IR DETERMINATION OF OH GROUPS IN THE HARDENING OF POLYURETHANES

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Four methods are given, all having the same relative error (5%) and limit of detection (0.1%).

Determination of isocyanate groups by reaction with amines [1] is used in measurements on the setting of polyurethane; but the conversion of isocyanate is not a sufficient criterion for chemical hardening when secondary reactions can give rise to dimers, urea and biuret structures, etc. The content of OH groups gives additional information, but the usual chemical methods of acetylation [2] or phthalation [3] are inapplicable in the presence of NCO groups.

We have devised spectroscopic methods for OH in polyurethane elastomers based on polyhydroxypropylene glycols (PPG).

Determination of OH in soluble polyurethanes. Diol polyethers may be used in research on mechanisms and choice of conditions; the resulting polyurethane is still soluble when the OH groups are adequately converted. This is true for many practical formulations in the initial stages of setting. Here it is convenient to use the OH absorption at 3594 cm⁻¹, which is observable in dilute solution in inert solvents (curve 1 of Fig. 1) and which is free from overlap by NH bands.

A dilute solution of PPG in CC1₄ shows bands at 3594 and 3480 cm⁻¹ in the OH region; the intensity ratio of these in a 0.5% solution is very largely independent of the molecular weight of the PPG if this is above 700. The optical density is measured relative to the straight line drawn tangential to the base. Calibration is by reference to the optical density D₃594 cm⁻¹ for a 0.5% solution of the initial polyether in CC1₄, the absorption coefficient being k = D₃594 /cOH · l, in which cOH is the concentration of OH and l is cell thickness.

The method has been tested on specimens based on polyhydroxypropylenediol and 2,4-TDI, the reaction at 40°C being carried to complete conversion of the NCO group and with excess of OH groups over NCO. The residual OH was determined by acetylation [2]. The table gives the results from both methods, which show that the absolute error does not exceed ±0.05%, which is quite sufficient for kinetic measurements.

The measurements were made with an SP-700 spectrometer fitted with a diffraction grating at a spectral slit width of 3 cm⁻¹ with a scan speed of 25 cm⁻¹/min. Quartz cells 10 mm thick were used.

Determination of OH in insoluble polyurethanes. Here the film must be used directly. Figure 1 gives results for films made from PPG and 2,4-TDI with various initial NCO:OH ratios.

With 100% conversion of OH (curve 2 of Fig. 1), the baseline was drawn through the 3100 and 3700 cm⁻¹ points, which eliminated superposition of the NH band on the OH band (curve 3 in Fig. 1).

The previous method may be used for the OH content in the early stages; when the material becomes insoluble, but retains a suitable viscosity, a film is prepared, the subsequent setting being completed in the cell with a suitable thermostat. The film thickness of 70 µm was set by an insert between polished NaCl or CaF₂ plates. The calibration curve (curve 1 in Fig. 2) was drawn up from model polyurethanes of known OH content. All the measurements were made with an H-800 spectrometer fitted with a NaCl prism; slit width 15 cm⁻¹, scan speed 50 cm⁻¹/min.

If it is known that secondary reactions do not occur under these conditions, it is convenient to use relative measurements and thereby eliminate the film thickness. Applying Beer's law to the 3480 and 3300 cm⁻¹ bands (measured relative to baseline 3 in Fig. 1), we have

\[ D_{3480} = k_{3480} c_{OH}, \]
\[ D_{3300} = k_{3300}^\text{NH} \cdot I_{\text{NH}} + k_{3300}^\text{OH} \cdot I_{\text{OH}}, \]  

in which \( c_{\text{OH}} \) and \( c_{\text{NH}} \) are the concentrations of OH and NH groups in the mixture and the \( k \) are the corresponding absorption coefficients. During setting

\[ c_{\text{OH}}^0 = c_{\text{OH}} + \frac{15}{17} \cdot c_{\text{NH}}, \]  
in which \( c_{\text{OH}}^0 \) is the initial OH content in wt. %.

\[ \frac{D_{3300}}{D_{3480}} = \frac{\frac{c_{\text{OH}}}{c_{\text{OH}}}^0}{\frac{c_{\text{OH}}}{c_{\text{OH}}}^0}, \]  

relation for model polyurethanes.

Solution of (1)-(3) gives

\[ \frac{D_{3300}}{D_{3480}} = \frac{15}{17} \cdot \frac{k_{3300}^\text{NH}}{k_{3480}^\text{NH}} \cdot \frac{c_{\text{OH}}^0}{c_{\text{OH}}} - \frac{15}{17} \cdot \frac{k_{3300}^\text{OH}}{k_{3480}^\text{OH}} + \frac{k_{3300}^\text{OH}}{k_{3480}^\text{OH}}. \]  

The line in Fig. 3 gives the constants of (4) as

\[ \frac{c_{\text{OH}}}{c_{\text{OH}}}^0 = \frac{0.95}{\frac{D_{3300}}{D_{3480}}} + 0.84. \]  

This reduces the problem to measurement of \( \frac{D_{3300}}{D_{3480}} \) for a film of any suitable thickness, (5) then giving the OH content.

The table gives results from tests of these two methods on model polyurethanes. The substantial error from use of the 3480 cm\(^{-1}\) band is due to the variation in thickness from specimen to specimen, it being difficult to reproduce 70 \( \mu \)m exactly.

Determination of OH from near-IR absorption. The use of thin films has the disadvantage of adhesion to the expensive NaCl or CaF\(_2\) plates. This makes it advantageous to use the first overtone of the OH stretching, since glass can be used in the cells in this region. Figure 4 shows this OH overtone; the band, which vanishes on setting, has a frequency of 6985 cm\(^{-1}\), though this is overlapped by absorption of the polyether, so measurements are best made relative to end-acetylated initial polyether (curve 3 of Fig. 4). The spectrum for material set with excess of isocyanate shows that the NH absorption hardly overlaps the OH (curve 1 of Fig. 4). All of these measurements were made with an SP-700 spectrophotometer fitted with a quartz prism (spectral slit width 35 cm\(^{-1}\), scan rate 750 cm\(^{-1}\) min), the cells being ordinary test-tubes up to 2 cm in diameter, since the narrow (3 mm) beam allows one to neglect the curvature of the surface. The