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Effect of hollow silica spheres on water vapor permeability of polyacrylate film

Yan Bao[1,2*] Chunhua Shi[1,2] Yongqiang Yang[1,2] Jianzhong Ma[1,2] Risong Sha

[1] College of Resources and Environment, Shaanxi University of Science & Technology, Xi'an 710021, China;

[2] Shaanxi Research Institute of Agricultural Products Processing Technology, Xi'an 710021, China

Abstract: Hollow silica spheres with different hollow size and shell thickness were synthesized via template method using PS spheres as templates and characterized by Transmission Electron Microscope, Scanning Electron Microscope, X-ray Diffraction and Brunauer-Emmett-Teller. Then the effects of hollow size, shell thickness and content of hollow silica spheres on water vapor permeability of polyacrylate films were investigated. The results showed that hollow silica spheres with smaller hollow size and thinner shell thickness were more conducive to the improvement of water vapor permeability of composite films because they provided more free volume for composite film. But too small hollow size or too thin shell thickness is unfavorable for water vapor permeability. Also, with the increase of the content of hollow silica spheres, the water vapor permeability of composite film first increased and then decreased. In short, the composite film containing 2.0wt% hollow silica spheres with hollow size of 150nm and shell thickness of 10nm showed the best water vapor permeability.

Keywords: hollow silica spheres, water vapor permeability, polyacrylate film, template method

1 Introduction

Polyacrylate resin has been widely used in wall coating [1], adhesive [2] and finishing agent for leather[3] and textile due to its excellent film-forming property, adhesiveness, gloss and color retention, anti-aging and environmental friendliness. But it has several

* Corresponding author. Tel.: +0086-29-86132559-607; Fax: +0086-29-86132559; E-mail address: baoyan0611@126.com (Yan Bao).

shortcomings, such as brittleness at low temperature and stickiness at high temperature, poor water/solvent resistance, short of

thermal stability and stain resistance, and poor permeability, which reduces its usability and limits its further application in special

areas. More specifically, when polyacrylate resin is used for leather or textile finishing, the poor hygienic property (air permeability

and water vapor permeability) affect significantly the wearing comfort of their products.

In fact, high-performance polymeric film with high air permeability or permselectivity has been used a lot in gas separation and

is developing rapidly [4-6]. And the previous research is mainly focus on the relationship between film structure and gas transport

properties. The free volume theory first suggested by Cohen and Turnbull [7] are widely accepted to expound the mass transfer in

polymer film [8-9]. However, little attention has been paid to the water vapor permeability of polymer film [10]. Due to molecular

polarity of water molecules, hydrogen bonds will form between them and the polymer chains. So the water vapor permeability of

polymer film can be influenced by hydrophilic groups in polymer chains as well as free volume in film structure [11]. In particular, the

number, size, and shape of free volume determine water vapor permeability of polymer film for the most part [12].

Hollow silica spheres with special hollow core, low density, large specific surface area and good permeability are of increasing

interest because of their potential applications in a wide range of industrial and biological applications [13-17]. Beginning with the

pioneer work of Caruso et al. [18], a variety of strategies have been employed to prepare hollow silica spheres, including template

method, emulsion approach [19], chemical etching [20] and shape evolution of silica nanoparticles [21]. Among them, template method is

the most common one due to its convenience, versatility, high repetition rate and many other advantages [22]. A typical process

involves the shell formation on the template surface to create a template/silica core-shell structure, followed by a template removal

process [23-25]. Many kinds of materials can be used as the templates to prepare hollow silica spheres, including polymeric spheres [26],

inorganic spheres [27], metal spheres [28] and spherical bacterium [29]. Among them, polystyrene (PS) spheres take preference over

others for their excellent mono-dispersity, uniform and narrow size distribution, and easy preparation. For example, PS spheres were

used by Wu and co-workers as templates to prepare hollow silica spheres [30] and PS/SiO$_2$ hybrid hollow spheres [31]. Yeh et al.

successfully fabricated multi-shelled mesoporous hollow silica spheres using PS spheres as templates via shell-by-shell method [32].

In our previous report, hollow silica spheres were used as inorganic nano-filler to increase the size and number of free volume and thereby to improve the water vapor permeability of polyacrylate film [33-34]. We introduced the formation of hollow silica spheres using PS spheres as hard templates and confirmed that hollow silica spheres can significantly improve the water vapor permeability of composite film. The hollow core provides free way for water vapor molecules, but the silica shell has certain barrier property. So we infer that the hollow size and shell thickness of hollow silica spheres may affect the diffusion of water vapor. Hence, in this paper hollow silica spheres with different hollow size and shell thickness were prepared through changing the size of PS spheres and the silica precursor content, respectively. Then hollow silica spheres with different hollow size, shell thickness or content were compounded with polyacrylate emulsion to prepare polyacrylate/hollow silica composite film. The relationship between water vapor permeability of composite film and structural parameters of hollow silica spheres were investigated. This work demonstrated that smaller hollow size and thinner shell thickness of hollow silica spheres were more conducive to improving the water vapor permeability of polyacrylate film. A brief procedure for the fabrication of composite film with well water vapor permeability is schematically described in Figure 1.

