



# Polypropylene nonwoven surface modified through introducing porous microspheres: Preparation, characterization and adsorption



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## ABSTRACT

A new porous fabric adsorbent (PM/PP nonwoven) was prepared by hydrogen bonding self-assembly method, in which poly(divinylbenzene-co-4-vinylpyridine) microspheres were introduced onto the surface of PP-g-AA (polypropylene grafted acrylic acid) nonwoven. The effects of the main conditions for self-assembly reaction such as mass ratio of microsphere to nonwoven, pH and the grafting degree of acrylic acid were studied. In addition, the adsorption mechanisms and interactions for three VOCs (styrene, cyclohexane, acetone) were systematically elucidated. The resulting 28.2% PM/PP nonwoven obtained a higher adsorption amount (52.8 mg/g) of styrene vapor, which was 88 times greater than that of original PP nonwoven. Meanwhile, the kinetic studies suggested that the Yoon and Nelson model is suitable to describe the adsorption mechanism of styrene over the modified nonwovens. Adsorption and pressure drop data showed that PM/PP nonwoven had good adsorption ability and air permeability due to its abundant functional groups and porous structures. Taken together, it is expected that PM/PP nonwoven would be a promising adsorbent for removal of VOCs from the gas streams.

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## 1. Introduction

Volatile organic compounds (VOCs), which are commonly found as solvents in industrial processes and domestic use, are considered as major air contaminants for inducing directly health troubles and for being precursors of tropospheric ozone [1,2]. The effects of VOCs on human health have been well documented: specifically, styrene is a human carcinogen associated with genetic disorders, while other aromatic VOCs are associated with damage to human organs and nervous system [3,4]. Therefore, several methods have been developed to remove them, including catalytic oxidation, membrane separation, biological treatment and adsorption [5–7]. Among these methods, adsorption has been considered to be superior to other techniques in view of its comparatively low costs, wide range of applications, simplicity of design and fewer secondary products [8]. The core of this process is to develop suitable and effective adsorbents. Recently, porous microspheres have been proved to be capable for removing VOCs as their controllable pore

structure, stable physical/chemical properties and high surface area which enabled their adsorption at low concentrations [9]. However, several shortcomings such as high pressure drop, inflexibility and poor portability limited its further application [10,11].

Thus, to overcome such limitations, the nonwoven could be introduced for improving the air permeability and flexibility of the adsorbent. That was because the nonwoven fabrics are complex three-dimensional (3D) fibrous materials containing fibers oriented in preferential or random directions that are bonded by thermal, chemical, or mechanical techniques. Meanwhile, the nonwoven consisting of polymer fibers provide an excellent platform for the integration of functional structures to improve the performance of the materials for a variety of applications [12,13]. These special structures help the nonwoven fabrics have a short transit distance, low pressure drops, and flexibility [14–16]. Hence, it is of significance to find an effective method to introduce the porous microspheres onto the surface of nonwovens.

Several studies have been carried out to develop the methods for attachment/binding of particles onto substrates. Fukahori et al. [17] and Iguchi et al. [18] produced photocatalytic papers, which are made of TiO<sub>2</sub> supported by ceramic fibers, using the wet-end addition process. Xia et al. [19] and Wang et al. [20] developed a facile and reproducible procedure for anchoring SiO<sub>2</sub> nanoparticles to carbon fibers by sol–gel technique. The oxidation resistance of the carbon fiber was improved by the SiO<sub>2</sub> coating. Aguedach

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et al. [21] and Raillard et al. [22] also coated paper with a mixture of TiO<sub>2</sub> and colloidal silica using a size press treatment. However, above three methods are mostly utilized for inorganic microsphere immobilization and the porous structures of microspheres cannot be retained.

Self-assembly is a powerful technology for fiber surface modification with their simplicity, versatility, and advantages for controlling the shape, composition and surface roughness [23]. Fundamentally, self-assembly process is based on a charge compensation mechanism between the electron donor and acceptor. So the preparation process could not alter the interior porous structures of materials. The alternate positive and negative layers of self-assembly material can be replaced with any particles containing appropriate polarity. Therefore, surface property of substrate that the spheres deposited on can be tailored with ease to have desirable property such as to enhance the anti-fouling property and filterability of modified composite membranes [24,25], to improve their pervaporation performance [26], and to protect underlining surface [27].

In this paper, porous microspheres (PM) were introduced onto the surface of polypropylene (PP) nonwoven which was employed as a matrix by graft polymerization and subsequent self-assembly. Through above methods, the PM/PP nonwoven (porous microspheres self-assembled polypropylene nonwoven) was prepared, and the reaction conditions were discussed. In addition, three VOCs (styrene, cyclohexane, acetone) with different molecular structures were used to investigate the adsorption mechanism and interactions ( $\pi$ - $\pi$  interaction, dipole-dipole interaction, and van der Waals forces). To study the effects of PM/PP nonwoven fabric on VOCs removal, the composition and morphology of the material were analyzed using the Brunaur-Emmett-Teller (BET) method, X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectrometer (FTIR), and scanning electron microscopy (SEM). These results showed that the PM/PP nonwoven fabric was successfully constructed. To examine the air permeability of nonwovens, a gas permeating experiment was also carried out. These results indicate that the PM/PP nonwoven with excellent adsorption and permeability performance have a promising future in VOCs and some polar gas emission controlling.

