Progress in Organic Coatings 120 (2018) 190–197

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Improvement of wetting properties of expanded perlite particles by an organic conformal coating

Mehmet Gürsoy[a], Mustafa Karaman[a,b,*]

[a] Department of Chemical Engineering, Selcuk University, Konya 42075, Turkey
[b] Advanced Technology Research & Application Center, Selcuk University, Konya 42075, Turkey

ARTICLE INFO

Keywords:
Surface coating
Plasma polymerization
PECVD
Expanded perlite
Hydrophilic coating

ABSTRACT

Expanded perlite particles were surface functionalized using poly(hydroxyethyl methacrylate) (PHEMA) thin film under radio frequency (RF) plasma conditions in a rotating-bed plasma enhanced chemical vapor deposition (PECVD) system. Using a rotating-bed system allowed effective agitation and mixing of the particles during depositions, which ensure uniform surface coating of highly porous and particulate materials. The effects of plasma power and plasma operation mode, namely pulsed and continuous modes on the deposition rates, structure, wettability and water holding capacities of expanded perlite particles were investigated. Chemical and morphological properties of uncoated and coated expanded perlites were determined by SEM, FTIR, contact angle, and BET analyses. Observed deposition rates changed between 10 and 35 nm/min., which were dependent on the deposition conditions. It was found that pulsing the discharge helped to minimize undesirable monomer fragmentation while providing better film structure. The most hydrophilic PHEMA thin films were fabricated at 50 W plasma power and under pulsed-plasma mode. When the expanded perlite was modified with PHEMA under suitable experimental conditions, the water holding capacity of untreated particles is increased by more than twenty percent.

1. Introduction

Fine particulate materials are being used in a wide range of applications in various areas, such as composites, filtration, agriculture, packaging, textiles, construction and catalysis. Surface modification of such particles is becoming more important as the final uses of such materials become more evident. For some special end-uses a suitable chemical finish must be applied to the surface of a particle without changing its surface geometry.

Up to now, surfaces of many micro- and nano- particles including graphene, carbon nanotubes (CNTs), fibres, activated carbon, and clay have been coated and/or encapsulated for many intended applications. For instance, activated carbons were treated with ammonia to enhance their CO2 capture capacity [1]. Multiwalled CNTs were non-covalently modified by poly(styrene-alt-maleic anhydride) and silica can be used for constructing superhydrophobic antistatic coatings [2]. The water/ethylene glycol repellency of graphene paper can be significantly improved by surface fluorination [3]. Cotton fibers were coated with thin titania film to improve their photocatalytic activities [4]. Clay platelets were encapsulated by a polymer via emulsion polymerization [5]. These were just few examples of surface modification of particulate solids, in which mainly wet protocols were applied to modify the surfaces of such particles. Most common bottom-up strategies to modify or encapsulate the surfaces of micro- or nano- structures in liquid phase are surface initiated atom transfer radical polymerization (ATRP) [6] and sol-gel [7] processes. Such wet strategies usually suffer from particle agglomeration because of strong liquid surface tension forces, which also prevents liquid penetration inside tiny pores and cavities of the porous substrates. There are very few wet coating studies that have been able to overcome the agglomeration problem. One of them was conducted by Zhang et al., they coated solid particles with a uniform polymer film using a hot-melt resin coating process [8]. Solvent-free and conformal nature of chemical vapor deposition (CVD) method, on the other hand, offers advantageous properties over wet coating techniques [9,10]. For instance, owing to not using any liquid-phase intermediate, CVD prevents possible agglomeration and sticking between particles [11]. Furthermore, continuous mixing and agitation of particles during depositions by using either fluidised or rotating-bed approaches can further increase the uniformity of coatings around individual particles [12–14].

Recently, expanded perlite has become an important porous fine material for various applications because of its superior features.

* Corresponding author at: Department of Chemical Engineering, Selçuk University Kampus, Konya 42030, Turkey.
E-mail address: karamanm@selcuk.edu.tr (M. Karaman).

https://doi.org/10.1016/j.porgcoat.2018.03.021
Received 13 January 2017; Received in revised form 13 March 2018; Accepted 20 March 2018

Expanded perlite is easy to obtain, lightweight, fire-proof, and reusable. It is also chemically inert, non-toxic and non-water-soluble. These properties create many usage areas for expanded perlites including construction, insulation, adsorption and agriculture. For example, expanded perlite is an important and popular “soil alternative” material. Owing to its hydrophilic nature, it absorbs water and dissolved nutrients, allowing the plants to use them as needed. Due to its porous structure, expanded perlite has also excellent oxygen retention ability. In solid-based farming, the plants roots are in the heavy soil. The significant fraction of water into the ground cannot be absorbed by the plant roots [15]. On the other hand, in hydroponic farming for which expanded perlite is an excellent growing medium, water with nutrients is fed directly to plant roots. So the resources are not wasted and can be used more efficiently. For instance, hydroponics farming needs just 5% of water which would be needed to grow same amount of plant in traditional soil-based farming [16].

The primary aim of this study was to improve the water retention capacity of expanded perlite. For this purpose, a hydrophilic monomer (2-hydroxyethyl methacrylate) (HEMA) was polymerized on the surfaces of expanded perlite particles in a rotating-bed plasma enhanced chemical vapor deposition (rotating-bed PECVD) reactor. Poly(2-hydroxyethyl methacrylate) (PHEMA) is a hydrophilic polymer because of its hydroxyl functionality. Moreover, while PHEMA does not completely dissolve in water, it swells in water [17]. For that reason, PHEMA coating is considered to be a good strategy for improving water retention capability of expanded perlite. The influences of plasma operation mode and plasma power on the chemical structure, morphology and water retention capability of plasma functionalized expanded perlites were investigated.