It has not been reported by others, so far, that adopting hollow silica spheres to improve the water vapor permeability of polyacrylate film. And the common methods to improve the water vapor permeable of polymer film are to increase the hydrophilic groups on polymer chain, or to increase the pores in film by laser processing [12, 35]. In comparison, a distinct advantage of this work is that it creates additional free volume by introducing hollow nano-filler, without changing the film-forming process or post processing on film, which avoids the deterioration in other basic performance of film. Water vapor molecules penetrate from one side of the composite film into hollow silica spheres through the shell and then get to the other side under the water vapor pressure, rather than diffuse directly through the film under concentration gradient or by small permeation resistance as others reported previously.
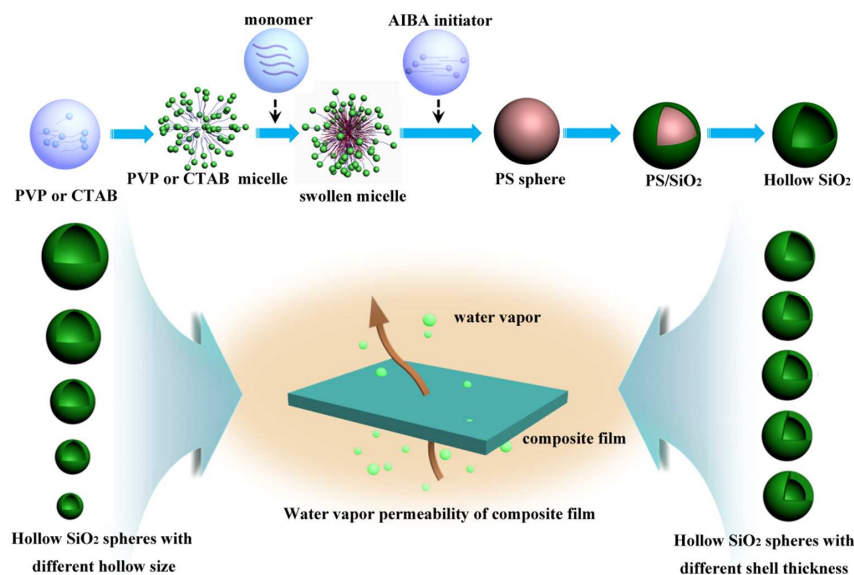
Figure 1 Fabrication diagram of the polyacrylate/hollow silica composite film

2 Experimental

2.1 Chemicals

Styrene (St) as monomer was purchased from Tianjin Fuchen chemical reagent factory. Polyvinylpyrrolidone (PVP, average Mw. 1000-1300, 000), cetyl trimethyl ammonium bromide (CTAB) as surfactant and tetraethyl orthosilicate (TEOS) as silica resource were purchased from Tianjin Kemiou chemical reagent Co., LTD. 2,2'-azobis(2-methylpropionamidine) dihydrochloride (AIBA) as initiator was purchased from Qingdao Kexin new materials science and technology Co., LTD. Tetrahydrofuran (THF) and ethanol were purchased from Hongyan regent factory. Polyacrylate was purchased from Lanxess chemical Co., LTD. All materials were analytical grade and used as received without any further purification.

2.2 Synthesis of polystyrene spheres

Mono-dispersed PS spheres were prepared using emulsion polymerization method and then served as templates for the growth of silica coatings. Typically, a certain amount of PVP (or CTAB) and 0.39g of AIBA were dissolved in 100mL of water with stirring at room temperature. When the solution became clear, 3.0g of St was added. The mixture was deoxygenated under a nitrogen atmosphere for 1h at room temperature, and then heated to 75□. The reaction was continued for 24h at 120 rpm to form PS spheres.

The obtained PS spheres colloid was then cooled to room temperature for further use. The PVP amounts were varied from 0.1 to 2.0g

and CTAB from 0.04 to 0.1g.

2.3 Synthesis of hollow silica spheres

First, the pH of PS spheres colloid was adjusted to 4.0 using sulfuric acid solution. Then, a specific amount of TEOS was

dissolved in 30g of PS spheres colloid. The hydrolysis and condensation reaction of TEOS was allowed for 24h under constant

stirring at 40℃, obtaining PS/SiO$_2$ core-shell spheres colloid. The PS/SiO$_2$ core-shell spheres solid product was separated from the

mother solution via centrifugation and washed with ethanol. The hollow silica spheres were obtained by scattering PS/SiO$_2$ core-shell

spheres in THF and dissolved for 24h at 50℃ under a constant stirring rate of 300 rpm. The amounts of TEOS were varied from 0.44

to 3.22g.

2.4 Preparation of composite film

Polyacrylate/hollow silica composite emulsion was prepared by physical blending method. The hollow silica spheres were

dispersed in 10mL of deionized water and 3mL of isopropyl alcohol under ultrasonic. Then the resulting dispersion was mixed with

polyacrylate latex for 6h at 80℃ to obtain polyacrylate/hollow silica composite emulsion. Polyacrylate/hollow silica composite film

was obtained through transferring polyacrylate/hollow silica composite emulsion into watch-glass to evaporate the solvent.

2.5 Characterization

The morphologies of hollow silica spheres were observed by transmission electron microscope (TEM, JEM-3010, operated at 50

kV) and scanning electron microscope (SEM, JSM-6700F, operated at 5.0 kV). Before TEM measurements, a few drops of hollow

silica suspension in ethanol were dropped on a copper grid before analysis to evaporate the solvent and prepare samples for

measurement. For SEM, hollow silica powders were dispersed on the sample platform and sputter-coated with gold prior to

examination.

The particle size and size distribution of PS spheres were determined by Zeta PALS dynamic light scattering (DLS) detector

(Nano-ZS, Malvern Instruments Ltd., UK) at 25°. The sample for DLS characterization was diluted with deionized water and treated

for 5 min under ultrasonic.

The pore size distribution of hollow silica spheres was measured using a specific surface area and porosity analyzer (NOVA 2200, Quantachrome, USA) at 77 K. The sample was degassed at 300℃ under vacuum for 3 h before the test.

The crystalline phase of hollow silica spheres was analyzed by X-ray diffractrometry (XRD, Rigaku, D/max-2200, Japan). The XRD sample was prepared by flattening the hollow silica spheres powder in the sample container using a glass slide. Radial scans of intensity versus scattering angle (2θ) were recorded from 10° to 70° using a CuKα radiation.

The water vapor permeability of composite film was tested according to the national standards of China. A water vapor permeability cup with area of 10 cm^2 was filled with 30g of deionized water. Then the film and a rubber washer were placed on the top of the cup successively to ensure a perfect sealing between cup and film. The cup was kept in a dryer contained with concentrated sulfuric acid for 24h, which was put into a constant temperature (37□) and humidity (90% RH) incubator. The water vapor permeability was valued by the following formula:

Water vapor permeability $[mg / (10\,\text{cm}^2 \cdot 24h)] = m_1 - m_2$.

