One-pot preparation of PS/silica hydrophobic coating by solution-casting using D-limonene as dispersing medium

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Abstract

Different polystyrene (PS) coatings were prepared and optimized by dissolving PS in D-limonene and subsequent dispersion of varying amounts of different chemically modified silica nanoparticles. Among the materials prepared, a PS coating filled with silica nanoparticles organo-modified with long alkyl carbon chains results in high hydrophobicity (120.8° as compared to bare PS coating – 67.0°) and excellent film-formation.

Keywords: PS/silica coatings, hydrophobicity, contact angle

Kulcsszavak: PS/szilícium-dioxid bevonatok, hidrofobitás, nedvesedési szög

1. Introduction

Highly hydrophobic coatings have been of particular interest over the last decade due to their extensive potential applications in anti-corrosion [1,2], self-cleaning [3,4], anti-fouling [5,6], anti-icing [7,8], and drag-reducing materials in a wide range of industries. Surfaces with water contact angles of at least 90° are referred to as hydrophobic surfaces whereas surfaces with water contact angles greater than 150° are referred to as superhydrophobic surfaces [9].

PS is a versatile plastic material that has found wide applications in food packaging, laboratory wares [10-13], electronics and automobile parts [11,12], etc. Due to its low cost of production, most consumer goods come in PS packaging in one form or another. This poses a serious problem to the environment as PS is shown to be relatively stable and is hard to be degraded even after 32 years as stated in a previous study [14]. Over the years, the amount of PS waste that accumulates in landfills and oceans increases. Based on global statistics, about 14 million metric tons of PS are produced each year, and only about 15 percent of that is being recycled due to cost and processing issues as PS is cheaper to produce rather than to recycle and that recycling polystyrene requires it to be contaminant free [15-18].

As a coating material, it has poor barrier characteristics to oxygen and water vapor [19], which is necessary for coating applications. However, several researchers have shown that added with inorganic fillers like silica, PS-based coating materials result in better coating materials [20-22].

Here, we prepared hydrophobic polymer coatings filled with silica nanoparticles from solution-casting using D-limonene as the dispersing medium. Highly hydrophobic coatings based on polystyrene (PS) optimized with different types of surface-modified silica nanoparticles were prepared. In this study,

one-pot method of preparation based on surface segregation phenomenon of nanoparticles on a polymer matrix was used. To make PS and silica dispersion, an environment-friendly solvent, D-limonene, was utilized. D-limonene is a natural solvent that is extracted from citrus fruits like oranges [23].

2. Experimental methods

2.1 Materials

Polystyrene (PS) (MW ~350, 000) and D-limonene (>97%) were purchased from Sigma-Aldrich Co. Three types of commercially available organo-modified nanosilica (SiO_2) particles: Aerosil R 812S, Aerosil R 816, and Aerosil R 972 were used in this study. Aerosil R 812S, Aerosil R 816, and Aerosil R 972 are silica nanoparticles chemically pre-modified with hexamethyldisilazane, hexadecylsilane, and dimethyldichlorosilane, respectively.

2.2 Preparation of PS/ SiO_2 coatings

PS (5.0 g) in D-limonene (150 mL) was heated to 40°C and stirred at 400 rpm for 2 hours. Afterwards, 30 mL each of the polystyrene dispersion was poured into four individual clean Erlenmeyer flasks, where silica nanoparticles were added to three of the flasks and then subjected to stirring. In summary, there are four treatments considered: (1) PS – control (no silica); (2) PS/AS1 – PS/Aerosil R 812S (99:1); (3) PS/AS2 – PS/Aerosil R 816(99/1), and PS/AS3 – PS/Aerosil R 972. Each dispersion was then coated onto clean glass cover slips via solution casting and allowed to dry overnight under ambient conditions. Of the three treatments containing silica nanoparticles, the sample exhibiting highest contact angle and good film formation was then optimized by having varying PS: SiO_2 ratios.

2.3 Wetting property measurement

The static water contact angle of each coated surface was determined by gently dropping 5 μ L of distilled water onto the coated surface using a micropipette. Five replicates were performed for each of the measurements. A photo of the droplet was captured immediately after the droplet was placed on the surface, and the water contact angle was calculated using ImageJ Low-Bond Axisymmetric Drop Shape Analysis (LB-ADSA) [24,25].

3. Results and discussion

3.1 Preparation of PS/SiO₂ coatings

The four treatment samples: (1) PS – control (no silica); (2) PS/AS1 - PS/Aerosil R 812S (99:1); (3) PS/AS2 - PS/Aerosil R 816(99/1), and PS/AS3 – PS/Aerosil R 972 when solution-casted on glass slides.

