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# Physicomechanical characterization of monodisperse multivesiculated polyester particles



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## ABSTRACT

This work describes physicomechanical properties of low-density polyester particles with multi-alveolar inner morphology, obtained via a water/oil/water double emulsion process. Monodisperse particle diameters were produced thanks to the use of a microchannel T-junction device for droplet generation. The drying conditions tested showed that rapid water evaporation at 120 °C, combined with slow diffusion towards the exterior, causes internal fracture and particle deformation. Interestingly, all particles present virtually identical internal damage and external deformation features under these drying conditions, demonstrating the uniformity in internal structures. Drying at 70 °C allows for efficient water removal with no damage. Thermomechanical transitions and thermal stability were analyzed by dynamic mechanical analysis (DMA in single-particle compression mode), dynamic scanning calorimetry (DSC) and thermogravimetry (TG). The effectiveness of curing conditions was evaluated by FTIR and DSC, allowing to identify the need of a thermal post-treatment for consumption of residual styrene. The consequent increase in degree of crosslinking produced a positive shift in glass transition temperature measured by DMA. Finally, mechanical reinforcement of the multivesiculated polyester particles was obtained by loading the polymer with surface-modified fumed silica, yielding 75% increase in storage modulus.

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## 1. Introduction

Multivesiculated polyester particles (MVPs) are an example of hollow polymeric microparticles that have been used as opacifying agents in paint and paper industries, taking advantage of the refraction index difference between the polymer and the air contained in the multiple inner voids [1,2]. They are produced in a conventional batch stirred tank reactor, with sizes ranging from a few to tens of microns. In a recent work, we have reported for the first time the synthesis of MVPs using a microfluidic system [3], allowing for obtaining particles with very narrow size distributions

and uniform morphologies, unlike the conventional stirred batch reactor process. The new process involves three steps. First, water is emulsified in an organic phase made of unsaturated polyester dissolved in styrene. This water-in-oil (w/o) emulsion is stabilized by hydrophilic acid-base ion-pairs formed by neutralization of terminal polyester carboxylic groups with an added amine, no surfactant addition being necessary [4]. A microchannel T-junction device is then used to generate monodisperse droplets of this w/o emulsion in an aqueous solution of protective colloid, forming a w/o/w double emulsion. The last step consists in chemically cross-linking (curing) the polyester–styrene phase via radical polymerization. This yields an aqueous dispersion of solid particles that, upon drying, loose water retained in the vesicles and become air-filled.

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We have previously studied the conventional stirred reactor process for MVPs production, in the context of use as waterborne paint opacifying agents [2]. The most relevant properties for this application are particle size distribution, internal vesiculation morphology, and dry film opacity. However, the possibility of fine-tuning monodisperse particle sizes via a microfluidic approach opens new potential fields of application, namely involving particles with larger diameters (tens to hundreds of microns). Indeed, considering the particular structure of these alveoli-filled particles, combined with the rigid cross-linked matrix of the polymeric walls, MVPs are interesting for novel uses such as low-density fillers for thermoplastic [5] or thermoset matrixes [6], and syntactic foams [7]. This entails a thorough characterization of new pertinent properties and processing conditions.

The present work investigates for the first time several physicochemical properties of multivesiculated polyester particles (glass transition, thermal stability, rigidity, degree of curing), synthesized as water dispersions with the help of a microchannel T-junction device. The thermomechanical characterization is based on dynamic mechanical analysis of single particles in compression mode. This constitutes a powerful methodology, valid thanks to the high homogeneity of the particles produced, both in terms of external dimension and internal morphology. The effectiveness of different curing and drying conditions is also analyzed, allowing identification of appropriate procedures. Finally, the effect of adding an inorganic nano-filler (functionalized silica) to the polymer matrix on the thermomechanical behavior of the particles is studied.

A photoinitiator is used for the chemical cross-linking process instead of the thermally activated peroxide-based initiator system used in previous works [8]. This allows for fast curing at room temperature under UV irradiation.

