



Application of hollow fiber flow field-flow fractionation with UV–Vis detection in the rapid characterization and preparation of poly(vinyl acetate) nanoemulsions

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ABSTRACT

Poly(vinyl acetate) (PVAc) nanoemulsions have wide applications in the construction and adhesives industries, with their unique properties being closely dependent on the PVAc nanoparticle (NP) size. Effective and robust analytical methods are needed to accurately characterize the NP size according to the specific requirements to satisfy quality controls and scale production demands. Herein, hollow fiber flow field-flow fractionation (HF5) with UV–Vis detection, which features instrumental simplicity, convenient operation, and low running costs, was proposed for the real-time size characterization of PVAc NPs. The results obtained by the proposed method were in good agreement with the size values obtained by TEM, thereby demonstrating the applicability and reliability of the HF5-based method for PVAc NP size characterization without tedious sample preparation requirements. In order to assess the parameters dominating PVAc NP size, the variables of emulsifier concentration, composite emulsifier ratio, reaction temperature, and stirring rate were investigated in detail. The results proved that the emulsifier component and string rates were the key parameters controlling particle size. Furthermore, NP growth processes were tracked by HF5 over 8 h, clearly indicating a gradual increase in PVAc NP size with time. The results firmly confirmed that HF5 has great potential in NP size control applications during the production and product quality evaluation of PVAc NPs.

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1. Introduction

Poly(vinyl acetate) (PVAc), commonly known as “white latex”, is a widely used polymer emulsion variety produced on an industrial scale [1–3]. PVAc emulsions have excellent inherent properties, including environmental friendliness, high bonding strength, low volatility, and excellent film-forming properties [4]. PVAc-based products, approved by the Food and Drug Administration, are commonly used in a large number of fields worldwide, and in particular in the construction and adhesives industries [5,6]. Previous studies have confirmed that the mechanical and adhesive properties of PVAc products are closely related to the particle size or molecular weight of PVAc polymers [7–10]. For example, PVAc particles of <100 nm in size (nanoparticles, NPs) exhibit increasing permeability, leveling, and rheological properties with decreasing size. Furthermore, the stability of PVAc NPs was shown to be significantly better than that of PVAc microspheres [11]. Therefore,

the need to produce well-defined PVAc NPs with a uniform size distribution has led to the requirement of real-time, robust, and high resolution characterization techniques for the quality monitoring and control of NP size.

A wide variety of analytical techniques have been applied in the characterization of PVAc particle size, including transmission electron microscopy (TEM), dynamic light scattering (DLS), and size exclusion chromatography (SEC). TEM is able to provide direct visualization of the size of individual PVAc particles as well as bulk size information following statistically counted particles appearing in the grid [12]; however, the labor- and time-intensive sample preparation procedures hinder its use as a rapid, real-time monitoring characterization technique during PVAc manufacture or on-site quality control. Further, given the relatively flexible nature of PVAc NPs, sample drying and electron beam irradiation during high-vacuum measurements could result in the shrinkage of particles [13,14], providing erroneous results. Conversely, DLS measurements are simple and fast, requiring no special sample preparation, which is beneficial for its use in real-time monitoring. Nevertheless, particle size characterization by DLS is based on the Brownian

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motion of particles scattering light, and therefore larger particles may lead to the overestimation of mean size value and size distribution [15,16]. This effect will lead to limited resolution, making DLS unsuitable for polydisperse samples containing a wide particle size range. SEC coupled with spectroscopic techniques has great potential in the separation and characterization of PVAc particles at high resolution [17–19]; however, there are concerns regarding the column lifetime due to the interaction between sample components with the packing material [14] and the exclusion limits, dominated by the packing material pore size [20].

Field flow fractionation (FFF), another widely used separation and sizing technique conducted in channels free from packing materials, has an excellent capacity to characterize particle species with hydrodynamic diameters spanning the nano and micron size range with high resolution [21–24]. Traditional flow FFF subtechniques (e.g., sedimentation FFF [25,26] and flow FFF [27–29]) are useful in the monitoring of size variation in the synthesis process of NPs. Hollow fiber flow FFF (HF5) is the latest variant technique of flow FFF [30]. Compared to the classical flow FFF channel, in which fractionation is achieved in a thin ribbon-like open channel, fractionation in HF5 is performed in cylindrical channels composed of a hollow fiber membrane [31,32]. In addition to the comparable or better separation ability with other flow FFF techniques, the key advantage of HF5 lies in its instrumental simplicity, convenient operation, and low running costs due to the inexpensive and disposable hollow fiber (HF) used [33,34]. Moreover, HF5 has shown great potential in monitoring the preparation or purification of polymer-based NPs due to its rapid (within minutes) separation of NPs or macromolecules [35,36]. However, despite these advantages, to the best of our knowledge, HF5 has not yet been applied in the rapid characterization and quality control of polymers during their preparation.

The present study aims to evaluate (1) the applicability of HF5 in the real-time separation and characterization of PVAc NPs during their synthesis, (2) the effects of the main experimental parameters, such as emulsifier concentration and composition, reaction temperature, and stirring rate on particle size, and (3) track particle growth processes.

