Fabrication of Hollow Silica Spheres and Its Application in Polyacrylate Membrane Forming Agent for Leather Finishing

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Abstract

Polystyrene/silica core/shell spheres were fabricated using mono-dispersed polystyrene as templates by hydrolysis and condensation of two different silica precursors. The polystyrene cores of polystyrene/silica core/shell spheres were dissolved subsequently in the tetrahydrofuran medium to form mono-dispersed hollow silica spheres. The structures and morphologies of hollow silica spheres were characterized by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). Then polyacrylate/hollow silica composite membrane forming agents were prepared via physical blending of polyacrylate and two different hollow silica spheres, and the water vapor permeability of their membranes were compared. The results showed that the structure of hollow silica spheres were very typical and obvious. The silica shell was continuous and uniform using tetraethylorthosilicate as precursor, which was accumulated by many silica seeds with size of 10~20nm, and the thickness of silica shell was about 16.7nm. However, the hollow silica spheres using tetraethylorthosilicate and vinyl triethoxy silane as precursors had mesoporous structure in the shell, and the pore size was about 3~40nm. The introduction of hollow silica spheres can significantly improve the water vapor permeability of polyacrylate membrane. At last, a possible mechanism for the formation of hollow silica spheres was proposed and the process of water vapor through polyacrylate/hollow silica composite menbranes was modeled.

Keywords: hollow silica spheres; water vapor permeability; membrane forming agent

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Polymeric membrane with high water vapor and gas permeability are widely used in breathable coating fabrics, medical appliances and special adhesives. Especially, water vapor permeability of polymeric finishing membrane for textile and leather influence the comfortable and hygienic properties of products significantly. The study of transport properties of water vapor through polymeric membranes is particularly interesting. Water vapor molecules transport through non-porous polymeric materials depends strongly on the amount of free volume or space not occupied by polymer chains in the material [1]. Free volume, whether static voids created by inefficient chain packing or transient gaps generated by thermally induced chain segment rearrangement, presents diffusing molecules with a low-resistance avenue for transport.

Due to its larger special surface area, nanoparticle increased the number of free volume including interfacial regions between nano-spheres and polymer chains and interstitial cavities in the nano-spheres agglomerate, resulting in a higher water vapor permeability of composites membrane [2]. However, the introduction of nano-spheres could not increase significantly the water vapor permeability of polymer membrane.

Due to special hollow structure, inner and outer surfaces and lower density, the hollow silica spheres are promising inorganic components in organic-inorganic composites [3-5]. However, the introduction of hollow silica spheres to improve water vapor permeability of membrane is rarely reported at present. In this paper, the different kinds of hollow silica spheres as the free volume were used to improve water vapor permeability of polyacrylate membrane. The introduction of hollow silica spheres can significantly improve the water vapor permeability of polyacrylate membrane, especially that with the mesoporous structure.

The uniform hollow silica spheres using TEOS and TEOS/VTES as silica precursors were firstly synthesized by hard templates method (PS spheres). Figure 1 displays the TEM images of hollow silica spheres using TEOS (a) and TEOS/VTES (b) as silica precursors. TEM images show that the clear and neat hollow silica spheres using TEOS and TEOS/VTES as silica precursors with a mean size of 170nm and cavity of 130nm have been obtained. The hollow silica spheres using TEOS (Figure 1a) as silica precursor are monodispersed and its shell is continuous and uniform. While hollow silica spheres using TEOS/VTES (Figure 1b) as silica precursors have aggregations at certain degree, and the shell is non-continuous with many mesoporous structure in it. To observe the morphology and structure of hollow silica spheres more clearly, SEM was also carried out. It can be seen from both Figure 2a and 2b that hollow silica spheres are well-defined and indeed show vivid hollow structure. The hollow silica shells using TEOS as silica precursor are very compact and consist of silica

seeds with a broad size distribution, which roughens the surfaces greatly. While the shells using TEOS/VTES as silica precursor are loose and non-compact, this corresponds to the mesoporous structure.

