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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.

## 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 stir-red 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.

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 physicomechanical 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 nanofiller (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., Switzer-land. 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 Ø 750 lm, 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 μL/min and 650 μL/min, respectively, yielding an average droplet size of about 400 μm. The fluids were driven by two precision syringe pumps (model 11 Plus, Harvard Apparatus). Temperature at the T-junction was kept constant at 25 $^{o}$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 μL/min and continuous phase = 750 μL/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 x 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 equip-ment 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 Miracle attenuated total reflectance setup. Dried samples were crushed in liquid nitrogen and then placed in a desiccator overnight, before being analyzed.

Dynamic mechanical analysis (DMA) was performed with a DMA 242 E Artemis (NETZSCH). The analyses were performed in compression mode on single particles using a sample holder with 3 mm diameter, at 2 K/min and 1 Hz. The maximum amplitude was 10 μm and the maximum dynamic force was 0.25 N.

The apparent density of the particles was determined by mercury porosimetry with a Poremaster 60 model from Quantachrome. The density of unvesiculated polymer was determined by helium picnometry. The organic phase (polyester, styrene and amine solution) was mixed with 3 wt.% benzoyl peroxide, and cured for 2 h at 60 °C, without water addition.

## 3. Results and discussion

The SEM image shown in Fig. 1a depicts particles dried at 70 °C for 24 h (reference drying conditions). The particle sizes are very uniform – the average diameter is 394 μm with a coefficient of variation of 3.5%. The external surface is smooth, as seen in Fig. 1b. Fig. 1c and d depict a fractured particle, showing a multi-alveolar morphology throughout the entire particle. This homogeneous vesiculation is a con-sequence of the stability of the water-in-oil emulsion during the droplet generation and curing stages [3]. The apparent density of these particles, determined by mercury porosimetry, is 0.60 g $cm^{-3}$. The density of non-vesiculated polymer, determined by picnometry, is 1.2 g $cm^{-3}$.

