

Research Article

Measurement Methods of Micro-structure of Porous Materials

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Abstract: Porous media is used in many areas of applied science and engineering and its characterization of porosity and micro-structure is very important, therefore, it is very necessary to know the measurements of pore structure of porous materials. In this study, some traditional methods that are used to measure micro-structure of porous material were briefly introduced in this study, including mercury porosimetry method, gas adsorption method, electronic microscope method, small angle X-ray scattering method and bubbling test method, followed by some emerging technology, including the combination of different methods, medical imaging technology and image processing software. Meanwhile merits and drawbacks as well as the existing problems of methods mentioned were analyzed and application range was described. At last, the developing trends and prospect of newly emerging methods, which is used to measure micro-structure of porous material, are also described briefly.

Keywords: Micro-structure, porous material, testing technology

INTRODUCTION

Porous materials, called porous media, are a kind of composite medium, which consist of solid matrix and fluid and widely exist in nature and human life. Its specific porous structure endows it with high specific surface area, large porosity, good permeability, excellent absorbability and other superexcellent physical and chemical properties, which makes it extensively applied in chemical industry, bio-medicine, environmental protection, functional materials, etc and play an important role in the development of economy, progress of technology and enhancement of human life.

Owing to its complicated internal structure and various pores, porous material has no characteristic length and is extremely irregular. All transfer coefficients present non-uniformity and uncertainty. Meanwhile, the actual heat and mass transfer process of porous materials is very different from that happens in homogeneous medium (Chen *et al.*, 2015). Therefore, the study on micro-structure of porous material has been an urgent issue.

Commonly, there are two kinds of testing methods to determine its micro-structure, namely, direct method and indirect method. Direct method means that micro-structure is observed by electronic microscope while indirect method implies that based on some physical phenomenon related with micro-structure of porous material, relevant physical parameters are firstly obtained through conducting experiments, then equivalent diameter is calculated under the assumption that all micro-pores are uniform and straight cylinders

(Li *et al.*, 2010). Concrete measurements include: mercury porosimetry method, gas adsorption method, filtration method, electronic microscope method, penetration method, small angle X-ray scattering method, bubbling test method and others, among which mercury porosimetry method and gas adsorption method are most diffusely adopted. Thereby, some commonly utilized methods and several newly born methods were introduced in this study, that is: mercury porosimetry method, gas adsorption method, electronic microscope method, small angle X-ray scattering method, bubbling test method, expecting this study will provide theoretical basis for the development of porous material.

DISCUSSION

Mercury porosimetry method: Washburn first proposed an idea that the micro-structure of porous material can be obtained by injecting non-wetting liquids into the micro-pores, which becomes theoretical basis of modern mercury porosimetry method. Washburn equation is shown as follows (Mohammed, 2015):

$$r = \frac{2\gamma_{Hg} \cos \theta}{P} \quad (1)$$

where,

γ_{Hg} = The interfacial tension of Hg

θ = Contact angle

r = Pore diameter

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P = Supplied pressure

Equation (1) shows an easy relationship between pore diameter and pressure. By relationships between the volume of non-wetting liquids into pores and the corresponding pressure, distribution of pore diameter can be obtained. Under a certain pressure, mercury can penetrate into pores with certain size, in which mercury injected into pores stands for the volume of internal pores. By gradually increasing pressure and at the same time calculating the quantity of mercury injected into micro-pores, the distribution of pore volume of porous material will be available. As a result, mercury porosimetry method is a major method to test the pore diameter distribution. Wang *et al.* (2006) analyzed pore size distribution and porosity of filter paper, coated paper and offset paper with mercury porosimetry method, results of which showed micro-structure of coated paper and pore size distribution can be accurately obtained. Xie *et al.* (2006) utilized this method, combined with Washburn equation and succeeded in analyzing the holistic porosity of shale, results of which showed comparing to gas adsorption method, heterogeneity of pore distribution had a minor effect on this method and this method can make up the defects of gas adsorption method in analysis of larger pores.

The most frequently used pore model in mercury porosimetry method is cylindrical pore, in which pore diameter is that of the model's, contact angle θ is considered as 140° and interfacial tension of Hg γ_{Hg} is regarded as 480 mN/m. Hence Eq. (1) is turned into general Eq. (2):

$$P \times r = 7.35 \times 10^8 \quad (2)$$

Seen from Eq. (2), pore diameter r is in inverse proportion to pressure P . When supplied pressure is zero, mercury will not enter the interior pores; only when pressure increases to a certain value will mercury penetrate into corresponding pores with specific size. By measuring the volume of mercury injected into pores under different pressure, the volume of corresponding pore can be obtained as well as the pore diameter, the relationship of which can be expressed by plot of $P \sim r$, thus distribution of pore diameter can be obtained.