## 2. Materials and methods

### 2.1. Materials

PP nonwoven fabric of 50 g/m<sup>2</sup> was obtained from the Haidexin Chemical Factory, Jiangsu, China. The nonwoven was washed by acetone and distilled water and dried at 323 K before use. 4-Vinylpyridine (4VP, 95% grade) and divinylbenzene (DVB, 80% grade) were purchased from Aldrich and distilled under vacuum. Acetonitrile and toluene (analytical grade, Tianjin Chemical Reagent II Co.) were dried with calcium hydride and purified by distillation before use. 2,2'-Azobisisobutyronitrile (AIBN, Chemical Factory of Nankai University) was recrystallized from methanol. Ethanol, methanol, acetone, styrene, cyclohexane and acrylic acid were purchased from Tianjin Guangfu Fine Chemical Research Institute and used without further purification.

### 2.2. Preparation of the PP-g-AA nonwoven fabric

The PP nonwoven fabric was washed with distilled water, 1 M NaOH, distilled water and acetone, and then dried in a vacuum oven at 323 K for 48 h. The samples were weighed, and then immersed in solutions of acrylic acid with different volume concentrations (vol%) of the ethanol/water (1/4, v/v) mixture solution. 1% mass percent of benzophenone was also added as to minimize the homopolymerization of acrylic acid during the grafting process.

The mixture was sealed in polyethylene bags and degassed by bubbling with high purity nitrogen flow for 20 min to remove oxygen and then directly subjected to electron-beam irradiated at room temperature using an accelerating voltage of 175 kV. The electron-beam irradiation graft polymerization reaction occurred on the surface of PP nonwoven and the irradiation doses were 40, 60 and 80 kGy. Afterward, the grafted PP nonwoven was taken out and extracted in a Soxhlet apparatus with toluene about 4 h to remove the unreacted monomers and homopolymers before self-assembly process. The resulting polypropylene grafted acrylic acid (PP-g-AA) nonwoven was dried in a vacuum oven at 323 K for 48 h to a constant weight and weighed. The degree of grafting was obtained using the following formula:

$$G(\%) = \frac{W_g - W_o}{W_o} \times 100 \quad (1)$$

where  $W_o$  and  $W_g$  are the weight of the original and grafted nonwoven, respectively.

### 2.3. Preparation of poly(DVB-co-VPy) microspheres

The poly(DVB-co-VPy) microspheres were prepared by distillation precipitation copolymerization of divinylbenzene and 4-vinylpyridine in neat acetonitrile. A typical procedure for such copolymerization was follows: divinylbenzene and 4-vinylpyridine with 2,2'-azobisisobutyronitrile (2 wt% relative to the whole comonomer) initiator were dissolved in 170 ml of acetonitrile and 30 ml of toluene as the pore-formed template were put in a dried 250-ml-two-necked flask attaching with a fractionating column, Liebig condenser, and a receiver. The flask was submerged in heating mantle, and the reaction mixture was heated from ambient temperature to boiling state within 15 min, and the reaction mixture was kept under refluxing state for 10 min. Then the solvent was distilled off the reaction system and the reaction was ceased after 100 ml of acetonitrile was distilled from the reaction system within approximately 1.5 h. Several important textural parameters of the microspheres are summarized in Table 1. After polymerization, the resultant poly(DVB-co-VPy) microspheres were purified by three cycles of centrifugation, decantation, and resuspension in acetone with ultrasonic treatment. Then the microspheres were dried in a vacuum oven until a constant weight was achieved. Finally, the obtained microspheres were suspended in acetonitrile (approximately 10 mg/ml) for the following self-assembly process.

### 2.4. Preparation of PM/PP nonwoven fabrics

Self-assembly process between the carboxyl groups of PP-g-AA nonwoven fabrics and the pyridyl groups of Poly(DVB-co-VPy) microspheres was performed as follows: the grafted nonwoven (0.5 g) and microspheres (0.5 g) were soaked in 50 ml acetonitrile, and the mixture was sealed in centrifuge tube on an SHA-B shaker. The self-assembly process was carried out at room temperature with gentle agitation by rolling the centrifuge tube in a horizontal position at approximately 150 rpm for 24 h. After self-assembly, the achieved nonwoven was washed and ultrasonicated consecutively with acetonitrile and acetone three times and dried in a vacuum oven at room temperature overnight. The effect of pH on the morphology of the composite nonwoven was determined by

**Table 1**  
Textural parameters of the porous polymer beads.

Sample	1	2	3	4
VPy:DVB (V/V, ml)	0:5	0.5:4.5	1:4	1.5:3.5
$S_{BET}$ (m <sup>2</sup> /g)	616	542	463	289
$V_t$ (ml/g)	0.131	0.117	0.096	0.083

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