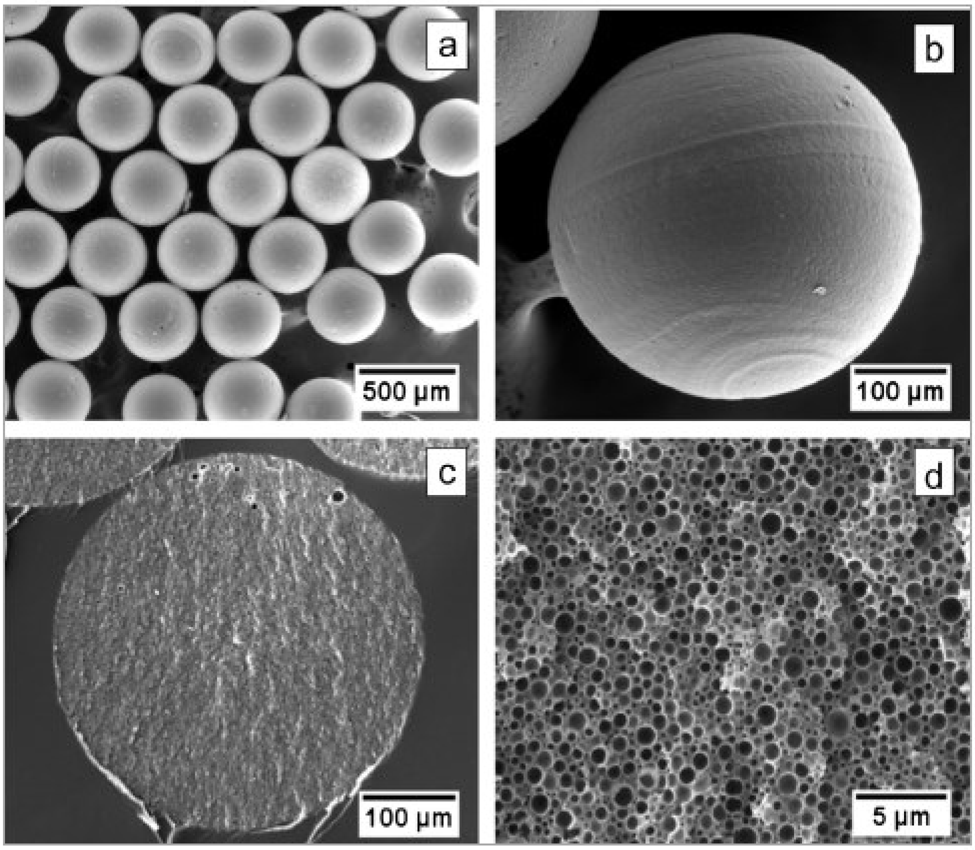


**Fig. 1.** SEM images presenting external (a and b) and internal (c and d) morphologies of MVPs after drying at 70 °C for 24 h (reference conditions).

Recalling that the weight proportion of water to organic phase in the formulation is 40:60, a theoretical apparent density of 0.67 g $cm^{-3}$ for the particles can be computed. This is in reasonable agreement with the experimental result, since the calculation assumes that no inward or outward water diffusion occurs during droplet formation and cure.

In order to shorten the drying time, a second set of conditions was tested. Particles were left in the oven at 120 °C for 150 min. Unexpectedly, as seen in Fig. 2a, all MVPs are deformed. During drying, the originally spherical particles expanded uniaxially, forming two almost separated semi-spheres (Fig. 2b). The external surface is smooth, as before. Images of fractured particles (Fig. 2c and d) show a large hollow core with an almost elliptical cross-section. Sudden exposure to 120 °C caused a significant inner pressure increase due to fast vaporization of water contained in the vesicles. This pressurized vapor did not diffuse fast enough towards the external surface, causing internal fracture and particle distortion. This inner bursting was probably aided by residual structural stresses originated during cure. The fact that, remarkably, all particles underwent the same type of deformation evidences the similarity of their internal structures.

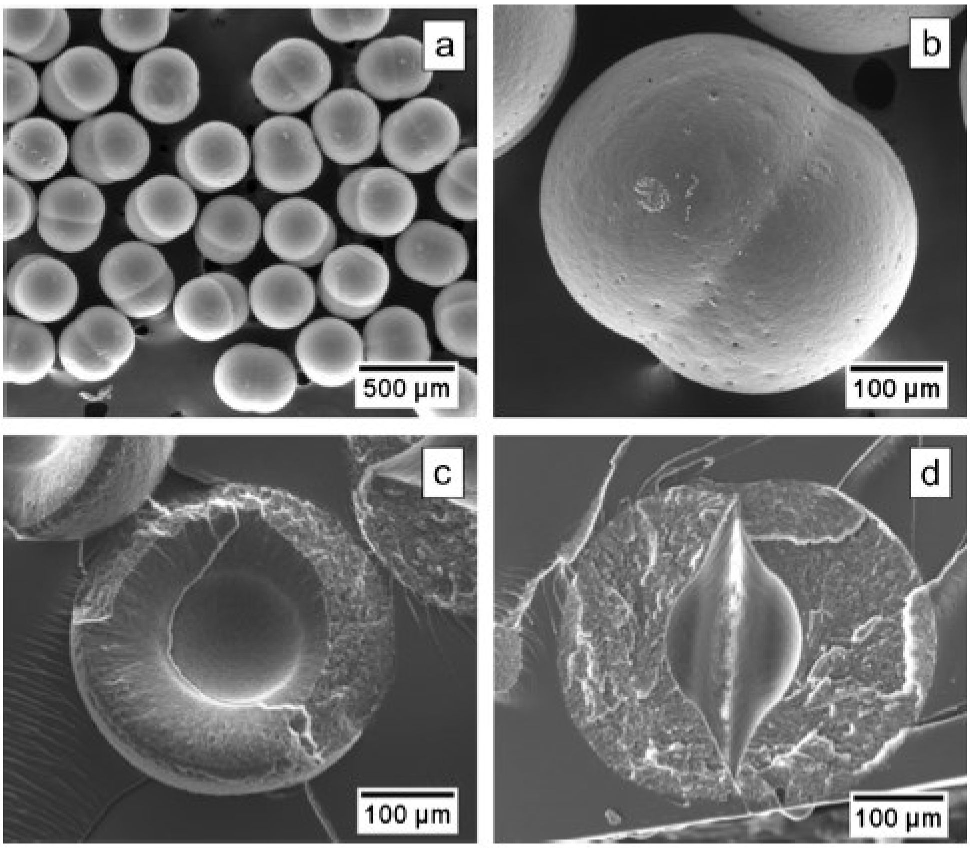


**Fig. 2**. SEM images presenting external (a and b) and internal (c and d) morphology of MVPs after filtering and drying at 120 °C for 150 min.