2. Experimental

2.1. Materials

Vinyl acetate (VAc), ammonium persulfate, sodium dodecyl sulfate (SDS), and octyl phenyl polyoxyethylene ether (OP-10) were purchased from J&K Chemical Ltd. (Beijing, China), and used to prepare PVAc NPs. Polystyrene (PS) latex standards having a nominal size of 20, 60, 80, and 100 nm were obtained from Thermo Fisher Scientific, Inc. (Waltham, MA, USA) and used for PVAc NP size characterization. A polyacrylamide (PAN) HF membrane with a molecular weight cut-off of 30 kDa, to be used as the separation channel in HF5, was bought from Synopex Inc. (Gyeongsangbuk-Do, Korea). Ultrapure water (18.3 M Ω) produced by a Milli-Q Gradient system (Millipore, Bedford, USA) was used throughout this work.

2.2. Synthesis of PVAc NPs

An emulsion polymerization technique of the VAc monomer with SDS was adopted to prepare PVAc NPs [37]. The effects of emulsifier dosage and composite emulsifier ratio, reaction temperature, and stirring rate were investigated to identify the main operation parameters controlling PVAc particle size. In a typical reaction, 1.72 g SDS, 0.43 g ammonium persulfate, and 200 mL ultrapure water were successively added into a three-neck round bottom flask. The mixture was stirred until it became transparent. Then, 86 g of monomer VAc were slowly added into the mixture. Finally, the aqueous solution was heated to 50 °C in a water bath under stirring at 100 rpm and incubated for 4 h. PVAc nanoemulsions sampled from the reaction solution were diluted 10 times with the carrier liquid (5 μ M SDS) prior to HF5 analysis.

2.3. Instruments

The HF5 system previously described [38] was slightly modified as shown in Fig. 1. Briefly, a plunger pump (1200, Agilent, USA) equipped with a degasser was used to deliver the carrier solution. Flow rates were adjusted by two metering valves (SS-31RS4, Nupro, Willoughby, OH, USA) for the entire duration of the experiments. Sample injection was performed using a model 7752i injection valve (Rheodyne, Cotati, CA, USA) with a 20- μ L loop. The HF separation channel, with dimensions of 0.85 mm \times 1.55 mm \times 24 cm (inner diameter (I.D.) \times outer diameter (O.D.) \times length), was constructed as previously described [34,38]. During a complete run, constituted of focusing/relaxation and elution, the conversion between the focusing/relaxation step and the elution step was achieved by electronically controlled valves (VICI, Valco Co., Houston, TX, USA). A UV–Vis detector (1200, Agilent, USA) at a wavelength of 254 nm was used to monitor the eluted particles. PEEK tubing (0.50 mm \times 1.58 mm, I.D. \times O.D.) was used to connect all of the abovementioned units.

TEM (H-7500, Hitachi, Japan; at 200 kV) and DLS (ZEN3600, Malvern, UK) were used to validate PVAc NP size information obtained through the HF5 system.

3. Results and discussion

3.1. Operation of HF5 separation

The operation procedure consisted of two steps, sample focusing/relaxation and elution, which were triggered and switched by automatically controlling valves (V1 and V2; Fig. 1). During the sample focusing/relaxation step, V1 (four-way valve) and V2 (three-way valve) were transferred to the MV1 and HF direction, respectively. The carrier solution containing 5 μ M SDS was transported by a pump and split in two by a tee connector before V1 as V_{in} (flow entering V1) and V_{out} (flow entering the back end of the fiber through V2). As previously reported [34], a metering valve (MV1) was used to adjust the ratio of V_{in} and V_{out} to 1:9. Sample injection was performed through an injection valve. Following a set focusing time (e.g., 3 min), elution was commenced by switching V1 and V2 toward the HF and UV–Vis detector directions simultaneously. V_{in} was increased to the desired value (e.g., 1.5 mL/min), while another metering value (MV2) was used to ensure that the flow field (radial flow rate, V_{rad}) was identical to that used during focusing/relaxation. Finally, the fractionated particles formed in the prior step were transferred to the detector according to their size.

In order to improve separation performance, the main operating conditions of HF5, namely carrier composition, focusing time, and flow rates, including V_{rad} and V_{in} in the elution step, were optimized using 60 and 100 nm standard PS NPs as models. A series of carrier liquids with an SDS concentration ranging from 0 to 1 mM were tested, and 5 μ M of SDS was finally chosen as the most suitable carrier in terms of

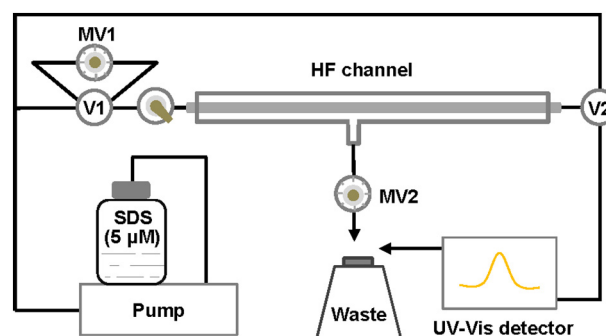


Fig. 1. Scheme of the HF5 system. V1, four-way valve; V2, three-way valve; MV1 and MV2, metering valves; IV, injection valve.

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