Mercury porosimetry method, due to simple theory, quick experiments and wide range of pore size (5 nm~350 μ m) that can be tested, is usually used to analyze porosity, specific surface area and pore structure of porous materials when pore size distribution is not uniform. Therefore this method is standard and typical to test pore diameter distribution of macro-pores and meso-pores. Yet, accuracy of the testing results will be affected by several factors. For example:

- Mercury will be compressed at high pressure and its viscosity will increase with the increase of

pressure (Qi *et al.*, 2012). So dilatometer and compressibility of mercury should be corrected when pore diameter distribution is under test.

- Contact angle θ is often regarded as 140° because of cylindrical pore model and surface of porous materials is considered homogeneous. However, under actual circumstance, contact angle is usually not 140° , which is because it will be affected by many factors, including rough surface, complicated geometry, chemical properties of the surface (strong polarity will lead to a change of pore diameter distribution), also purity of mercury and water that is adsorbed to porous materials have a major influence on contact angle. The entire situation stated above make contact angle have a wide range. Moreover, even if contact angle has an error of 1° , the results will have a deviation of 20% so it is better to use the measured value as contact angle.
- Purity of mercury will influence interfacial tension, thus it is better to use mercury of AR.
- For those porous materials which have weak structure, or can be damaged utterly at high pressure and the compressibility of porous materials shall be revised and analyzed.

Gas adsorption method: Static adsorption capacity of nitrogen is often applied in this method and its main process is: porous material placed in gas system is made to develop physical adsorption at very low temperature. When temperature is at liquid nitrogen temperature and relative pressure is 0.05~0.99, adsorption and desorption of nitrogen will occur in the surface of porous materials and 22 adsorption numbers at different pressure can be available, then adsorption and desorption isotherms can be depicted. Through the analysis of isotherms, distribution of pore size, specific surface area, porosity and pore volume shall be accessible. Zhang *et al.* (2011) analyzed specific surface area of sponge palladium in conditions of different degassing time and temperature by low temperature nitrogen adsorption method and obtained adsorption-desorption isotherms of sponge palladium; meanwhile BJH equation was employed to study distribution law of pore size with adsorption isotherm and precision of the results was good in this method. Dong *et al.* (2007) tested pore structure of cotton fiber by adsorption and desorption isotherms and DFT, through comparison to electronic microscope, they concluded nitrogen adsorption method is an effective method and can obtain much more information about the pore size. As nitrogen belongs to inert material and it is not easy to develop chemical adsorb at liquid nitrogen temperature, the original characteristic of materials will not be altered during testing process (Yang *et al.*, 2013).

Nitrogen adsorption method is based on adsorption law of gas on surface of solid and the mechanism is micropore filling. By analysis of thermodynamics and kinetics of this process, multi-molecular absorption equation, i.e., BET equation, was found and this is a well-developed and extensively adopted method, which is based on the adsorption isotherms principles of nitrogen. At liquid nitrogen temperature, adsorption capacity of nitrogen on surface of solid is determined by relative pressure of nitrogen P/P_0 , where, P is partial pressure of nitrogen and P_0 is the saturated vapor pressure of nitrogen at liquid nitrogen temperature. When $P/P_0 < 0.05$, it is not easy to establish adsorption equilibrium; when $0.05 < P/P_0 < 0.35$, adsorption amount and P/P_0 accord with BET equation, which is the basis of nitrogen adsorption method to test Specific surface area; when $P/P_0 > 0.4$ and pressure continues to increase, there will generate capillary condensation phenomenon and form condensation liquid in macropores for pore diameter will become thin after adsorbing multi-layer molecules. As a result, internal surface area shall be reduced and adsorption equilibrium will be broken. Gas is adsorbed into the pores and condenses into liquid, thus making adsorption amount sharply increase. When all pores are filled with liquid adsorbent in surface of porous material, adsorption amount would become maximum. At this time, capillary condensation model, i.e., BJH cylinder model, is utilized to analyze pore size distribution according to the branch of desorption in adsorption isotherm. By experiments and theoretical analysis, pore volume as well as pore size distribution can be determined. Calculation formula is as follows (Chen *et al.*, 2011):

$$r_k = -\frac{2\gamma V_m}{RT \ln \frac{P}{P_0}} + 0.345 \left(-5 \ln \frac{P}{P_0}\right)^{\frac{1}{3}} \quad (3)$$

where,

- r_k = Pore diameter
- V_m = Molar volume of nitrogen
- γ = Surface tension of nitrogen at boiling point
- P/P_0 = Relative pressure of nitrogen
- T = Absolute temperature

