Work 4

Texture characteristic of membrane materials – mercury porosimetry

This laboratory work introduces the method of mercury porosimetry which is important for determination of textural characteristic of solid materials. This method is especially used to study of catalysts, membranes, sorbents, raw materials, ceramics or construction materials, corrosion degree of historical buildings or statues etc. We can measure pieces of solids or powders and gain porosity value and pores size distribution of various materials.

Theory

Mercury porosimetry is based on the capillary law governing liquid penetration into small pores. This law says, in the case of a non-wetting liquid like mercury (contact angle is bigger than 90°), that mercury penetrates into pores under external pressure only. For cylindrical pores it is expressed by the Washburn equation:

$$g\rho h\pi r^2 = -2\pi r\gamma.\cos\Theta,$$

where g [m/s^2] is gravity acceleration, ρ [g/m^3] mercury density, h [m] is height of mercury column in pore, r [m] pore radius, γ [N/m] the surface tension of mercury and Θ is the contact angle. This equation we can modify to:

$$g\rho h = P = -2\gamma.\cos\Theta / r,$$

here P [N/m^2] is the applied pressure. We can see the radius pore is inverse proportional to the applied pressure so, the higher pressure the narrower pores are filled with mercury.
The volume of mercury V penetrating the pores is measured directly as a function of applied pressure. This $P - V$ information serves as a unique characterization of pore structure.

Pores are rarely cylindrical, hence the above equation constitutes a special model. Such a model may not best represents pores in actual materials, but its use is generally accepted. The surface tension of mercury varies with purity, its usually accepted value and the value

recommended here is 485 dynes/cm. The contact angle between mercury and solid containing the pores varies somewhat with solid composition. A value of 130° is recommended in the absence of specific information.

The sample is suitable for our measurement, if the mercury is non-wetting to this material and of course if the material does not react with used liquid (mercury).

Experiment

The measurement is realized by analyzer unit Autopore IV of Micromeritics company. The unit has got two parts. There are two low pressure ports on the top, where the evacuation of sample and low pressure analysis from 0,01 MPa to 0,20 MPa takes place. That means the pore radius from 100 μm to 3 μm approximately are analysed. The high pressure chamber is used for high pressure analysis from 0,20 MPa to 400 MPa. It covers the range of pore radius from 3 μm to 1,5 nm.

During analysis the applied pressure increases step by step to desired value and mercury volume penetrating the pores is measured. From these data (pressure and corresponding value of intrusion volume) we can gain the pore size distribution. The whole analysis is controlled by computer.

Important notice!

Mercury is poison. It can enter the body through the skin, lungs or digestive system. Health hazards from mercury can be prevented by limiting the average concentration of mercury. This is achieved through proper ventilation in the work area, proper clean-up of mercury spills and good personal hygiene to prevent contamination of hands.

Work instruction for 2 tasks:

I. Calibrating penetrometer

We use special vessel – penetrometer -for measurement and we need to know its precise volume. So the first task is to obtain the empty volume of a penetrometer.

1. Seal the penetrometer and weigh the empty assembled penetrometer.
2. Install the penetrometer in the low pressure port.
3. Perform the low pressure analysis.
4. Remove the penetrometer filled by mercury from the low pressure port, weigh it and calculate volume of penetrometer using the weight and density of mercury.

II. Measuring of sample porosity and pore size distribution

The second task is to measure porosity and pore size distribution of particular sample (usually of membrane).

1. Weigh the sample and load it to the another penetrometer (previously calibrated).
2. Seal the penetrometer and weigh the assembled penetrometer with sample together.
3. Install the penetrometer in the low pressure port.
4. Perform the low pressure analysis.
5. Remove the penetrometer from the low pressure port, weigh the penetrometer with sample and mercury together.
6. Install the penetrometer in the high pressure port and perform it.
7. Process the data.

Every equipment manipulation is possible with assistant only!

Final report includes:

- Introduction (briefly method theory, definitions of structural properties, technique, …)
- Penetrometer calibration - determination of penetrometer volume
- Calculation of sample structural properties (bulk density, apparent density and porosity)
- Graphs (use the logarithmic scale of X-axis):
  1) cumulative curve X-axis = pore radius ***(r)*** calculated from Washburn equation,
     Y-axis = cumulative intrusion volume ***(V)***
  2) differential curve X-axis = pore radius ***(r)*** calculated from Washburn equation,
     Y-axis = diferential volume ***(dV)***
  3) frequency curve X-axis = pore radius ***(r)*** calculated from Washburn equation,
     Y-axis = derivation of cumulative curve ***[-(dV/d log r)]***
- Conclusion

Relations:

BULK DENSITY
ρ_{bulk} = sample weight/ solid volume (with pores)

APPARENT DENSITY
ρ = sample weight/ solid volume (without pores)

POROSITY
ε = pores volume/ (solid volume + pores volume) = $1 - (\rho_{bulk}/ \rho)$