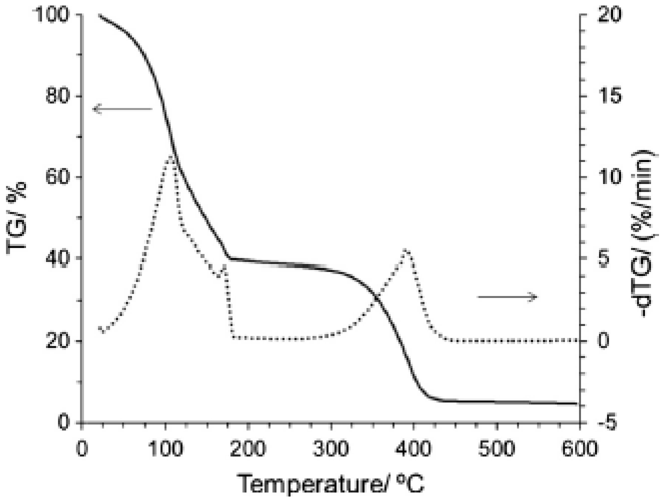


**Fig. 3.** Thermogravimetric analysis results for a freshly filtered sample of MVPs.

The drying of MVPs was studied by thermogravimetric (TG) analysis. The weight loss and first derivative (dTG) curves are presented in Fig. 3, for undried particles. Several distinct weight loss events can be identified. Water evaporation from surface and interparticular space occurs from the moment the test begins, showing a maximum rate at 100 °C, as expected. At about 110 °C the weight loss curve shows a change in slope, possibly corresponding to slower, diffusion-controlled, water vapor escape from inner vesicles. The small peak observed in dTG curve after 165 °C may be associated with faster water release caused by the inner bursting phenomenon described before. The slow heating ramp applied in this analysis may explain why this occurs at a higher temperature than previously, when the particles were instantly exposed to 120 °C. At around 180 °C all water has been removed, and a plateau is observed until 300 °C. At higher temperatures the polymer undergoes thermal decomposition.

Fig. 4 shows the TG and dTG curves for a sample previously dried at 70 °C for 24 h. Only the polymer decomposition step is evident, above 325 °C, confirming that water had been efficiently removed.