2. Materials and methods

2.1. Materials

Expanded perlite (Tesar Püskürtme Granit, Turkey) and flat silicon wafer (100, *p*-type) were used as substrates. *n*-heptane (≥99%) and 2-hydroxyethyl methacrylate (97%) (HEMA, Fig. 1a) were purchased from Sigma-Aldrich. The chemicals were used as received with no further modification and purification.

2.2. Polymerization by PECVD

Plasma polymerization of HEMA was carried out using a rotating-bed PECVD system (Fig. 1b). Detailed description of the experimental apparatus is given elsewhere [13]. In that system, expanded perlite particles were placed into a cylindrical Pyrex tube, which was used as a vacuum chamber. In order to provide effective agitation of the particle bed during the depositions, the chamber was rotated at a speed of 30 rpm using a stepper motor. Mixing of particles during the depositions allowed continuous exposure of all surfaces of expanded perlite particles to the plasma discharge. HEMA monomer was vaporized in a temperature-controlled glass jar and its vapor was delivered to the reactor through a needle valve. Flowrate of HEMA vapor was kept constant at 0.35 sccm. Temperatures of glass jar which contains HEMA monomer and manifold pipeline were maintained constant at 50 °C and 60 °C, respectively, using PID temperature controllers. During the plasma deposition experiments, the reactor pressure was kept constant at 200 mTorr, which was measured by a capacitance type pressure gauge (MKS, Baratron). Effects of applied plasma power and plasma operation mode (either continuous or pulsed (duty cycle = 30%)) on the wettability of PHEMA-coated expanded perlite particles were investigated. In all plasma polymerization experiments, a flat silicon wafer was also placed in the reactor for characterization purposes.

2.3. Materials characterization

Thicknesses of PHEMA thin films on reference silicon wafers were measured using an AEP 500LS profilometer. Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and Brunauer–Emmett–Teller (BET) method were employed to analyse the chemical and the morphological properties of the surfaces of expanded perlite before and after PHEMA coatings. FTIR spectra were obtained in a Bruker Vertex 70 FTIR spectrometer between 400 and 4000 cm^{-1} wavenumbers at a resolution of 4 cm^{-1} using an attenuated total reflectance (ATR) accessory. SEM experiments were performed using a Zeiss LS-10 scanning electron microscope. The BET data were measured on an Autosorb-IQ2 instrument (Quantachrome).

2.4. Water contact angle measurements and water swelling experiments

The effect of PHEMA coating on wetting properties of expanded perlites was investigated. For this purpose, water contact angles were measured both on flat and particulate substrates. The wettability of PHEMA-coated silicon wafer surfaces was measured by microliter sessile drop contact angle analysis with a video capture system (Model OCA 50, DataPhysics Instruments GmbH) using 2.0 μL de-ionised water. To determine the wettability of PHEMA coated expanded perlite surfaces, Washburn capillary rise method [18] was utilized instead of direct contact angle measurement method, which is not suitable for the contact angle analysis of particulate solids. The schematic diagram of Washburn method is given in Fig. 2. In this method, particles are packed into an open-ended glass capillary column, which is then immersed in water. As time passes, water penetrates into the column, the

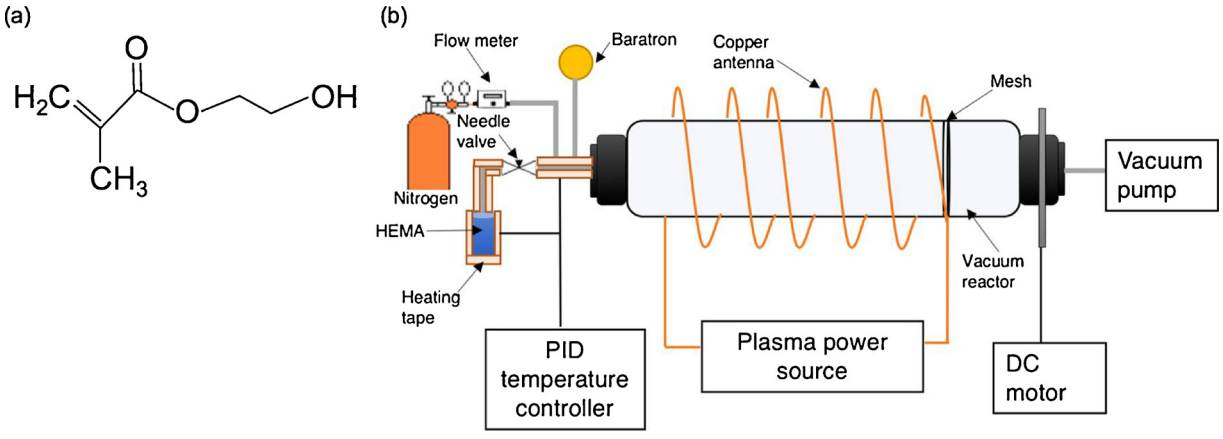

Fig. 1. The chemical structure of HEMA (a) and the schematic diagram of experimental system (b).