Gas adsorption method is regarded as one of the best methods to test micro-structure of solid as much statistical information can be obtained, say specific surface area, pore volume, pore size distribution; moreover this method can reveal general characteristics of material. Nevertheless, this method has serious errors when testing larger pores since the adsorbed gas is much more difficult to saturate in larger pores and adsorption equilibrium is harder to arrive. As a result, it cannot be used to test the range of pore size and pore structure comprehensively. For meso-pores and micro-pores with pore diameter being less than 50

nm, the results are precise while for macro-pores, some serious errors will be generated. Hence maximum pore diameter is 100 nm or so for this method. When the specific surface area of material is smaller, argon or krypton adsorption method is exploited instead as their molecular diameters and saturated vapor pressure are much lower and range of pore size that can be tested will be much wider.

Electronic microscopes: Since 1970s, there has been a great progress in electron microscope, including Scanning Electron Microscope (SEM), Transmission Electron Microscopy (TEM), High Resolution Transmission Electron Microscopy (HRTEM), Scanning Tunneling Microscope (STM), Atomic Force Microscope (AFM), Environmental Scanning Electron Microscope (ESEM), etc. They develop a completely new prospect, making observation way of nature transform from macrocosm to super microcosm. Among electronic microscopes, Scanning Electron Microscope (SEM) with high resolution has an explicit advantage in morphology observation and dimension measurement of materials with nanoscale due to simple operation. Besides, high magnification makes images clearer, intelligent operation can be realized without being affected by human factors and it can be combined with numerous hardware and software, so accuracy of this method is relatively high and this method has numerous functions, making it extensively used in analysis of micro-structure.

In this method, the surface of sample is irradiated in the way of raster scanning with ultrafine and focused electron beam being light source and then images are formed through the message generated by interaction between incident electron and sample. In this method, not only surface morphology of particle can be observed, but also distribution of particle size and amount of particle can be analyzed and measured if combined with Energy Dispersive Spectrometer (EDS). Because of high accuracy, Scanning Electron Microscope (SEM) has an irreplaceable role in particle size analysis. For example, Fang *et al.* (2007) studied the variation characteristics of micro-structure of marine soft soil during consolidation by contrast of SEM images at different consolidation pressure. Teng and Hui (1991) made a research on surface characteristic of quartz grain, results of which showed Scanning Electron Microscope (SEM) is indispensable for indicating micro-structure and appropriate use of Scanning Electron Microscope (SEM) is a reliable assurance to obtain micro-structure of porous materials.

In spite of extensive application of electronic microscope in analysis of micro-structure, yet, it belongs to qualitative analysis of two-dimension and the attained porosity cannot reflect practice thus it cannot be used to test distribution of pore size, volume

and surface area of pores; furthermore, although this method belong to nondestructive testing, the preparation of sample usually goes through cutting, inlaying, polishing and other pretreatments, which brings some defects to this method, such as: sample preparation is difficult and sample is vulnerable. What's more, despite that nano-scaled pores can be observed by this way, however, human factors will have a major impact on measuring the pore size. Besides, the amount of sample prepared is limited; the range of particle size cannot be determined by several photographs as the representativeness of results is poor. In addition, there exists radiation damage to porous material brought by electron beam with high energy.

Small Angle X-ray Scattering method (SAXS): He *et al.* (2006) discovered SAXS phenomenon and raised the theory of SAXS. Later, Guinier, Porod and Debye successively developed SAXS theory and established its application, which has become the basis of SAXS method to study various systems.