The m_1 and m_2 were the total mass of deionized water, composite film and water vapor permeability cup, weighted up promptly and after 24h respectively. Figure 2 is the apparatus for measuring water vapor permeability of composite film.
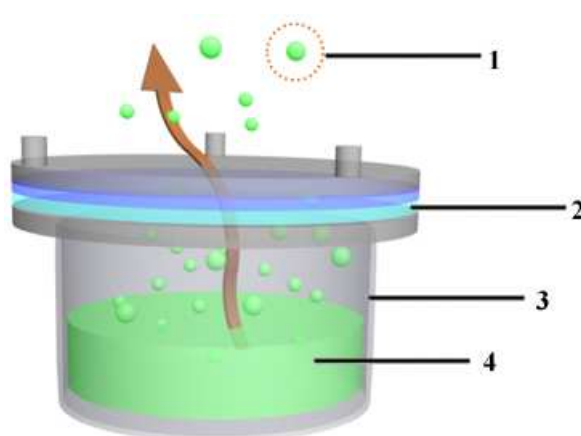

Figure 2 The apparatus for measuring water vapor permeability of composite film: (1) water vapor; (2) composite film; (3) water

vapor permeability cup; (4) deionized water

3 Results and discussion

3.1 Effect of hollow size of hollow silica spheres on water vapor permeability of composite film

The water vapor transporting through polyacrylate/hollow silica composite film is a complex process, which mainly includes

three routes. The first one: Diffusion in polyacrylate matrix. When polyacrylate film is covered on the top of water vapor, the water

vapor molecules that diffused to the lower surface of film are firstly fixed by the hydrogen bond with hydrophilic groups (i.e.

hydroxyl groups, carboxyl groups, ester groups) in the film. Then the water vapor molecules transport in polyacrylate film under the

concentration gradient of water vapor and then across the film taking hydrophilic groups in the film as the "stairs". The second one:

Diffusion in interfacial regions between hollow silica spheres and polyacrylate matrix. Because of the smaller size than interfacial

regions, water vapor molecules can jump into these regions and diffuse from one region to another under the water vapor pressure,

and finally to get through the composite film. The third one: Diffusion through hollow silica sphere. Under the water vapor pressure,

the water vapor molecules traverse the interfacial region and are absorbed by the hydroxyl groups of hollow silica spheres. Owing to

the mesoporous structures and hydroxyl groups on the shell, hollow silica spheres can provide loose channel for water vapor

molecules. So water vapor molecules will eventually transport through the shell to the core of hollow silica spheres. With the

accumulation of water vapor molecules in the core of hollow silica spheres, the water vapor pressure is so high that water vapor

molecules transport out from the core of hollow silica spheres to the polyacrylate matrix. In all diffusion routes of water vapor

molecules, the diffusion rate can be reflected from diffusion coefficient (D). The idealized diffusion coefficient of composite film

can be illustrated by the following equation:

$$D = \frac{A}{\tau} \exp(-B \frac{v}{v_\mathrm{f}}) \tag{1}$$

where A, B are defined as constants (A is related to the size and shape of the penetrants; B depends not only on the type of

penetrants but also on the polymer itself); v is the specific volume of the polymer; v_f is the free volume of the polymer. Free

volume is the necessary condition for water vapor through composite films. With the increase of free volume, the value of D

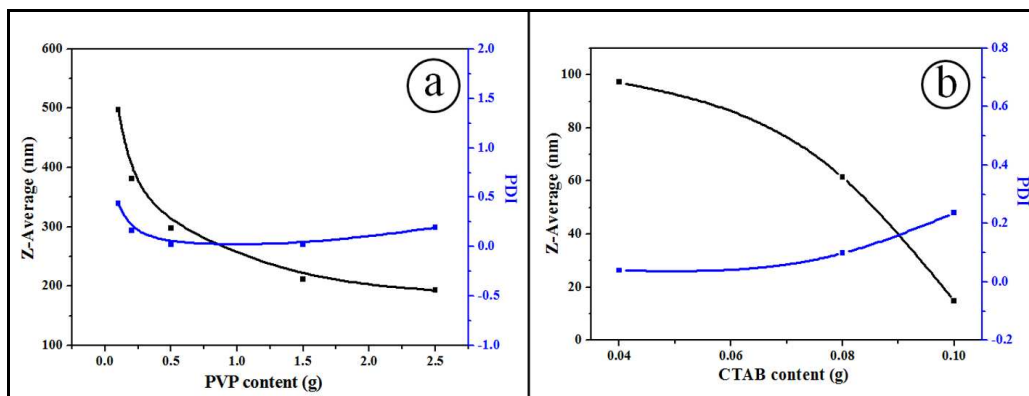increases and the water vapor permeability of film will also increase.

Figure 3 Effect of (a) PVP and (b) CTAB content on the size of PS spheres
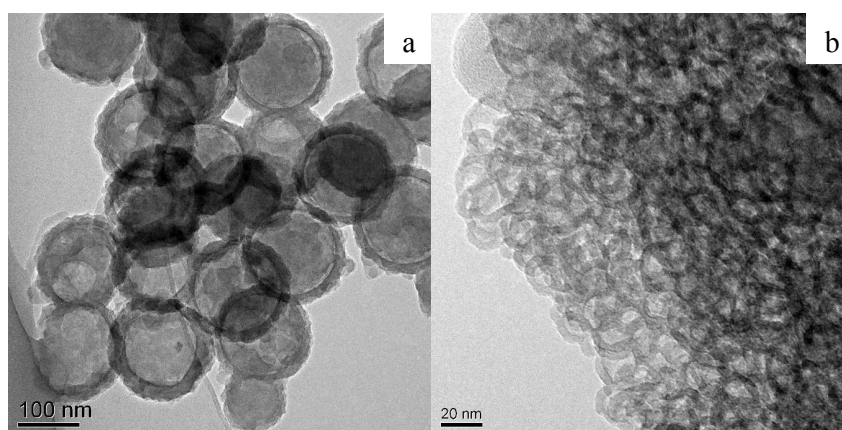

