



# Fabrication of poly(ethylene glycol) particles with a micro-spherical morphology on polymeric fibers and its application in high flux water filtration

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## ABSTRACT

Polymeric coatings with micro-spherical morphology have a high surface area, which is advantageous for resins for heterogeneous chemical catalysis, for adsorption processes, nano-reactors, and anti-fouling coatings for water treatment membranes. The fabrication of stable, non-leachable micro-spherical polymers on solid surfaces is challenging. Here we introduce a straightforward method for fabricating polymeric particles with micro-spherical morphology on poly(ethylene terephthalate) fibers used as media for water filtration in microfiber technology. UV-initiated grafting with poly(ethylene glycol) methacrylate (PEGMA) monomers using benzophenone in aqueous solutions resulted in stable spherical particles coated on poly(ethylene terephthalate) threads, as revealed by FTIR, gravimetric degree of grafting, and SEM analyses. The micro-spherical morphology was unique to grafting with PEGMA monomers, whereas other types of methacrylate monomers resulted in smooth coatings. Grafting with PEGMA on high-flux water filtration cassette made of poly(ethylene terephthalate) fibers lead to enhanced performance and better dust removal capacity of the filter. The improved performance in coarse filtration is beneficial for treatment of water for agriculture, pretreatment facilities for freshwater supply, cooling water systems, and wastewater treatment. The protocol developed in this study is highly promising for both industrial and medical applications.

## 1. Introduction

There is considerable interest in the development of polymeric coatings with predefined specific morphologies. A micro-spherical morphology, as opposed to a smooth, flat coating, has the advantage of a high surface area which is beneficial for anti-fouling coatings for water treatment membranes and filters; it can aid other numerous applications, such as materials with high sorption capacity, nanoreactors, resins for heterogeneous chemical catalysis, and anti-adherence coating for medical implants [1–4]. Additionally, polymeric anti-fouling coatings with a micro-spherical surface morphology may be an attractive route for improving membranes and filters due to the high permeability of such coatings as compared with a flat coating.

Several methodologies have been reported for preparing polymeric materials with spherical morphology. The main strategies are the

polymerization of core-shell nanoparticles, suspension polymerization and emulsion polymerization, self-assembly of amphiphilic-diblock copolymers, template-directed synthesis, and electrospinning (see a recent review [5]).

Polymeric micro-spherical particles that are bound to polymeric surfaces have also been described (see a feature article [6]), but much less extensively than polymerizations occurring in the bulk. Uchida and Ikada performed graft-polymerization of 2-(dimethylamino)ethyl-methacrylate by UV initiation on poly(ethylene terephthalate) (PET) film [7]. Atomic-force microscopy (AFM) of the resulting PET surface showed that in water the grafted polymer brushes stretch out from the surface, forming a brush structure. Significant progress in preparing polymeric spherical particles on flat surfaces was achieved by Yang and colleagues [8], who identified synthetic procedures for the direct fabrication of spherical particles bound covalently to polymeric surfaces,

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which were therefore highly stable [9]. These procedures were based on UV-initiated polymerization with benzophenone (BPh) as a photo-initiator. One-step co-polymerization of the amphiphilic monomer N-vinylpyrrolidone with an emulsion of methyl-methacrylate and divinylbenzene stabilized with surfactants gave spherical particles 0.35–1.3  $\mu\text{m}$  in diameter immobilized on the surface [10,11]. The spherical particles were either hollow or solid, depending on the exact monomer composition [9]. Photo-grafting of NVP with methylene-bisacrylamide as an inverse micro-emulsion [12] gave spherical particles with a bimodal size distribution of 45 nm and 110 nm. A two-step procedure comprising surface initiation by UV with BPh followed by addition of the monomer emulsions resulted in mono-dispersed spherical particles 30 nm in diameter as a monolayer or multilayers attached to the surface [11–13].

An example of the potential use of a spherical polymeric coating is the surface hydrophilization of water treatment membranes and filtration media for overcoming organic- and bio-fouling. Poly(ethylene glycol) (PEG) was shown to resist the non-specific binding of proteins to surfaces [14,15], and was successfully incorporated in the design of water treatment membranes by several groups to reduce membrane fouling [4,16]. The PEG moiety was either grafted on the membrane surfaces or incorporated in the polymer blend as an additive. Previous studies of coating polymeric membranes by our group showed that redox-initiated graft polymerization with hydrophilic methacrylate monomers was an efficient method for generating antifouling coatings on reverse osmosis, nanofiltration, and ultrafiltration membranes [17,18]. Mechanistic studies showed that both the swelling properties and the chemical nature of poly(ethylene glycol) contributed to the antifouling behavior of the coating [19,20].

This study describes a method for the fabrication of grafted polymeric spherical particles on flat polymeric fibers used for coarse filtration. The method is simple, conducted in aqueous media without the use of surfactants, and is based on the one-step graft-polymerization of a single monomer, poly(ethylene glycol) methacrylate, using UV irradiation. Graft-polymerization on PET fibers resulted in a coating of spherical particles 1–10  $\mu\text{m}$  in diameter. When PEGMA was grafted on PET fibers of water filter cassettes enhanced performance and better dust removal was achieved. This method may be highly suitable for the surface hydrophilization of polymeric surfaces, and is especially useful for coating polymeric membranes and filters for water treatment due to the high permeability of coating by spherical particles, and its simplicity (one-step procedure), execution in aqueous solution, and use of low-cost and commercially available reagents.