Small Angle X-ray Scattering method (SAXS) is used to analyze physical structure and measure distribution of pore size in modern times. It not only can test pore size of open pores, but also can assess pore size of closed pores. By contrast to other testing methods, Small Angle X-ray Scattering method (SAXS) can better measure micro-structure of materials on the whole. Furthermore, internal structure of sample will not be damaged in this method, thus samples will keep its authenticity and integrity. As a result, Small Angle X-ray Scattering method (SAXS) becomes an extensively used method in practice. Zhao *et al.* (2014) obtained internal characteristic, pore structure parameter and pore amount as well as pore size distribution of particulates exhausted by diesel during oxidation process by the method of thermo gravimetric analysis and Small Angle X-ray Scattering (SAXS). Wang and Zeng (2004) measured distribution of particle size of several oxides with nano-scale by X-ray diffractometer in the method of Small Angle X-ray Scattering (SAXS), then confirmed this method was viable to test the granularity of nanometer powder.

When X-ray with slender light penetrates porous granules, then is scattered by electrons inside the grain and dispersed in a very small region near elementary beams, this phenomenon is called Small Angle X-ray Scattering (SAXS). Scattering intensity is in direct proportion to the square of electron density difference between that of particle and ambient medium, then by scattering intensity formula of the electrons in the system and derivation, an approximate expression of Guinier formula that is to state the scattering of whole system can be obtained, which is shown as follows (Hiroyuki and Yuta, 2015):

$$I(2\theta) = I_e MN^2 \exp\left[-\frac{4\pi^2}{3\lambda^2} R^2 (2\theta)^2\right] \quad (4)$$

Conduct logarithmic transformation on both sides simultaneously into Eq. (5):

$$\lg I(2\theta) = \lg I_e MN^2 - \frac{4\pi^2}{3\lambda^2} R^2 (2\theta)^2 \lg e \quad (5)$$

where,

2θ = Scattering angle

$I(2\theta)$ = Scattering intensity at angle of 2θ

I_e = Scattering intensity of a single free electron

M = The pore number within unit volume of porous media

N = The difference of electrons between the framework of porous media and pore space within unit volume

λ = Wave length of X-ray

R = Gyration radius of particles

Equation (5) refers to a straight line between $\lg I(2\theta)$ and $(2\theta)^2$ and its slope is $-4\pi^2 R^2 \lg e / 3\lambda^2$, from which gyration radius can be calculated. When particles can be regarded as sphere, there lies a relationship of gyration radius and radius of particle, which is shown below and from which average radius of particle can be computed:

$$R = \frac{3r^2}{5} \quad (6)$$

To sum up, if only average pore diameter of particle needs to be measured and doesn't need high precision, Small Angle X-ray Scattering method (SAXS) is convenient, time-saving and economical. Images obtained from this method can make internal structure and arrangement condition of pores reappear, the difference between two samples shall be obviously unfolded and three-dimensional morphology of porous materials can be detected such as thickness, dimension of pore wall and pore size, etc. According to international requirements, superfine powder with particle size being 1~300 nm can be tested. Generally, the number of particles participating in the scattering can reach up to hundreds of millions; therefore the results are representative statistically. What's more, internal structure of porous media not only can be observed qualitatively, but also analyzed quantitatively. Whereas, some certain substances can strongly absorb the characteristic X-ray of anode target and fluorescence radiation phenomenon forms, which will cause small angle X-ray scattering not to accurately measure micro-structure of porous materials.

Bubbling test method: Bubbling test method, which takes advantage of physical laws of fluid flow in micro-channels, is a commonly applied method to measure pore size as it veritably reflects the actual situation of fluid flow in micro-channels.

The basic operating process of this method is as follows: porous material first utterly soaks into fluid A which has good wettability, then another fluid B, say compressed air, pushes fluid A out from micro-channels. When the pressure of fluid B increases to a certain value, fluid A will be pushed out from micro-channels and form first drop; Then continuously increasing pressure of fluid B makes the micro-channels of fluid A transform into that of fluid B. As a result, more fluid A flushes out from pores and fluid B will be filled with pores until all fluid A is eliminated (Yu *et al.*, 2010). During the process, flux and pressure shall be recorded simultaneously. When the relationship of flux and pressure is a straight line, it means all pores of the sample have been opened, which denotes measurement can be finished.