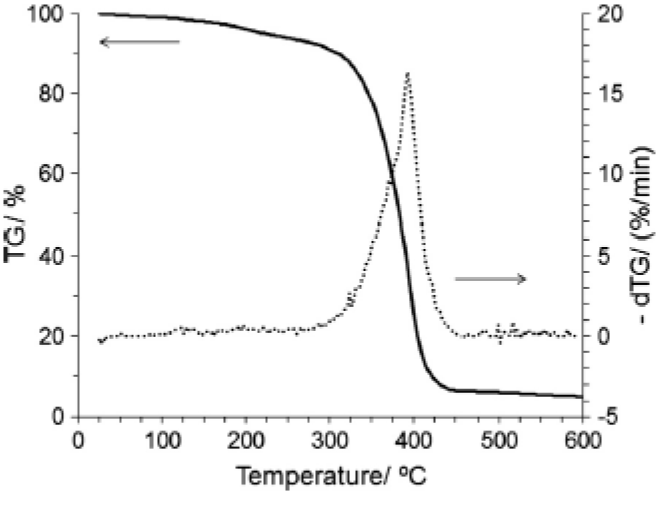


**Fig. 4.** Thermogravimetric analysis results for a MVPs sample dried at 70 °C for 24 h.

Fig. 5 presents a DSC thermogram for MVPs dried at 70 °C for 24 h. The onset of polymer thermal decomposition occurs at about 300 °C, as previously indicated by TG analysis. In addition, a small exothermic peak seems to occur in the range 120–140 °C. This is consistent with typical maximum exotherm temperatures in cure of unsaturated polyester with styrene [9]. It was therefore hypothesized that this exothermal event corresponded to residual cure of styrene that had not evaporated during the low temperature drying conditions (styrene boiling point is 145 °C). To test this hypothesis, a sample was dried at 70 °C for 24 h and then post-cured in the oven at 120 °C for 150 min. The DSC result is presented in Fig. 6, together with the previous thermogram (Fig. 5), in the relevant temperature range between 50 and 300 °C. No exothermic peak is visible in the post-cured sample. In addition, the existence of a negative step in the heat flow curve, between 100 and 200 °C, becomes clear. This indicates glass transition of the material, as will be corroborated below by DMA. It must be noted that after this post-cure treatment the particles showed no evidence of deformation, since all inner water had been removed during drying at 70 °C.

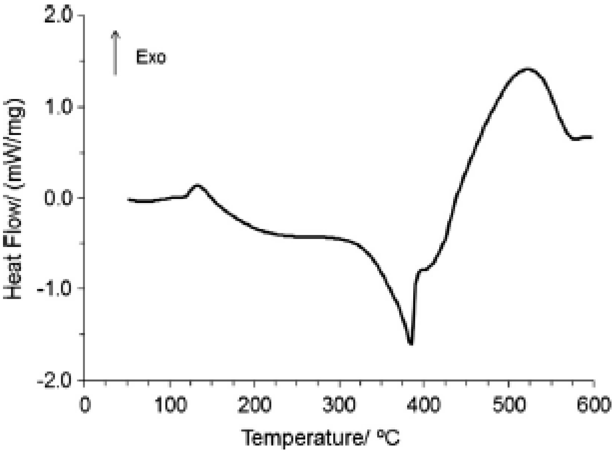


**Fig. 5.** DSC thermogram obtained for MVPs dried at 70 °C for 24 h.

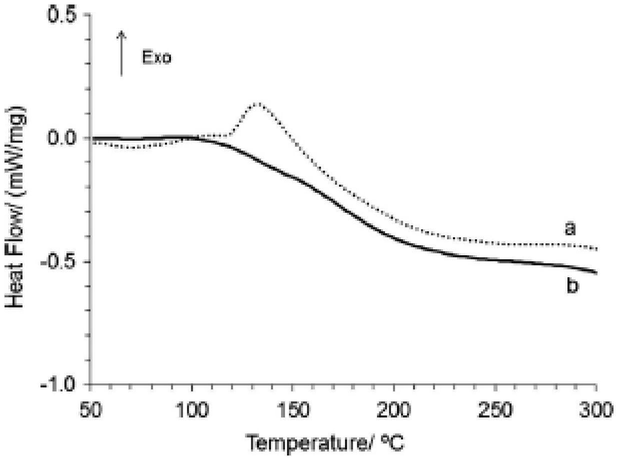


**Fig. 6.** DSC thermograms obtained for: (a) reference MVPs; and (b) post-cured MVPs (150 min at 120 °C).

FTIR analysis can be used to monitor curing of unsaturated polyester with styrene, using the C = O peak from polyester at 1720–1730 cm$^{-1}$ as reference, and following the relative evolution of peaks at 912 cm$^{-1}$ and 982 cm$^{-1}$, which correspond to C = C double bonds in styrene monomer and in polyester chain, respectively [10,11]. The FTIR spectra of unreacted organic phase, reference MVPs, and post-cured MVPs are presented in Fig. 7. The computed peak intensity ratios are shown in Table 1.