## 2. Experimental

### 2.1. Materials

Styrene and unsaturated polyester (70 wt.% solution in styrene, acid value 15–20 mg KOH/g and Brookfield viscosity 1000–2000 mPa s) were kindly provided by Resiquímica (Mem Martins, Portugal). Poly (vinyl alcohol) (Mowiol 47–88, Mw > 205,000 g/mol, degree of hydrolysis = 88%) was kindly provided by Clariant International Ltd., Switzerland. Triethanolamine (TEA, puriss. p.a.) and photoinitiator diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide/2-hydroxy-2-methylpropiophenone blend (TPO/HMPP) were supplied by Sigma–Aldrich and used as received. Hydrophobic fumed silica (AEROSIL R8200) was supplied by EVONIK Industries.

### 2.2. Multivesiculated particle production

The unsaturated polyester solution was first neutralized with TEA and then diluted in styrene. After addition of UV photoinitiator to the organic phase, the final proportion of polyester, TEA, styrene and TPO/HMPP is 45.9%, 2.5%, 48.2% and 3.4%, respectively.

Water was then emulsified in the organic solution (40/60 wt.% ratio) by stirring for 15 min at 1000 rpm with a helix-type impeller. This w/o emulsion was then injected in a T-junction device (stainless-steel tee fitting reference ZT1, internal diameter  $\varnothing$  750  $\mu$ m, supplied by VALCO VICI) to generate monodisperse droplets in a continuous phase consisting of 2.3 wt.% PVA aqueous solution. The apparatus is described in detail in our previous work [3]. The selected operating conditions consisted on dispersed and continuous phase flow rates of 5  $\mu$ L/min and 650  $\mu$ L/min, respectively, yielding an average droplet size of about 400  $\mu$ m. The fluids were driven by two precision syringe pumps (model 11 Plus, Harvard Apparatus). Temperature at the T-junction was kept constant at 25 °C with a thermostatic bath.

For incorporation of nano-filler, functionalized fumed silica powder (5 wt.%) was dispersed in the initial organic phase by an IKA T-18 Ultra-Turrax disperser at 3000 rpm, for 10 min in an ice bath, to avoid overheating. The suspension was then left to rest for 30 min to remove microbubbles and allow reaching room temperature. The synthesis process then proceeded as described previously, although the fluid flow rates had to be adjusted in order to obtain particles of the same size (dispersed phase = 3  $\mu$ L/min and continuous phase = 750  $\mu$ L/min). This was due to increased viscosity of the organic phase after addition of silica.

The multivesiculated droplets were then collected in a vessel with magnetic stirring, filled with the same PVA solution, and irradiated by an UV lamp (Vilbert Lourmat – BLB 365 nm, 2  $\times$  6 W lamps). The particles produced in each trial were subjected to at least 30 min of UV irradiation.

### 2.3. Characterization methods

Optical microscopy images of collected droplets were obtained using an Olympus IX-51 microscope equipped with an Olympus i-speed LT camera. ImageJ software was used for measuring droplet diameters, in order to confirm particle size distributions.

After curing, particles were filtered in a steel mesh to remove secondary particles, and washed continuously with distilled water to remove PVA retained at the surface. The sample was then dried in an oven at constant temperature for varying times.

A FEI Quanta 400FEG ESEM/EDAX Genesis X4M equipment was used for scanning electron microscopy (SEM) analysis at Centro de Materiais da Universidade do Porto (CEMUP). Samples were sputtered with gold/platinum. To allow visualization of internal structures dried particles were embedded in epoxy resin. After hardening at 50 °C overnight, the resulting material was fractured in liquid nitrogen.

Simultaneous thermogravimetry (TG) and differential scanning calorimetry (DSC) analysis were performed in a STA 449 F3 Jupiter (NETZSCH). Samples masses between 10 and 15 mg were placed in an alumina crucible. The heating rate was 10 °K/min, under nitrogen flow.

Fourier Transform Infrared Spectroscopy (FTIR) was performed on a MB154 model from ABB BOMEM using a

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