Figure 4 TEM images of hollow silica spheres using PS spheres with a diameter of (a) 150nm and (b) 14nm as templates

Hollow silica spheres with different hollow size were obtained using PS spheres with different size as templates. And the size of

PS spheres was controlled by adjusting the type and amount of emulsifier in emulsion polymerization, as showed in Figure 3. Figure

4 is the TEM images of hollow silica spheres fabricated using 150nm and 14nm PS spheres as templates, respectively. Figure 4a

proves that the hollow size of hollow silica spheres is consistent with the size of PS spheres. The hollow silica spheres are neat and

mono-dispersed with a mean outside size of 190nm and inner size of 150nm. In Figure 4b, fine hollow silica spheres can be clearly

observed. The shell is loose and its thickness is about 3nm. However, these hollow silica spheres reunited seriously due to the large

special surface energy. To further prove that the hollow size of hollow silica spheres can be determined by templates dimensions,

SEM was carried out. Figure 5 is the SEM images of hollow silica spheres prepared by PS templates with some other size: 150nm,

200nm, 300nm and 400nm. We can see obviously that the out size of hollow silica spheres increased with the increase of templates

dimensions. The broken section of hollow silica spheres shows that the shell is very thin, since the TEOS amount is only 1.33g.

These phenomena confirm the variation of hollow size along with the change of PS particle size.
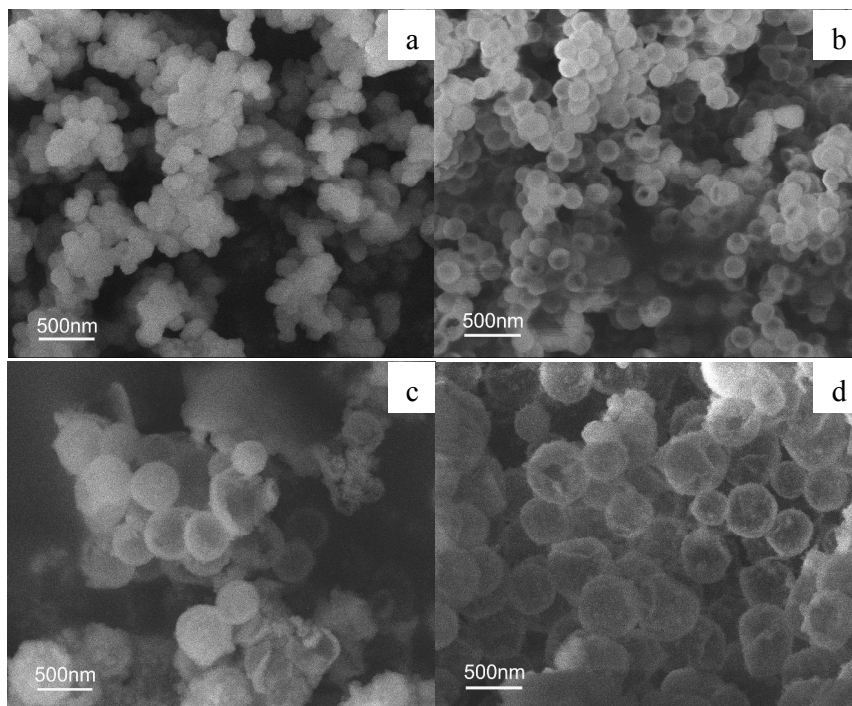

Figure 5 SEM images of hollow SiO$_2$ spheres with different hollow size: (a) 150nm; (b) 200nm; (c) 300nm; (d) 400nm

The effect of hollow silica spheres with different hollow size on water vapor permeability of composite films is given in Figure

6. It showed that the water vapor permeability of pure polyacrylate film is lower than that of composite films. This result is

correspond to our previous research, further confirming that the hollow silica spheres are in favor of increasing the number of free

volume and thereby the water vapor permeability of polyacrylate film. Also, hollow silica spheres with smaller hollow size are

conducive to increase the water vapor permeability of composite film. But the water vapor permeability decreased sharply when the

hollow size of hollow silica spheres is getting very small. This can be illustrated by the reunion of small hollow silica spheres, which

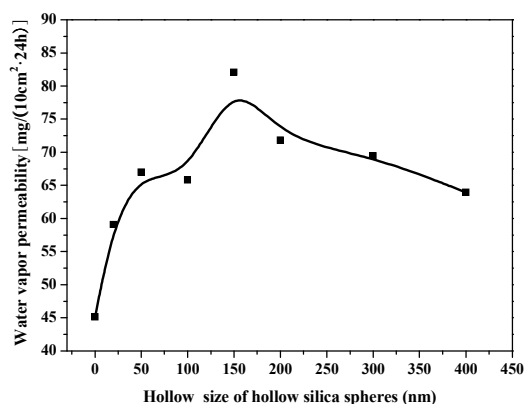decreased their dispersion degree in composite film.