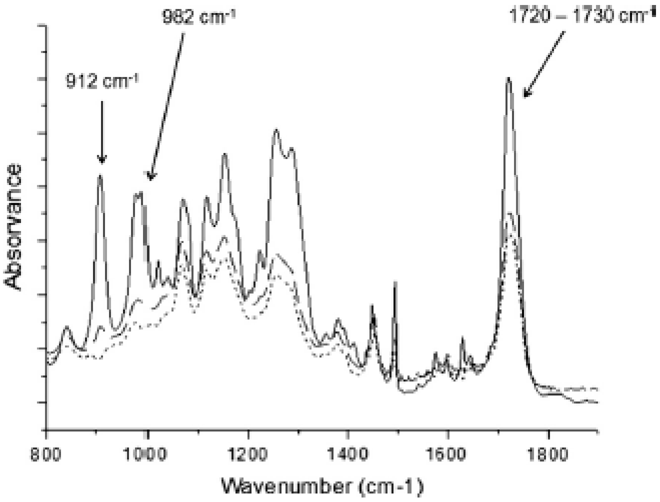
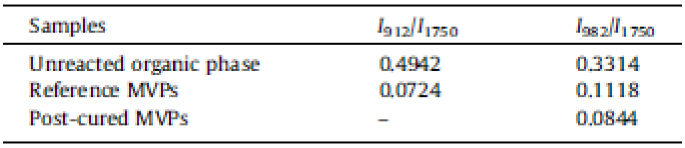


**Fig. 7.** FTIR spectra obtained for: uncured organic phase (solid line); reference MVPs (dashed line); MVPS post-cured at 120 °C for 150 min (dotted line).

**Table 1.** FTIR peak intensity ratios



| Samples | $I_{912}/I_{1750}$ | $I_{982}/I_{1750}$ |
|---|---|---|
| Unreacted organic phase | 0.4942 | 0.3314 |
| Reference MVPs | 0.0724 | 0.1118 |
| Post-cured MVPs | – | 0.0844 |

As expected, the signals corresponding to both types of double bonds decrease after particle production, and are even lower in the post-cured sample. This confirms that the thermal post-treatment yields higher degree of cure.

Dynamic mechanical analysis (DMA) was performed on particles produced with and without post-cure. Fig. 8 presents the storage modulus and damping coefficient (tan $\delta$) curves for the two samples. Since the equipment software is not configured for samples with spherical geometry, an equivalent cylinder was considered (cylinder height = sphere diameter, cylinder diameter = half sphere diameter). The computed values of dynamic storage modulus (E0) should only be considered for comparison between different samples and not as a quantitative evaluation of the particles' rigidity.

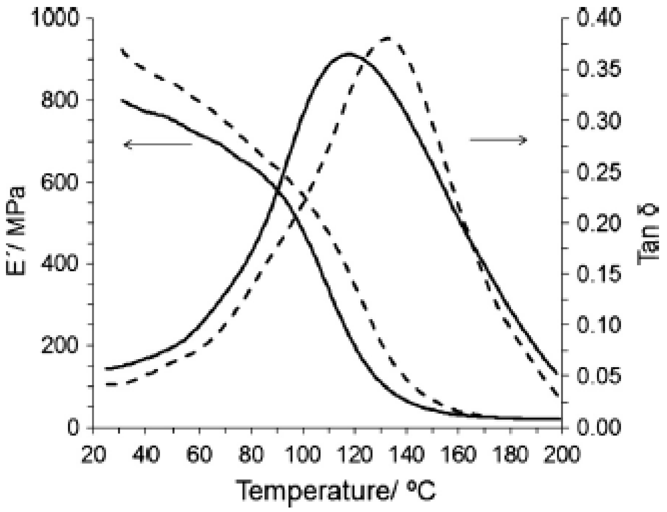


**Fig. 8**. Storage modulus and tanδ curves obtained by DMA for reference MVPs (solid line) and post-cured MVPs (dashed line).

A continuous decrease in storage modulus is observed for both samples, indicating gradual softening with temperature. A sharper decrease in E´ in the range between 100 and 140 °C indicates occurrence of glass transition. The fact that significant softening occurs above 100 °C helps explaining the observed plastic deformation due to internal bursting at 120 °C. From Fig. 8, the initial values of E´ are slightly higher for the post-cured particles than for the reference, which would be in agreement with a higher degree of cross-linking. However, the differences become slight when standard deviations for measurements with 3 different particles are considered: 828 ± 3 MPa for reference MVPs and 876 ± 45 MPa for post-cured MVPs. On the other hand, the glass transitions, observed as a broad peak in damping coefficient, are distinctly different. Tg, taken from the maximum in tan d, is 121.0 ± 3.9 °C for reference MVPs and 135.7 ± 3.4 °C for post-cured particles. This increase in $T_g$ is coherent with higher cross-linking, as a consequence of cure reaction progress during post-treatment.

