POLYVINYL ALCOHOL

New specifications prepared at the 61st JECFA (2003) and published in FNP 52 Add 11 (2003). An ADI of 50 mg/kg bw was established at 61st JECFA (2003).

SYNONYMS Vinyl alcohol polymer, PVOH, INS No. 1203

DEFINITION Polyvinyl alcohol is a synthetic resin prepared by the polymerization of vinyl acetate, followed by partial hydrolysis of the ester in the presence of an alkaline catalyst. The physical characteristics of the product depend on the degree of polymerization and the degree of hydrolysis.

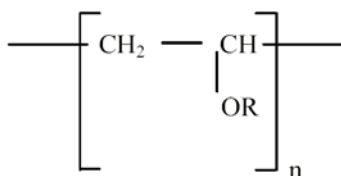Chemical names Ethenol homopolymer

C.A.S. number 9002-89-5

Chemical formula $(C_2H_3OR)_n$ where R=H or $COCH_3$ (randomly distributed)

Structural formula

Where R=H or $COCH_3$ (randomly distributed)

DESCRIPTION Odourless, translucent, white or cream-coloured granular powder.

FUNCTIONAL USES Coating, binder, sealing agent and surface-finishing agent.

CHARACTERISTICS

IDENTIFICATION

Solubility (Vol. 4) Soluble in water, sparingly soluble in ethanol.

pH (Vol. 4) 5.0 – 6.5 (1 in 25)

Infrared spectrum (Vol. 4) The infrared absorption spectrum of a potassium bromide dispersion of the sample corresponds to that of a poly vinyl alcohol standard (see Appendix).

Colour reaction A Dissolve 0.01 g of the sample in 100 ml of water with warming and let the solution cool to room temperature. To 5 ml of the solution, add one drop of iodine TS and a few drops of boric acid solution (1 in 25). A blue colour is produced.

Colour reaction B Dissolve 0.5 g of the sample in 10 ml of water with warming and let the solution cool to room temperature. Add 1 drop of iodine TS to 5 ml of solution and allow to stand. A dark red to blue colour is produced.

Precipitation reaction Add 10 ml of ethanol to the remaining 5 ml of solution prepared for Colour reaction B. A white, turbid or flocculent precipitate is formed.

PURITY

<u>Loss on drying</u> (Vol. 4)	Not more than 5.0% (105°, 3 h)
<u>Residue on ignition</u> (Vol. 4)	Not more than 1.0%
<u>Water insoluble substances</u> (Vol. 4)	Not more than 0.1% Substitute a 100-mesh screen for the sintered-glass filter specified in Volume 4
<u>Particle size</u>	Not less than 99.0% material to pass through a 100 mesh sieve Determine by sieving for 30 min 100g of sample through a 100 mesh sieve and weigh the material passing through the sieve.
<u>Methanol and methyl acetate</u>	Not more than 1.0 % of each See description under TESTS
<u>Acid value</u>	Not more than 3.0 See description under TESTS
<u>Ester value</u>	Between 125 and 153 mg KOH/g See description under TESTS
<u>Degree of hydrolysis</u>	Between 86.5 and 89.0% See description under TESTS
<u>Viscosity</u>	4.8 - 5.8 mPa•s (4% solution at 20º) See description under TESTS
<u>Lead</u> (Vol. 4)	Not more than 2 mg/kg Determine using an atomic absorption technique appropriate to the specified level. The selection of sample size and method of sample preparation may be based on the principles of the methods described in Volume 4, "Instrumental Methods".

TESTS

PURITY TESTS

<u>Methanol and methyl acetate</u>	Place 2.0 g of the sample into a 100 ml screw-cap bottle, and add a magnetic stirrer. Add 98 ml of water and 30 µl of acetone. Close the bottle tightly with the screw cap and heat in a water-bath, stirring continuously. Once the solution becomes clear, remove the bottle from the water bath and allow it to cool to room temperature. Prepare a standard by taking 2 ml of a mixed solution of methanol and methyl acetate (1.2 % v/v solution), 98 ml of water and 30µl acetone; proceed as above starting from "close the bottle…Temperature".