Figure 6 Effect of hollow size of hollow silica spheres on water vapor permeability of composite films

The free volume introduced by the core of hollow silica spheres with different hollow size can be calculated by equation 2:

$$v_f = N_{(HSs)} V_{(PS)} \tag{2}$$

where $N_{(HSs)}$ is the number of hollow silica spheres, $V_{(PS)}$ is the volume of a single PS sphere. Because the number of hollow

silica spheres is equal to the number of PS spheres ($N_{(PSs)}$, equation 3) in this system, the free volume introduced by hollow silica

spheres can be calculated by equation 4:

$$N_{(PSs)} = N_{(HSs)} \tag{3}$$

$$v_f = N_{(PSs)} V_{(PS)} \tag{4}$$

And the number of PS spheres can be calculated by equation 5:

$$N_{(PSs)} = \frac{V_{(PSs)}}{V_{(PS)}} = \frac{m_{(PSs)}/\rho_{(PS)}}{V_{(PS)}} = \frac{m_{(PSs)}/\rho_{(PS)}}{4\pi r^3_{(PS)}/3} \tag{5}$$

In which $V_{(PSs)}$ and $m_{(PSs)}$ are the total volume and mass of used PS spheres, respectively, $V_{(PS)}$ is the volume of a single PS

sphere and $\rho_{(PS)}$ is the density of PS sphere, $r_{(PS)}$ is the radius of used PS sphere. According to equation 5, the equation 4 can be

converted into equation 6:

$$v_f = \frac{m_{(PSs)}/\rho_{(PS)}}{V_{(PS)}} V_{(PS)} = m_{(PSs)}/\rho_{(PS)}$$

(6)

Because $m_{(PSs)}$ used in different experiments is the same and $\rho_{(PS)}$ is constant, the free volume introduced by hollow silica

spheres with different hollow size is also the same. This result illustrates that the core size of hollow silica spheres has little impact on water vapor permeability of composite film.

However, the effect of $N_{(HSs)}$ on water vapor permeability of composite film should not be neglected. The $N_{(HSs)}$ in composite film can be calculated by equation 7:

$$N_{(HSs)} = \frac{V_{(HSs)}}{V_{(HS)}} = \frac{m_{(HSs)} / \rho_{(SiO_2)}}{4\pi [r^3_{(HS)} - r^3_{(PS)}]/3} \tag{7}$$

where $\rho_{(SiO_2)}$ is the density of silica, $V_{(HSs)}$ and $m_{(HSs)}$ are the total volume and mass of silica obtained via hydrolysis of TEOS, respectively, $r_{(HS)}$ is the radius of hollow silica sphere, and $r_{(PS)}$ is the radius of PS sphere. Because the number of hollow silica spheres is equal to the number of PS spheres, $r_{(HS)}$ can be represented by $r_{(PS)}$ based on equation 5 and 7. The relationship between $r_{(HS)}$ and $r_{(PS)}$ is shown in equation 8:

$$r^3_{(HS)} = [\frac{m_{(HSs)}\rho_{(PS)}}{m_{(PSs)}\rho_{(SiO_2)}} + 1] \cdot r^3_{(PS)} \tag{8}$$

Plug equation 8 into equation 7, the equation 7 will be deformed into equation 9:

$$N_{(HSs)} = \frac{3m_{(PSs)} / \rho_{(PS)}}{4\pi} \cdot \frac{1}{r^3_{(PS)}} \tag{9}$$

Because the mass of PS spheres used in the different experiments is the same and $\rho_{(PS)}$ is constant, the $\dfrac{3m_{(PSs)} / \rho_{(PS)}}{4\pi}$ can be represented with "b". Equation 9 can be expressed by equation 10:

$$N_{(HSs)} = \frac{b}{r^3_{(PS)}} \tag{10}$$

The equation 10 illustrates that the number of hollow silica spheres with smaller hollow size in composite film is more than that with large size, which increased the distribution index of free volume in composite film and thereby increased the water vapor permeability of composite film. At the same time, the hollow silica spheres with smaller hollow size have bigger specific surface area than that with larger hollow size. The interfacial areas between hollow silica spheres and polymer matrix are accordingly increased, resulting in increased water vapor permeability of composite film.

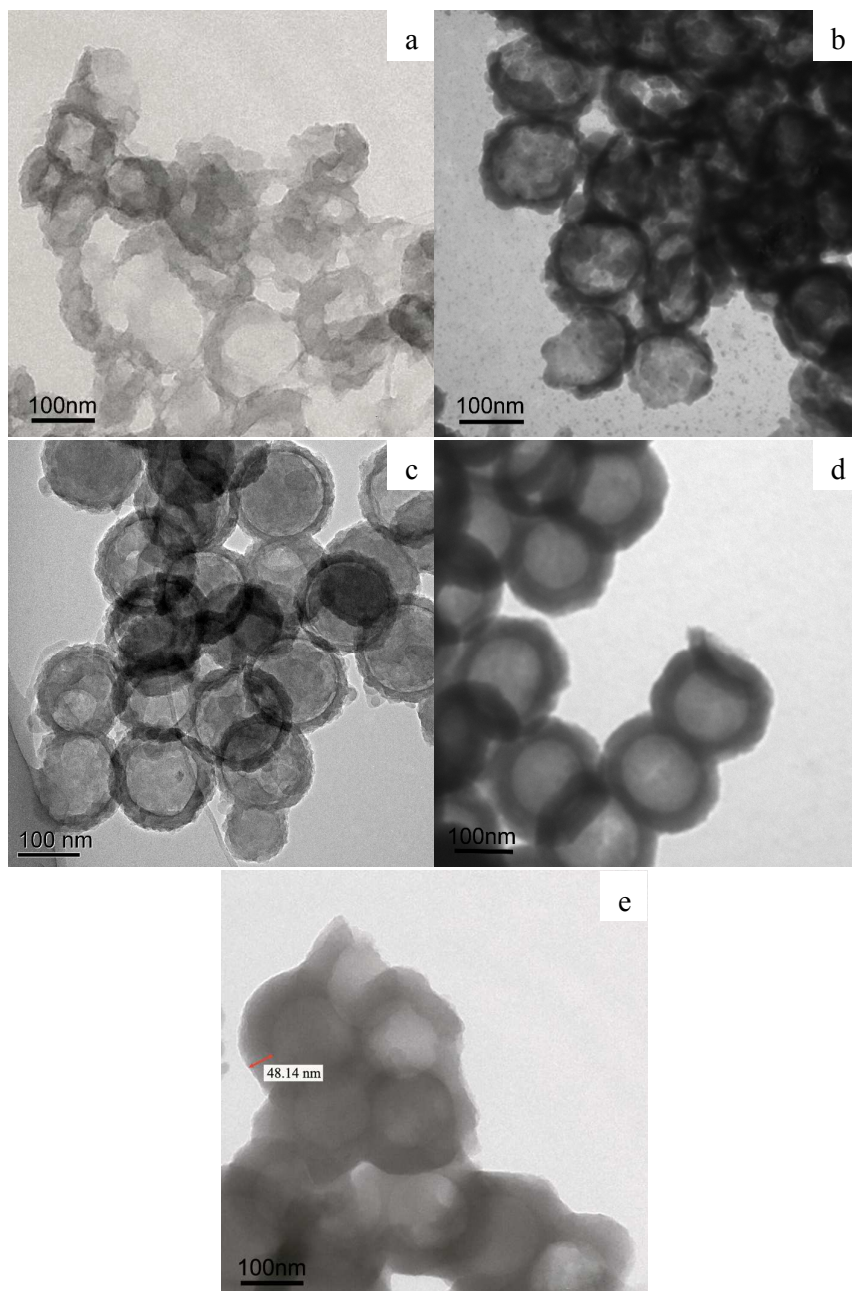**3.2 Effect of shell thickness of hollow silica spheres on water vapor permeability of composite film**