As shown in Fig. 1, the PS dispersion containing no silica nanoparticles formed a transparent film. PS/AS1 and PS/AS2, both result in homogeneous dispersion of the nanosilica particles, though, not transparent as the PS film (no silica). PS/AS3 exhibited poor homogenous film-formation, as a result of the silica particles poorly dispersed within the PS matrix.

Fig. 1 Glass cover slips coated with a) PS/AS1, b) PS/AS2, c) PS/AS3 and d) PS (control)

1. ábra Üveg fedőlapok a) PS/AS1, b) PS/AS2, c) PS/AS3 és d) PS (etalon) bevonattal

The method for contact angle analysis was first calibrated by comparing the water contact angles of PS and glass used to the ones previously reported elsewhere. The average water contact angle of PS is $\sim 68^\circ$ while that of glass is $\sim 40^\circ$ [26]. Using the low-bond axisymmetric drop shape analysis (LB-ADSA) method [24,25], the water contact angles of PS and glass subtract were found to match previously documented data. As shown in Fig. 2, all PS films filled with nanosilica showed higher contact angle values than the bare PS coating, indicating more hydrophobic effect to the PS matrix by organo-modified silica incorporation. Though PS/AS1 results to an even coating from visual inspection than PS/AS2, the latter exhibited higher contact angle (Mean = 120.6°). Among the films with incorporated silica, PS/AS3 results in lowest contact angle value and poor dispersion of the particles. Statistical analysis of all treatments showed a significant difference in the observed contact angles of the coatings.

Fig. 2. Contact angle measurements of the glass substrate used and different PS coatings applied on glass

2. ábra Nedvesítési szög üvegen és különböző PS bevonatokon

From the results of film casting and contact angle measurements, PS film modified with Aerosil R 816 exhibited homogeneously dispersed particles in a PS matrix with high hydrophobicity (high contact angle). Based on an initial PS/silica ratio of 99/1, varying ratios of PS/Aerosil R816 were then prepared.

As expected, the non-wetting behavior of PS-AS2 improved with increasing concentration of modified silica (Fig. 3). However, at SiO₂ concentration greater than 3.0% (relative to PS) decreased hydrophobicity and poor film formation were noted due to cracking brought about by particle aggregation.

Fig. 3. Measure contact angles (upper) and photos (lower) taken of various PS films incorporated with different amounts of Aerosil R816 (PS/AS3) applied on glass

3. ábra Nedvesítési szög (felső sor) és a hozzájuk tartozó minták amelyekre különböző mennyiségű Aerosil R816 (PS/AS3) bevonatot vittek fel (alsó sor)

Fig. 4 showed PS coatings (left) filled with Aerosil R 816 (PS/AS3) at varying ratios: 99.5:0.5 and 99.9:0.1. The other two (right) correspond to glass slides coated with PS only and uncoated glass, respectively. Water droplets (colored) are applied on the surfaces to compare non-wetting behavior. Though not as clear as the unfilled PS coating, PS-filled with silica nanoparticles solution-casted using D-limonene as solvent can result in more hydrophobic coatings where optical property can be fine-tuned by changing the silica concentration.

Fig. 4. PS films incorporated with different amounts of Aerosil R816 (PS/AS3) applied on glass compared to just bare PS coating and uncoated glass slide

4. ábra Különböző mennyiségű Aerosil R816 (PS / AS3) bevonattal ellátott PS-fóliák összehasonlítva tiszta PS bevonattal és bevonat nélküli üveggel

To check on the uniformity of the prepared film from the solution casting of PS filled with Aerosil R816 (PS/AS3), at 99.9:0.1 weight ratio with D-limonene as the dispersing medium, water droplets were placed at various places across the films. As shown in Fig. 5, uniform water droplets can be observed displaying high contact angles, that were previously determined to have an average value of 120.8° (as opposed to the contact angle observed in PS only, 67.0°).

Fig. 5. Deposited water droplets deposited on the surface of PS:Aerosil R816 (PS/AS3) film (at 99.9:0.1 weight ratio) solution casted from D-limonene as solvent

5. ábra A PS: Aerosil R816 (PS / AS3) film (99,9: 0,1 tömegarányú) felületére helyezett vízcseppek

4. Conclusions

In summary, we were able to prepare a highly hydrophobic PS-based coating filled with organo-modified nanosilica particles from solution-casting using D-limonene as the dispersing medium. The film's properties such as non-wetting behavior, film-formation characteristic and optical property can be fine tuned with the type of organo-modified silica particles to be added as well as the silica concentration. From the three commercially available silica nanoparticles used: Aerosil R 812S, Aerosil R 816, and Aerosil R 972 which are silica nanoparticles chemically pre-modified with hexamethyldisilazane, hexadecylsilane, and dimethyldichlorosilane, respectively – the PS films modified with Aerosil R 816 at 0.1:99.9 weight ratio (relative to PS) result in homogeneous, highly hydrophobic (120.8°) coatings as contrasted to PS only (67.0°).

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