<u>GC Conditions:</u>
    Column: Sunpak A (3.2 mm i.d. x 3 m) or equivalent
    Column temperature: 160°
    Injector temperature: 160°
    Detector temperature: 160°

Inject 0.4 $\pm$ 0.1µl of the standard solution into the gas chromatograph and record the peak areas (PAs) for methanol, methyl acetate and acetone.
Inject 0.4 $\pm$ 0.1 µl of the sample solution and record the peak areas (PAs) for

methanol, methyl acetate, and acetone.
Calculate the methanol and methyl acetate content using the formulae:

$$\text{Methanol (wt\%)} = PA(\text{methanol})/PA(\text{acetone}) \times PR_1 \times 0.024 \times 100/2$$

$$\text{Methyl acetate (wt \%)} = PA(\text{methyl acetate})/ PA(\text{acetone}) \times PR_2 \times 0.024 \times 100/2$$

where
  0.024 = conversion factor to obtain the masses of methanol and methyl acetate added to 30 µl acetone (density = 0.8) for the methanol/methyl acetate standard;
  PR_1 and PR_2 are the peak area ratios $PA(\text{acetone})/PA(\text{methanol})$ and $PA(\text{acetone})/PA(\text{methyl acetate})$, respectively, of the standard 1.2% methanol and methyl acetate aqueous solutions.

Acid value

Add 250 ml of water and a stir bar into a 500-ml round-bottom flask, attach a reflux condenser and begin heating in a boiling water bath. Add 10.0 g of the sample and continue heating for 30 minutes while stirring continuously. Remove the flask from the water-bath and continue stirring until the solution reaches room temperature. Take 50 ml of the solution, add 1 ml of phenolphthalein TS and titrate with 0.05 M potassium hydroxide until the pink colour persists for 15 seconds; record the titre in ml (V). Calculate the acid value, A.

$$A = (56.1 \times V \times M)/W$$

Where
  56.1 = the formula weight of KOH
  M = molarity of the KOH solution
  W = weight of sample (g).

Ester value

Accurately weigh about 1.0 g of sample into a 250-ml round-bottom flask, add 25 ml 0.5 M alcoholic potassium hydroxide, 25.0 ml of water and a few glass beads. Attach a condenser and allow the contents to reflux for 30 minutes in a boiling water-bath. Let cool to room temperature, remove the condenser, add 1 ml of phenolphthalein TS and titrate immediately with 0.5 M hydrochloric acid; record the titre in ml (V_1).

Carry out a blank test under the same conditions. Titrate with 0.5 M hydrochloric acid and record the titre in ml (V_2). Calculate the saponification value, S:
  $$S = 56.1(V_2 - V_1) \times M/W$$
Where
  56.1=formula weight of KOH
  M = molarity of the hydrochloric acid solution
  W = weight of the sample in (g).
Calculate the ester value, E:
  $$E = S - A$$
Where
  S = saponification value
  A = acid value

Degree of hydrolysis

Convert the saponification value obtained during the determination of the ester value to the "dried basis" (S_{db}):

$$S_{db} = (S \times 100)/(100 - LOD)$$

Where

LOD= Loss on Drying.

The degree of hydrolysis is:

$$100 - [7.84 \, S_{db}/(100 - 0.075 \, S_{db})]$$

Viscosity

Calibration of *capillary-type* viscometers

An oil of known viscosity is used to determine the viscometer constant (k*)*.

Ostwald-Type Viscometer: Fill the tube with the exact amount of oil (adjusted to 20.0±0.1º), as specified by the manufacturer. Use either pressure or suction to adjust the meniscus of the column of liquid in the capillary tube to the level of the top graduation line. Allow the liquid to flow into the reservoir against atmospheric pressure by opening both the filling and capillary tubes. If either tube is not open, false values might be obtained. Record the time (seconds), for the liquid to flow from the upper mark to the lower mark of the capillary tube (efflux time).

Ubbelohde-Type Viscometer: Place a quantity of the oil (adjusted to 20.0 ± 0.1º) in the filling tube, and transfer to the capillary tube by gentle suction. Keep the air vent tube closed in order to prevent bubble formation in the liquid. Adjust the meniscus of the column of liquid in the capillary tube to the level of the top graduation line. Allow the liquid to flow into the reservoir against atmospheric pressure by opening both the filling and capillary tubes. If either tube is not open, false values might be obtained. Record the efflux time (seconds).