Figure 7 TEM images of hollow silica spheres using different amount of TEOS: (a) 0.44g; (b) 0.66g; (c) 1.33g; (d) 1.99g; (e) 3.22g

The shell thickness of hollow silica spheres is another factor influencing the water vapor permeability of composite film. Hollow

silica spheres with different shell thickness were prepared by simply tailoring the amount of TEOS with 150nm PS spheres as

templates. Figure 7 is the TEM images of hollow silica spheres using different amount of TEOS. With the increase of TEOS amount

from 1.33g to 1.99g to 3.22g, the shell thickness of hollow silica spheres increased gradually, from 20nm to 30nm and then to 50nm

(Figure 7c~e). These results illustrate that the shell thickness of hollow silica spheres is proportional to the TEOS amount. So in theory, when the amount of TEOS was 0.44g and 0.66g, the shell thickness of hollow silica spheres should be 6.6nm and 10nm, respectively. However, the shell of hollow silica spheres collapsed when the amount of TEOS was 0.44g as shown in Figure 7a. We can see that there are many shell fragments and non perfect hollow silica sphere is found in the picture. This is because that the shell of hollow silica spheres is too thin to consolidate their morphology, leading to their collapse in the preparation. When the amount of TEOS was 0.66g, there are a small part of hollow silica spheres whose shell collapsed (Figure 7b). But most of them are of full spherical, with the shell thickness of about 10nm.

Polyacrylate/hollow silica composite films were prepared using the above hollow silica spheres with different shell thickness. And their water vapor permeability was tested under the same conditions. The effect of shell thickness of hollow silica spheres on water vapor permeability of composite film can be observed in Figure 8. The tendency of water vapor permeability of composite films is of parabola shape with the increase of the shell thickness of hollow silica spheres. The composite film has the best water vapor permeability when the shell thickness of hollow silica spheres is 10nm. This process of water vapor molecules across hollow silica spheres can be attributed to the crystalline phase and pore size distribution of the shell of hollow silica spheres. Figure 9a is the XRD pattern of hollow silica spheres. There is only one broad peak between 17° and 38°, suggesting the loose amorphous structure of hollow silica spheres [36]. This loose structure makes it easy for water vapor molecules passing through hollow silica spheres. Also, there are many pores on the shell of hollow silica spheres as shown in Figure 9b. Narrow peak at 2.0nm and 5.6nm is regarded as the internal pores originated from the diffusion of PS core. This indicates that the shell of hollow silica spheres is of porous structure. The water vapor molecules can easily traverse into and out the hollow core of hollow silica spheres by right of the mesoporous on the shell of hollow silica spheres under the water vapor pressure difference. If the shell thickness of hollow silica sphere ($h_{(HS)}$) is increased, the water vapor molecules would experience more roads to across the composite film and decrease the water vapor permeability. At the same time, the increase in shell thickness of hollow silica spheres influences the free volume of composite film. The free volume introduced by hollow silica spheres can be represented by equation 11:

$$v_f = N_{(HSs)} \cdot \frac{4\pi r^3_{(PS)}}{3}$$ (11)

According to equation 7, the number of hollow silica spheres ($N_{(HSs)}$) with different shell thickness can be represented by equation

12:

$$N_{(HSs)} = \frac{m_{(HSs)} / \rho_{(HS)}}{4\pi[(r_{(PS)} + h_{(HS)})^3 - r^3_{(PS)}]/3}$$ (12)

where $h_{(HS)}$ is the shell thickness of hollow silica spheres. So, the equation 11 can be converted into equation 13:

$$v_f = \frac{m_{(HSs)} r^3_{(PS)}}{\rho_{(HS)}[(r_{(PS)} + h_{(HS)})^3 - r^3_{(PS)}]}$$ (13)

From equation 13, we can infer that the free volume introduced by the core of hollow silica spheres in composite film decreased with

the increase of shell thickness, leading to a decreased water vapor permeability of composite film. At the same time, with the increase

of shell thickness of hollow silica spheres, the number of hollow silica spheres is reduced according to the equation 12. So the

interfacial region between hollow silica spheres and polyacrylate matrix is decreased accordingly, which also decreased the water

vapor permeability of composite film. However, when the shell is too thin to consolidate the morphology of hollow silica spheres, the

water vapor permeability of composite film is decreased (Figure 8). This is because that the shell collapsed and the free volume

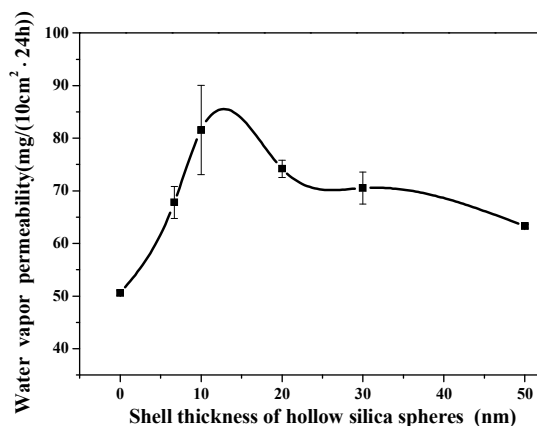introduced by the core of hollow silica spheres disappeared.