For most actual porous materials, all pores can be treated as capillary tubes with different sizes and various shapes, thus, porous materials are supposed to consist of parallel capillary tubes. The more different pores are, the slower fluid flow will be, avoiding turbulent flow. Viscous fluid obeys Poiseuille's law when it goes through cylinder capillary in laminar flow conditions, which is shown in Eq. (7). Pore diameter of capillary is calculated by equation (Wang *et al.*, 2012):

$$r = \frac{2\gamma \cos \theta}{\Delta P} \quad (7)$$

$$Q = \frac{n \pi r^4 \Delta P}{8bl\mu} \quad (8)$$

where,

- Q = Flow capacity of fluid B at average pressure
- ΔP = Pressure difference at both sides of porous material
- b = Kezenaier constants
- l = Thickness of porous material
- μ = Viscosity coefficient of fluid
- γ = Interfacial tension of fluid A
- θ = Contact angle of liquid and solid
- r = Average pore size of porous material

Flow will increase with increase of pressure difference for opened pores. On the other hand, the increase of pressure difference also makes minor pores unfold, which is favorable to increase of flow. The effects of the two situations make the relationship between flow Q and pressure difference ΔP nonlinear. Yet, when pressure difference increases to a certain degree and all pores are opened, pore size r is fixed

value and Q and ΔP will show a linear relation, also, flow Q will be determined by Poiseuille's law utterly. Therefore, r_{min} , r_{ave} and r_{max} , which is significant to evaluate micro-structure of porous material, can be computed through Eq. (7) according to the plot of Q - ΔP . Huang *et al.* (1996) measured the distribution of pore size of inorganic ceramic micro-filtration membrane in this method and studied the effects of different solvents, including ethanol, isobutanol and toluene, then compared to mercury porosimetry method, the results of which showed the two methods agreed to each other.

The most obvious advantages of this method are simple apparatus, easy operation and good reproducibility, pore size of 0.1~100 μm can be tested in this method. Furthermore, it can better reflect the actual situation of fluid passing through micro-channels. Additionally, the data obtained from measurement can be directly applied, thus avoiding the intricacy brought by graphical solution. For unfolded pores, this way is feasible; yet, it cannot measure pore size of half-unfolded pores or folded pores. But there are still some points that need to keep in mind:

- As bubble is limited by surface tension of liquid, when fluid A is being pushed by fluid B from the very tiny micro-channels, the pressure is required to be high.
- Pores size under 0.1 μm cannot be tested.
- When testing pore size and its distribution, expansion effect of gas must be considered.

Emerging methods and the developing trends: Since the methods above all have their own advantages and disadvantages, different methods can work together to test pore size of porous material, such as mercury porosimetry method is joint with nitrogen adsorption method, which can express pore size comprehensively from micro-pores to macro-pores; SEM, combined with mercury porosimetry method and nitrogen adsorption method, can evaluate systematic features of porous material qualitatively and quantitatively, where SEM is first applied to judge whether macro-porous or micro-pore is major, if macro-porous occupies more space, mercury porosimetry method is considered; if not, nitrogen adsorption method or other methods that are used to test micro-pore are preferred.

Recently, with the fast development of hardware and software of computers, image processing software emerges continuously and their processing ability has been improved immensely. On the basis of existing hardware and equipment, more and more epidemic and cheap image processing software are selected to analyze microstructure instead of expensive image analyzers. Pierre (1998) analyzed particle size distribution of clastic sediments by NIH Image.

As medical image diagnosis develop very rapidly, several medical imaging technology are being extensively applied in medicine, including Computed Tomography (CT), digital radiography, radionuclide imaging, Magnetic Resonance Imaging (MRI), elastosonography, magnetic source imaging, Positron Emission Tomography (PET) and infrared image (Luo and Zhou, 2010). Meanwhile, there emerge new imaging technology and the existing technology is improving from plane to stereoscopic, from local to whole, from static to dynamic. Since the newly-rising imaging technology has been developed rapidly and adequately, it will be a completely new field if translated and applied in analysis of micro-structure.

CONCLUSION

Some methods that are used to measure pore size of porous materials were introduced in this study, including mercury porosimetry method, nitrogen adsorption method, electronic microscope method, small angle X-ray scattering method, bubbling test method and other emerging methods.

Traditional measurements play an important role and lay a solid foundation in the development of structure analysis and application of porous material. Nevertheless, those methods are based on the assumption that all pores are uniform and straight, which is quite different from pores in actual. Even if there exist no errors in actual measurement, the results will deviate from real pore size due to the hypothesis stated above, which cannot be avoided in indirect method. On the other hand, for the direct method, resolution of electron microscope image is low and graphics capability is not compact, which is a problem lying in medical imaging technology. As has been stated above, some cheap and powerful image processing software can be a support.

In conclusion, the author thinks it will be a new developing direction to study more profile of pores in the long run; at the same time, it is a great originality to bring image processing software to micro-structure analysis. Also with the improvement of traditional testing technology and emergence of new methods, the research of porous material will be further developed in the future.

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