The viscosity constant for *capillary-type* viscometers is given by:

$$k = v/dt,$$

Where, v is the known viscosity (mPa•s) of the oil used for viscometer calibration; d is the density (g/ml) of the liquid tested at 20º/20º; and t (seconds) is the efflux time.
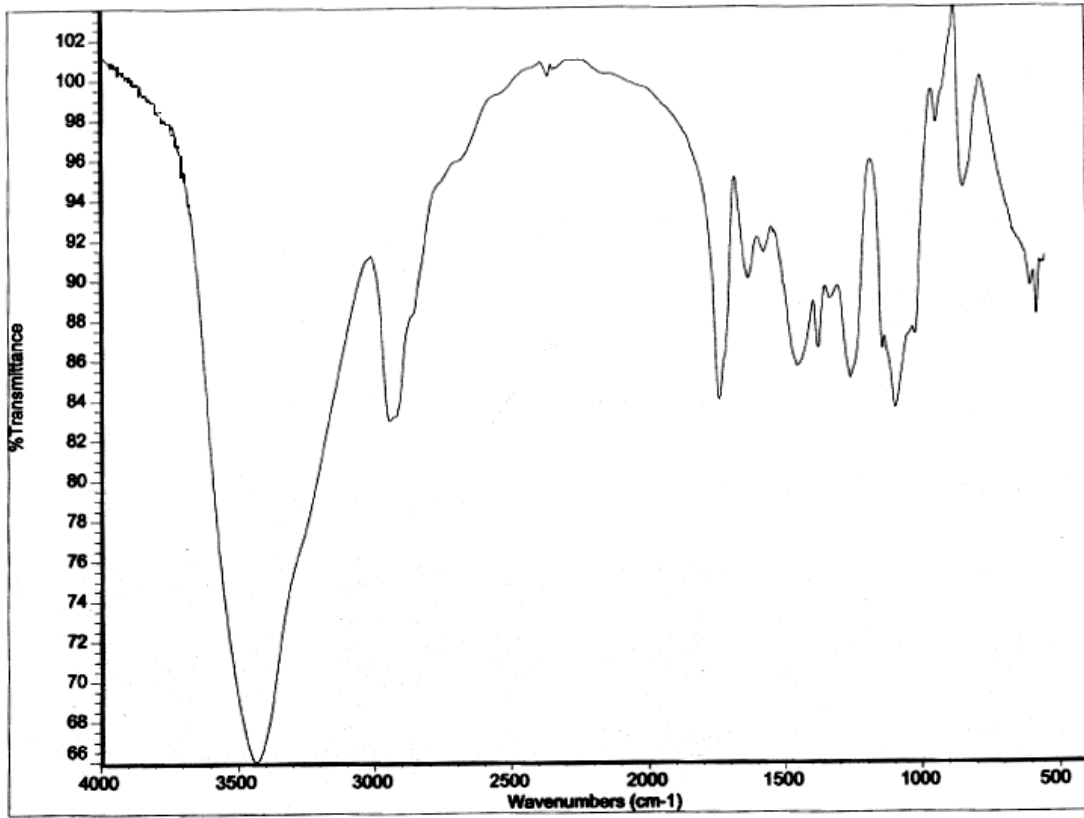
Procedure:

Weigh a quantity of undried sample equivalent to 6.00 g on the dried basis. Into a tared 250-ml flask containing a magnetic stir bar and approximately 140 ml of water, quickly (seconds) transfer the sample, while simultaneously stirring slowly and continuously. Once the sample appears thoroughly saturated, slowly increase the stirring rate to minimize the entrainment of air in the mixture. Heat the mixture to 90°, and maintain it at this temperature for approximately 5 minutes; discontinue heating and continue stirring for 1 hour. Add water in small amounts to attain a total mixture weight of 150 g, and resume stirring until the mixture appears homogenous. Filter the mixture through a tared 100-mesh screen into a 250 ml conical flask, cool the filtrate to about 15°, mix, and determine its viscosity at 20º using an appropriate viscometer (follow the manufacturer's instructions). NOTE: The temperature at which the viscosity measurement is made must be strictly controlled.

For measurements using *capillary-type* viscometers, the viscosity is given by:

$$v = kdt$$

where t is the efflux time for the sample solution and d is its density at 20º.

Appendix

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