Figure 8 Effect of shell thickness of hollow silica spheres on water vapor permeability of composite film
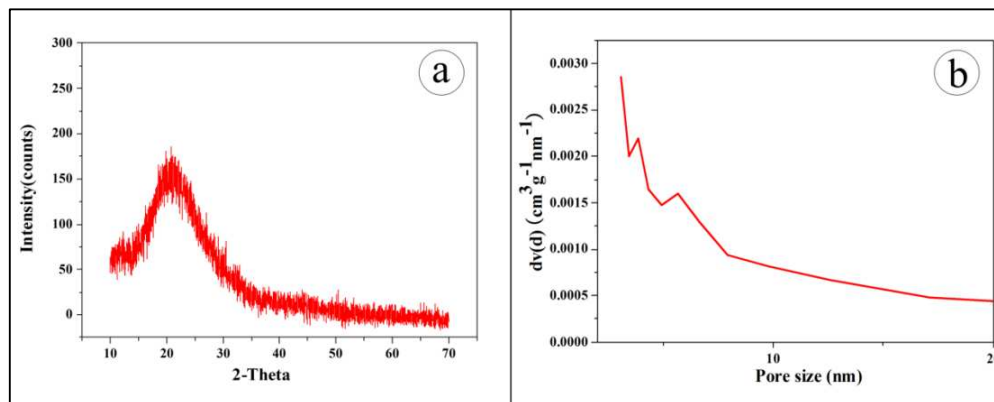
Figure 9 (a) XRD pattern and (b) pore size distribution of hollow silica spheres

3.3 Effect of content of hollow silica spheres on water vapor permeability of composite film

The content of hollow silica spheres is also an important factor influencing the water vapor permeability of composite film. Figure

10 shows the influence of the content of hollow silica spheres on water vapor permeability of composite film. It is worth noting that

the water vapor permeability of composite film is increased with the increase of the content of hollow silica spheres, when less than

2.0wt%. This is explained by the fact that the introduction of hollow silica spheres increases the free volume in the composite film

and interfacial region between hollow silica spheres and polymer chains. And the more hollow silica spheres were introduced, the

more free volumes and interfacial regions were produced in the composite film. Therefore, the water vapor permeability of composite

film was improved. However, when the content of hollow silica spheres was more than 2wt%, the water vapor permeability of

composite film decreased slightly. The agglomeration of hollow silica spheres is the principal factor causing this result. Due to high

specific surface energy, the hollow silica spheres are prone to agglomerate at a higher content, which decreases the distribution index

of hollow silica spheres in composite film. At the same time, the interfacial region between hollow silica spheres and polyacrylate

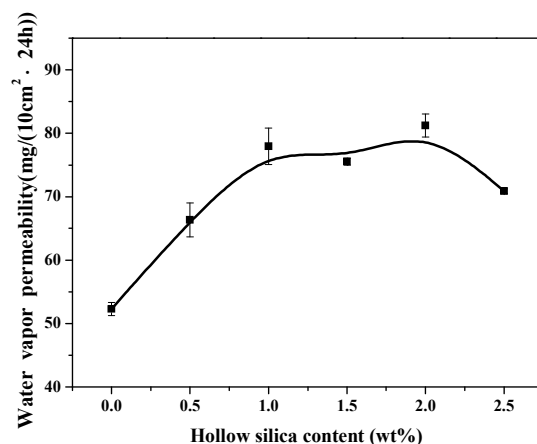matrix is decreased, resulting in reduced water vapor permeability.

Figure 10 Effect of the content of hollow silica spheres on water vapor permeability of composite film

3.4 Water vapor permeability mechanism of polyacrylate/hollow silica composite film

Free volume is the necessary condition for water vapor permeability of composite film. And the introduction of hollow silica spheres can increase the free volume in composite film. The schematic illustration of water vapor molecules transporting through hollow silica sphere is shown in Figure 11. Due to many mesoporous and hydroxyl groups in the shell of hollow silica spheres, the water vapor molecules can transport into the hollow core through the shell. When the number of water vapor molecules in the hollow core is large enough, these molecules will transport from the hollow core to the polyacrylate matrix under the water vapor pressure. The hollow cores of hollow silica spheres act as the "shortcut" and "storage station" for water vapor molecules to increase the water vapor permeability of composite film. The schematic illustration of water vapor molecules transporting through polyacrylate/hollow silica composite film containing hollow silica spheres with different hollow size, shell thickness and content are shown in Figure 12. In the case of the same mass, although the free volume introduced by the core of hollow silica spheres with different hollow size is the same, the number of hollow silica spheres with smaller hollow size is more than that with larger hollow size. Thus, the distribution index of free volume and the area of interfacial region increased, which provide more opportunities for water molecules to across the composite film (Figure 12. Hollow size). Similarly, with the same mass, the number of hollow silica spheres with thinner shell is more than that with thicker shell. But different from the influence of hollow size, the free volume introduced by the core of hollow silica spheres with thinner shell is larger than that with thicker shell. So, the effect of shell thickness on water vapor

permeability is greater than hollow size. The routes for water vapor molecules transporting in composite film are further shorten,

which leads to the increase of the water vapor permeability (Figure 12. Shell thickness). Moreover, the content of hollow silica

spheres also affects the number of hollow silica spheres and the free volume in composite film. Therefore, the water vapor

