



# Preparation of aqueous dispersion of thermoplastic sizing agent for carbon fiber by emulsion/solvent evaporation

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## ABSTRACT

In this work, different sizing agent aqueous dispersions based on polyetherimide (PEI) were elaborated in order to improve the interface between carbon fibers and a thermoplastic matrix (PEEK). The dispersions were obtained by the emulsion/solvent evaporation technique. To optimize the stability and the film formation on the fibers, two surfactants were tested at different concentrations, with different concentrations of PEI. The dispersions obtained were characterized by dynamic light scattering (DLS) and the stability evaluated by analytical centrifugation (LUMiFuge). The selected dispersions were tested for film formation ability by scanning electron microscopy (SEM), and the sizing performance was assessed by observation of the fiber/matrix interface by SEM. The results revealed that an aqueous dispersion of PEI, stabilized by sodium dodecyl sulfate as the surfactant, led to very stable sizing agent aqueous dispersion with ideal film formation and better interface adhesion.

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## 1. Introduction

Carbon fiber is widely used as a reinforcing material in composites, especially in advanced composites [1,2]. As carbon fibers are brittle, many problems, such as filament breakage and fluffing, arise due to mechanical friction during the manufacturing process [3–5]. Therefore, carbon fibers are generally sized or coated by a sizing layer on the surface, which is usually obtained from a solution or emulsion consisting of polymeric components [6,7]. Sizing eases fiber handling and can also provide a coupling agent for the fiber/matrix bond [8–11]. The nature of the sizing is often kept secret by manufacturers of carbon fibers. However, sizing is chosen according to the nature of the matrix and is generally a pre-polymer or polymer. Most of the composites are made from epoxy resin, and sizing agents are often of the same nature [5,12–14]. This is a problem when the matrix is a high-temperature thermoplastic polymer since the degradation temperature of this type of sizing is around 250 °C [15]. For polyimides, PEEK and other high-temperature thermoplastic polymers, the functional groups provided by the traditional epoxy-compatible sizing do not react chemically with these polymers and weak interfacial shear strengths result [16]. Moreover, for composites molded with polyimides or PEEK, high processing temperatures during manufacture and continuous use

in high-temperature environments degrade the epoxy sizing and, consequently, weaken the fiber/matrix interface, producing voids and delaminations [17–19]. All of these observations underline the importance of having sizing that is suitable for high-temperature thermoplastic matrices. From a practical point of view, the sizing formulation should be easy to use, non-toxic and environmentally friendly. In this paper, we report the first example of preparation an aqueous dispersion of a thermoplastic sizing agent for carbon fiber by emulsion/solvent evaporation.

## 2. Experimental

### 2.1. Materials

The polyetherimide PEI (Ultem 1000) was obtained from Sabic®. The sodium dodecyl sulfate (SDS) and the chloroform were provided by Sigma–Aldrich, the benzalkonium chloride (BC) was from Fluka (C<sub>12</sub> 60%, C<sub>14</sub> 40%). The AS4 carbon fiber tow, provided by Hexcel, was treated unsized and contained 12,000 fibers. The polyetheretherketone (PEEK) provided by Victrex was a 100 μm thick film. The remolding agent was CIREX 041WB from SICOMIN.

### 2.2. Preparation of PEI dispersions by emulsion/evaporation

In order to reduce the toxicity and to respect the environment, organic solvents must be avoided in the final sizing agent formulation. For these reasons, we decided to elaborate aqueous

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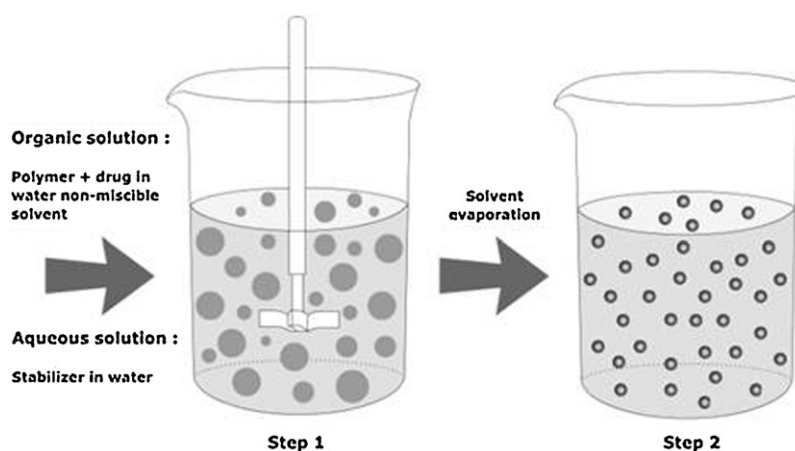


Fig. 1. Schematic representation of the pharmaceutical emulsification/evaporation process.

dispersions. These can be made by a variety of methods [20–23] leading, at the end, to stable hydrophobic particles in water. The preparation process described here was largely inspired by emulsion/solvent evaporation, an encapsulation technique used in the pharmaceutical industry to prepare aqueous dispersions of polymer nanoparticles or microspheres.

