((D_{916}/D_{849})\) was measured from spectra obtained on a Perkin-Elmer, Model 180, IR spectrophotometer according to the procedure described by Fujii et al.\(^8\), using the absorptions at 916 cm\(^{-1}\) and 849 cm\(^{-1}\). A value of density ratio greater than 0.30 indicates syndiotacticity, whereas a value less than 0.25 indicates isotacticity in the PVA polymer\(^9\). For an atactic polymer, density ratio values lie in the range 0.25-0.30.

Preparation of standards—The amorphous standard was prepared by dissolving PVA - 057 in water and rapidly precipitating it by the addition of acetone. The precipitated material was allowed to dry in air. The crystalline standard was prepared by heating ALCOTEX - 1017 in triethylene glycol until dissolution occurred at 180°C. The solution was cooled slowly to room temperature, resulting in the precipitation of crystalline PVA, which was filtered and washed with methanol. The crystalline PVA standard thus obtained is insoluble in water and has a density ratio value of 0.32.

Collection of X-ray intensity data—X-ray scans were obtained by chart recording between 10 and 50°(2θ) angular range. CuKα X-rays were employed as incident beam and monochromatization of diffracted intensities was achieved electronically. The X-ray system consisted of a vertical Philips X-ray diffractometer set-up to collect transmitted intensities from any sample using a curved crystal focalizer accessory to reduce the broadening caused by the instrument. A 0.0 divergence slit and a 0.3 mm receiving slit were used. X-ray diffraction powder photographs of polymers were taken using a cylindrical film type camera, keeping a specimen-to-film distance of 3 cm.

Computation of the degree of crystallinity—X-ray intensities from the polymer sample (S), crystalline standard (C) and amorphous standard (A) were read from the chart scans at 0.25° increments in 2θ. These values formed the input for a computer programme written in FORTRAN IV and executed on an IBM 360 computer. The programme carries out the normalization of diffraction data, so that the areas under the curves between 10 and 50° (2θ) are the same for all samples and then computes the differential intensities (S-A), and (C-A), at each incremental position in 2θ. It then calculates the linear regression of (S-A) on (C-A) and the degree of crystallinity is defined by the slope of this regression line.

Results
The normalized X-ray diffractograms of crystalline and amorphous standards of PVA are shown in Fig. 1. The crystalline peaks have been indexed on the basis of an orthorhombic unit cell\(^13\) for PVA and it is rather convenient for the present analysis, as the isotactic PVA in literature has the same crystalline structure as syndiotactic PVA\(^16\)-\(^18\). X-ray diffraction photographs of the crystalline and amorphous standards are shown in Fig. 2.

X-ray diffractograms of the control (unoxidized sample) and various oxidized PVA samples are shown in Fig. 3. The X-ray crystallinities of the various PVA samples are given in Table 1. X-ray diffraction powder photographs of the control and fully oxidized PVA samples are shown in Fig. 4.

IR absorption spectra of the control and various oxidized PVA samples (Fig. 5) show interesting differences between the polymers in the stereospecific region (950 - 800 cm\(^{-1}\)) as well as in the region of the crystalline band at 1141 cm\(^{-1}\). The band at 916 cm\(^{-1}\) is specific for syndiotacticity, whereas the origin of the band at 849 cm\(^{-1}\) is attributed to the isotacticity in the polymer. The values of the density ratio \(D_{916}/D_{849}\) for the control and the oxidized PVA samples are given in Table 1. An important observation made from Fig. 5 is that in the initial stages of oxidation (i.e. up to a reaction period of 20 min), the intensity of absorption band at 1141 cm\(^{-1}\) reduces, but in the final stages of reaction this band becomes sharp.

Fig. 6 shows a semi-log plot of X-ray crystallinity and IR density ratio (which provides a measure of tacticity) as a function of oxidation reaction period.
Table 1—Results of Hypochlorite Oxidation of PVA and Characterization of Crystallinity and Tacticity in Oxidized Poly(Vinyl Alcohol) Samples

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Reaction period min</th>
<th>Wt of the insoluble polymer g/g</th>
<th>IR density ratio $D_{916}/D_{849}$</th>
<th>X-ray crystallinity %</th>
<th>Correlation coefficient</th>
<th>Available Cl$_2$ consumed per PVA unit m mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(control)</td>
<td>-</td>
<td>0.33</td>
<td>88</td>
<td>0.75</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>0.90</td>
<td>0.29</td>
<td>46</td>
<td>0.58</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>0.85</td>
<td>0.26</td>
<td>42</td>
<td>0.55</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>0.65</td>
<td>0.26</td>
<td>29</td>
<td>0.43</td>
<td>170</td>
</tr>
<tr>
<td>5</td>
<td>90</td>
<td>-</td>
<td>-</td>
<td>38</td>
<td>0.53</td>
<td>192</td>
</tr>
<tr>
<td>6</td>
<td>120</td>
<td>0.55</td>
<td>0.25</td>
<td>30</td>
<td>0.46</td>
<td>220</td>
</tr>
<tr>
<td>7</td>
<td>150</td>
<td>-</td>
<td>-</td>
<td>36</td>
<td>0.53</td>
<td>247</td>
</tr>
<tr>
<td>8</td>
<td>180</td>
<td>-</td>
<td>-</td>
<td>42</td>
<td>0.60</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>360</td>
<td>0.32</td>
<td>0.26</td>
<td>43</td>
<td>0.64</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>720</td>
<td>0.25</td>
<td>0.30</td>
<td>41</td>
<td>0.59</td>
<td>-</td>
</tr>
<tr>
<td>11</td>
<td>1440</td>
<td>0.30</td>
<td>0.31</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*Fraction insoluble in alcohol-water (80:20) mixture.

Discussion

Data presented in Table 1 give an overview of the effect of hypochlorite oxidation on the various physico-chemical characteristics of PVA. As the duration of oxidation increases, the amount of fraction soluble in 80:20 alcohol-water mixture increases and that of the insoluble fraction decreases, as is evident from the decrease in the weight of the oxidized polymer. Syndiotacticity in PVA favours a much faster reaction rate\(^ {13} \). As a result, the IR density ratio decreases from 0.33 (for the control PVA) to 0.29, 0.26 and 0.25 in oxidized PVA samples obtained after 15, 60 and 120 min of reaction respectively. During this period, the consumption of oxidant increases progressively up to 247 m moles (out of 310 m moles initially present). Thus, after 150 min of reaction, there is practically no further oxidation, but the amount of oxidized PVA obtained decreases considerably with further increase in the reaction period (from 150 to
Fig. 4—X-ray photographs of (a) control PVA and (b) fully oxidized PVA

Conclusion

During the hypochlorite oxidation of PVA, the degradation of polymer chains occurs. Oxidation is virtually completed after 150 min of reaction, but depolymerization continues to occur with further increase in the reaction period, reducing the yield of oxidized PVA. During the reaction, the X-ray
crystallinity and the tacticity of the polymer undergo changes. The X-ray diffraction method can be used for quantitative characterization of structural order in PVA and oxidized PVA. Both X-ray and IR methods show a similar trend while characterizing the oxidation products of PVA.

Acknowledgement

The authors are thankful to Dr T. Radhakrishnan, Director, ATIRA, for permission to publish this work. They express their appreciation to Shri N.R. Kothari for the help in computer analysis of data and to Shri K.M. Patel for the help in collecting X-ray data.

References