## 2. Experimental section

### 2.1. Materials

Benzophenone (BPh), potassium persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ), potassium meta-bisulfite ( $\text{K}_2\text{S}_2\text{O}_5$ ) and the following monomers were all purchased from Sigma-Aldrich (St. Louis, MO, USA): methacrylic acid (MA), 2-hydroxyethyl methacrylate (HEMA), and poly(ethylene glycol) methacrylate (PEGMA; number-average molecular weight of 360 g/mol and 526 g/mol). PEGMA-200 was purchased from Polyscience Inc. (Warrington, PA, USA).

### 2.2. Polyethylene terephthalate (PET) fiber filtration cassette

The PET fiber filtration cassettes, as well as free bundles of PET fibers, were supplied by Amiad Water Systems (Galil Elyon, Israel). The filtration cassette is part of the *AMF Filter*<sup>®</sup> (by Amiad Water Systems), based on microfiber technology. It should be noted that all measurements in this study were made while the cassettes were detached from the *AMF filter*. The dimensions of the fiber cassette are 58 mm (width)  $\times$  86 mm (length), the filtration area of the cassette on both sides is 9976 mm<sup>2</sup> (100 cm<sup>2</sup>). Fig. 1 shows the PET fibers and a filtration

cassette. The fibers are distributed transversely, and the porosity of the filter material, which is made of fibers is  $\psi = 0.58$ . The penetration coefficient,  $K$ , is  $3 \times 10^{-10} \text{ m}^2$ . Attenuated total reflection (ATR) Fourier-transform infrared (FTIR) spectroscopy showed that the PET fibers were in their crystalline form (see Section 3).

### 2.3. UV-initiated graft polymerization on PET fibers

All the substrates were washed twice in methanol using an ultrasonic bath for 30 min, and were dried at room temperature for 1 h. Next, the PET threads were immersed for 15 min in acetone containing 0.1 MBPh, then dried in an oven at 45 °C for 2 h to remove the solvent. For the graft polymerization step, the PET surfaces were placed for 15 min in a glass Petri dish containing 15 mL of an aqueous solution of the monomers to swell. The Petri dish was covered with a cover glass (wavelength cutoff > 300 nm) and placed in a UVACUBE-100 UV chamber (Honle, Grafelfing, Germany) containing a mercury lamp. The UV intensity inside the chamber was measured by a UV light meter (model YK-34UV, Lutron Electronic, Taipei, Taiwan), and was found to be  $4.8 \pm 0.5 \text{ mW/cm}^2$ . The grafted fibers on the cassettes were washed at room temperature for 1 h, and free bundles of PET fibers were washed by Soxhlet extraction for 10 h. Finally, the fibers were dried overnight at room temperature.

### 2.4. Redox-initiated polymerization

To a stirred aqueous solution of PEGMA-360 (1.2 M), potassium persulfate and potassium meta-bisulfite were added to a final concentration of 0.01 M. The polymerization mixture was then dialyzed against water using a 25 mm  $\times$  16 mm cellulose-based dialysis tube with a molecular-weight cutoff of 14,000 kDa (Sigma-Aldrich). The resulting polymers in aqueous solution were then freeze-dried using a FreeZone 2.5 Plus lyophilizer (Labconco, Kansas City, MO, USA) for 48 h to give a white solid.

### 2.5. Characterization by ATR-FTIR spectroscopy

ATR-FTIR of the outer surfaces was performed using an Equinox 55 instrument (Bruker Optics, Ettlingen, Germany) equipped with a liquid nitrogen detector. ATR has a penetration depth of < 200 nm using wavenumbers above 2600  $\text{cm}^{-1}$  and > 300  $\text{cm}^{-1}$  for wavenumbers lower than 2000  $\text{cm}^{-1}$ , thereby allowing chemical information regarding the top layers to be obtained. Each measurement comprised 64 scans with a wavenumber resolution of 4  $\text{cm}^{-1}$  by placing the studied surface on top of a diamond crystal slit at a temperature of  $21 \pm 1$  °C. The basic Opus software provided by Bruker was used to record the spectra and select the corresponding backgrounds for the ATR crystal. Although high wavenumbers are useful for the characterization of certain functional groups such as hydroxyl groups or amines, most information is obtained between 1800 and 700  $\text{cm}^{-1}$ , which is the wavenumber range encompassing the characteristic bands of the PET functional groups.

### 2.6. Characterization by scanning electron microscopy (SEM)

The surface morphology of the grafted films was observed by SEM (JEOL, model JSM-5200, Peabody, Massachusetts). For better electrical conductivity, each sample surface was coated with a thin gold layer before scanning. SEM observation was employed primarily to elucidate the morphology of the new coatings.

### 2.7. Characterization of critical micelle concentration (CMC)

The amphiphilic characteristics of surfactants encourage them to locate mainly at the boundaries between two phases. At concentrations above the CMC, density forces the surfactants to associate into micelles within the bulk surfactant emulsion, thereby dramatically changing the

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