permeability of composite film varied with the content of hollow silica spheres (Figure 12. Content).
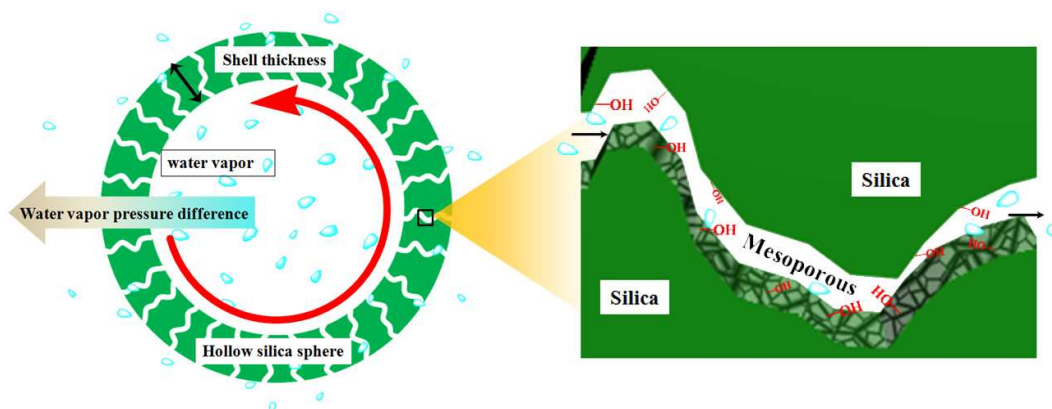

Figure 11 The schematic illustration of water vapor molecules transporting through hollow silica spheres
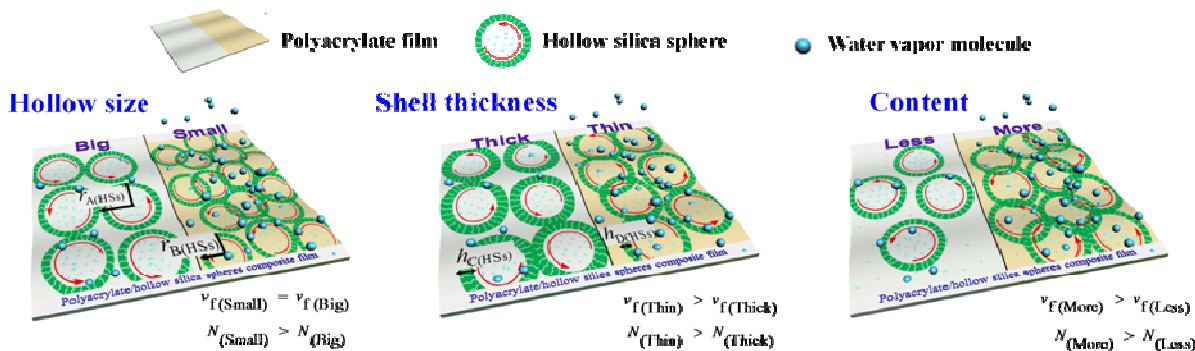

Figure 12 Schematic illustration of water vapor molecules transporting through polyacrylate/hollow silica composite films containing

hollow silica spheres with different hollow size, shell thickness and content

4 Conclusions

In conclusion, uniform hollow silica spheres with different hollow size and shell thickness were synthesized by adjusting the type

and amount of emulsifier in preparing PS spheres and the amount of TEOS, respectively. The hollow size, shell thickness and content

of hollow silica spheres have significant effects on water vapor permeability of polyacrylate film, since they can influence the free

volume in it. Hollow silica spheres with thin shell will increase both the size and the number of free volume, while those with small

hollow size will only increase the free volume distribution in composite film. Therefore to some extent, hollow silica spheres with small hollow size and complete thin shell are in favor of improving the water vapor permeability of composite film. In this study, hollow silica spheres with hollow size of 150nm and shell thickness of 10nm are the most favorable for the water vapor permeability of polyacrylate film. In addition, with the increase of the content of hollow silica spheres, the water vapor permeability of composite film first increases and then decreases. The reason is that within a certain range, adding more hollow silica spheres will introduce more free volume in composite film, but too many of them will reunite, reducing the distribution index of free volume. The study broadens the application area of hollow silica spheres. The prepared polyacrylate/hollow silica composite film has potential applications in coatings for leather, textiles, synthetic leather and so on.
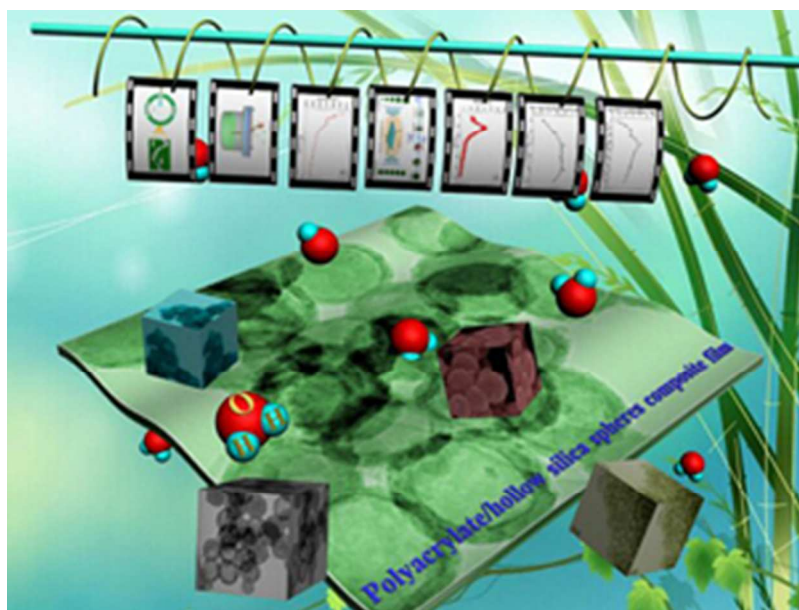
Acknowledgements

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