The effect of adding a nano-filler to the cross-linked polyester matrix was also studied. Hydrophobic fumed silica Aerosil R8200, surface-modified with hexamethyldisilazane and with primary particle size of 12 nm, was used. Reinforcement of polyester systems with fumed silicas has been previously reported in literature [12–14]. 5 wt.% silica powder was added to the organic phase prior to emulsification of the aqueous phase, yielding a homogenous and stable dispersion. Fig. 9 shows SEM images of the particles obtained. Significant surface roughness is now evident in Fig. 9a and b, contrarily to the smooth external morphology previously encountered on the unfilled particles. This may be a consequence of silica presence in combination with slight retraction of the polymer matrix upon curing [15,16]. Internal particle vesiculation (Fig. 9c) is quite homogeneous and apparently unaltered by filler addition. Silica nanoparticles are not clearly visible, but their presence was confirmed by EDS (Fig. 10).

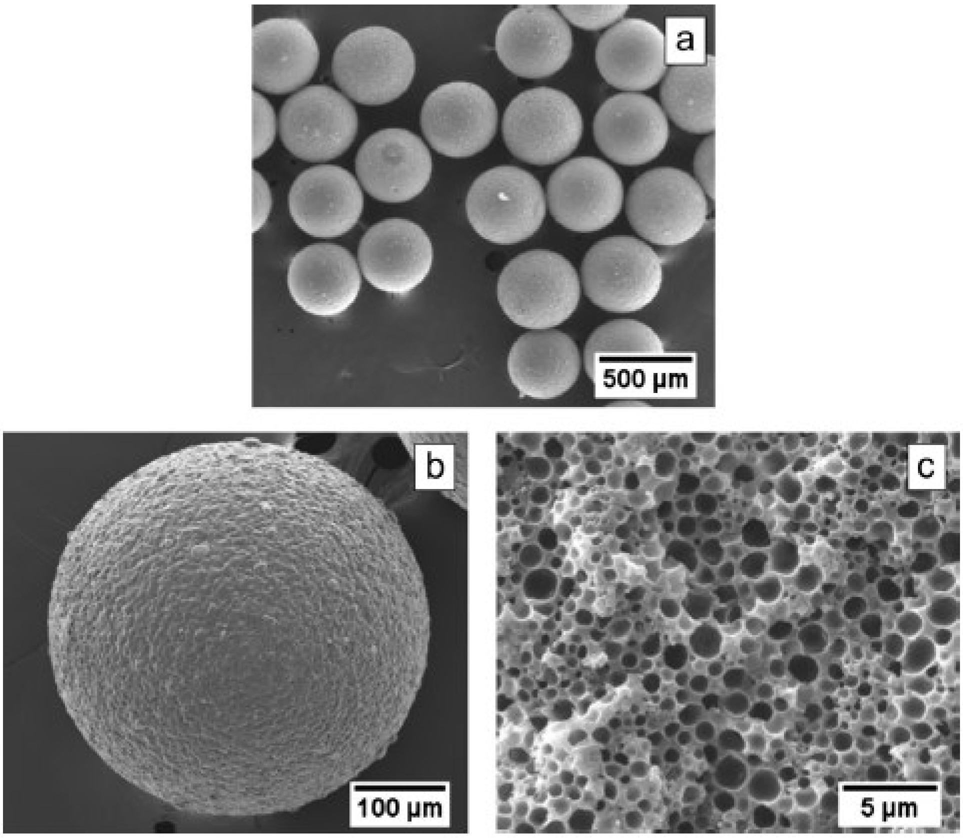


**Fig. 9**. SEM images presenting external and internal morphology of MVPs produced with 5 wt.% nano-silica addition to organic phase.