Emulsion/solvent evaporation involves a two-step process (Fig. 1): the emulsification of a polymer solution containing the encapsulated substance, followed by particle hardening through solvent evaporation and polymer precipitation. During the water emulsification, the polymer in solution in the volatile, water-immiscible solvent is broken into microdroplets by the shear stress produced by either a homogenizer or a sonicator in the presence of a surface-active agent until the polymer precipitates [24–27].

This method was used to prepare a stable aqueous dispersion of PEI as the sizing agent. We used two different surfactants, sodium dodecyl sulfate (SDS) and benzalkonium chloride (BC) at different concentrations (0.3%, 0.5% and 1 wt%). The final concentrations of PEI were 0.1%, 0.3%, 0.5% and 1 wt%. The PEI dispersion at 0.5 wt% in a 0.5 wt% surfactant solution was prepared as follows. In a 5-mL flask, 0.1005 g of PEI was dissolved in 2 mL of chloroform. This solution was poured into another flask containing 20 mL of the surfactant solution. The mixture was emulsified by ultrasound shearing (Vibra Cell, Bioblock Scientific 600W, 20 Hz). The shearing lasted 5 min at power 4. A water bath was used to maintain the solution at room temperature. Then, magnetic stirring of the emulsion at 1200 rpm for 12 h allowed total evaporation of the chloroform.

### 2.3. Characterization of PEI dispersions

#### 2.3.1. Particle size analysis

Dynamic light scattering (DLS) was performed using a Malvern Instruments Nano ZS with a He–Ne laser (633 nm) at a scattering angle of  $173^\circ$  and at  $25 \pm 1^\circ\text{C}$ . The hydrodynamic mean diameter of the nanoparticles was determined using the software provided by Malvern Instruments. The Contin model was applied to obtain size data. All the auto-correlation function fits were checked and found to be in accordance with the experimental data. Five measurements were made on each sample with an accuracy of about 2 nm.

#### 2.3.2. Evaluation of stability using analytical centrifugation

A separation analyzer (LUMiFuge, L.U.M. Berlin, Germany) was used to determine the separation behavior of dispersions under the influence of various centrifugal forces ( $5\text{--}1000 \times g$ ). This apparatus is based on a low-speed centrifuge combined with an optoelectronic measuring system that records the light transmission over the entire sample cuvette (Fig. 2). The cuvettes containing the

suspension are positioned in the horizontal plane on the rotor of the centrifuge. During centrifugation a light source positioned above the rotor emits radiation (near-infrared) onto the sample. Transmitted light is detected by a CCD line sensor below the rotor plane and is analyzed by a microcontroller, which generates a light-transmission profile of the sample area for every measurement step.

This technique is very appropriate for the study and optimization of very stable aqueous dispersions. The centrifugal force accelerates the destabilization of the dispersion and rapidly determines the shelf life of the dispersion [28]. Moreover, the possibility of studying 8 samples at the same time enables different formulations to be compared immediately [29,30]. The dispersions are naturally stable over 6 months so we chose to simulate 3 years of aging. The data acquisition corresponded to 255 profiles recorded every every seconds at 4000 rpm. The temperature was  $20^\circ\text{C}$ .

### 2.4. Sizing treatment of carbon fiber and composite preparation

#### 2.4.1. Sizing of carbon fiber

Different methods can be used to size carbon fibers, such as electrodeposition [31,32] or electropolymerization [33,34], but the most common is bath coating. We tested the sizing at laboratory scale so, in this case, the most suitable technique was to spray the dispersion directly on to the fiber surface. An unsized fiber tow was strained by a weight to keep it vertical, allowing uniform spraying of the sizing at the fiber surface (Fig. 3). After sizing, the fibers were dried at room temperature.

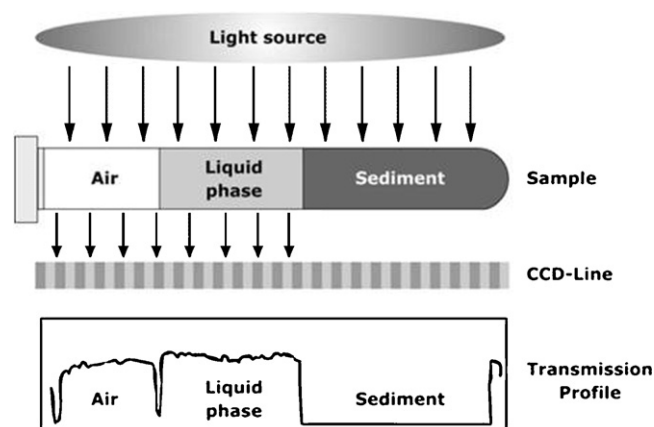


Fig. 2. Measuring principle of the separation analyzer (LUMiFuge).

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