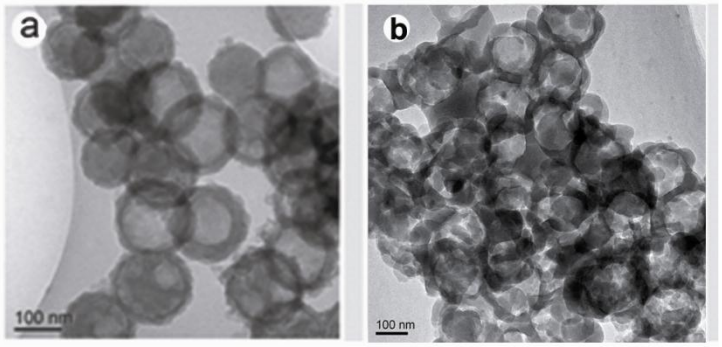

Figure 1. TEM image of hollow silica spheres using TEOS (a) and TEOS/VTES (b) as silica precursors.

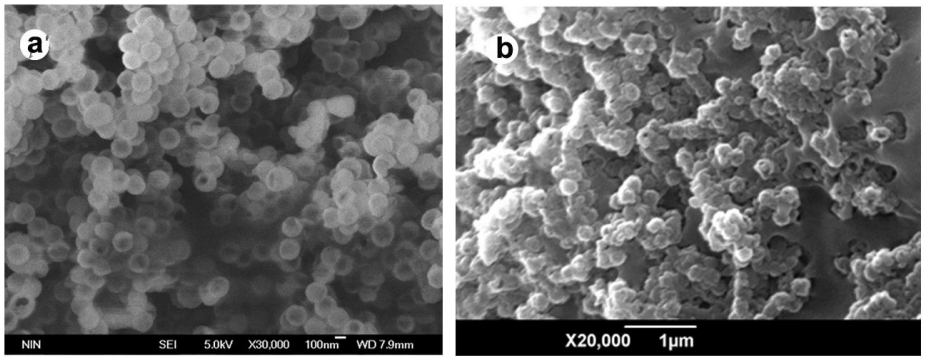

Figure 2. SEM images of hollow silica spheres using TEOS (a) and TEOS/VTES (b) as silica precursors.

The polyacrylate/hollow silica composite membrane was prepared through introducing as-prepared hollow silica spheres into polyacrylate latex by physical blending and transferring composite emulsion into watch-glass to evaporate the solvent. The water vapor permeability was measured according to the principle of pressure difference between out surface and inner surface of composite membrane. The concentrate gradient of water vapor in the membrane is the driving force of diffusion and hydrophilic groups are the “stairs” of water vapor molecules to across the membrane. Table 1 illustrates the water vapor permeability of pure polyacrylate membrane and composite membranes with 2% of hollow silica spheres using TEOS and TEOS/VTES as silica precursor. The result indicates that the water vapor permeability of polyacrylate/hollow silica composite membranes were much higher than that of pure polyacrylate membrane. Especially, the water vapor permeability of polyacrylate/hollow silica composite membrane using TEOS/VTES as silica precursors is superior to that using TEOS. The introduction of hollow silica spheres have special hollow core structure increase the number of free volume, especially, hollow structural region, interfacial region of nanospheres

and polymer chains and interstitial cavities in the nanospheres agglomerates, which may be the reason that water vapor permeability of composite membranes with hollow silica spheres are higher than pure polyacrylate membrane.

Table 1. Water vapor permeability of pure and composite polyacrylate membranes

Samples	Pure membrane	Composite membrane[a]	
		Hollow silica spheres[b] (TEOS)	Hollow silica spheres[c] (TEOS/VTES)
Water vapor permeability [mg(10cm^2·24h)]	45.98	69.33	74.01

[a] Composite membranes with 2% of hollow silica spheres.

[b] Hollow silica spheres using TEOS as silica precursor.

[c] Hollow silica spheres using TEOS/VTES as silica precursor.

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