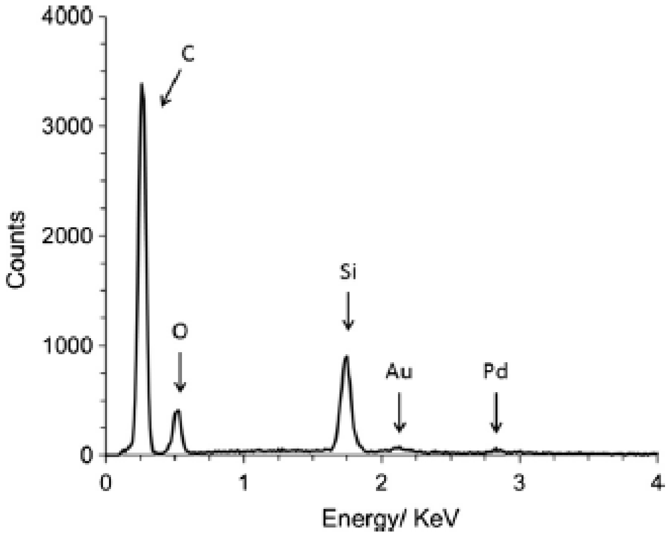


**Fig. 10.** EDS spectrum obtained for inner region of MVPs produced with 5 wt.% nano-silica addition to organic phase.

MVPs filled with nano-silica were analyzed by DMA. Fig. 11 shows that silica-reinforced particles present a 75% increase in storage modulus below glass transition. Nano-silica loading also promotes a positive displacement in the damping coefficient peak, causing $T_g$ to increase from

121 °C to about 140 °C. This is a consequence of homogeneous nano-filler dispersion and good interaction with the polymer matrix [13].

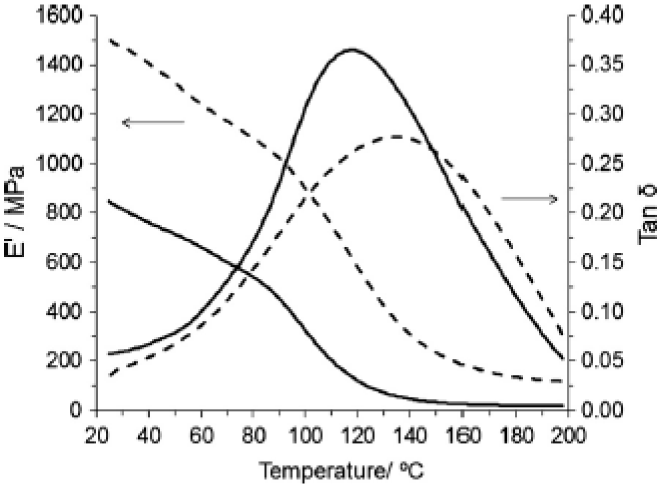


**Fig. 11.** Storage modulus and tan δ curves obtained by DMA analysis for organic phase produced without nano-silica (solid line) and with 5 wt.% nano-silica content (dashed line).

## 4. Conclusions

Monodisperse polyester particles with multivesiculated internal structure were obtained from a water/oil/water double emulsion. The droplets were generated with a microchannel device and then cured under UV radiation. The conclusions obtained from the characterization work performed can be summarized as follows:

– Uniform and densely distributed vesiculation was achieved throughout the particles.

– Drying at high temperature (i.e. 120 °C) originates internal fracture and particle deformation due to inner pressure increase. This is the result of the combined effects of rapid water evaporation and slow diffusion towards the exterior. The problem should be increasingly significant as particle size increases, due to longer diffusion paths.

– Efficient removal of trapped water was obtained at low temperature (70 °C) and long drying time (24 h).

– The cross-linked polyester that forms the particles exhibits a glass transition above 100 °C, clearly detected by DSC and DMA. Thermal degradation occurs above 300 °C.

– In order to maximize consumption of residual styrene, a post-cure thermal treatment at 120 °C is necessary. This promotes further crosslinking, which translates into an increase in glass transition temperature.

– Effective mechanical reinforcement is possible by loading the polymer with surface-modified fumed silica. 5 wt.% loading yielded 75% increase in storage modulus below $T_g$. The presence of these nanoparticles originated a significantly rougher external particle surface, which may be of interest for promoting mechanical anchoring of a surrounding polymeric matrix.

## Acknowledgements

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