This article was published in Polymer Engineering & Science, 54, 396-403, 2014

http://dx.doi.org/10.1002/pen.23571

Effect of Curing Conditions on the Properties of Multivesiculated Polyester Particle Dispersions

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Multivesiculated polyester particles were synthesized from a double emulsion system comprising water and a solution of unsaturated polyester in styrene. A suspension of solid micro-particles containing multiple water-filled vesicles is obtained after curing (i.e., cross-linking) the dispersed organic phase. These have several applications, like opacifying agents in paint formulations. The effects of curing time and temperature on relevant properties of the final product (particle size distribution, dry film opacity, dispersion viscosity, and stability) were investigated. Results showed that more than 1 h was necessary when curing at room temperature, in order to avoid coalescence and loss of opacity upon drying. On the other hand, well-individualized particles were obtained within a few minutes when curing above 60^{o}C, and the internal alveolar structure was preserved after drying. Furthermore, high curing temperatures enhanced not only the final dry film opacity, but also originated less viscous and more stable particle dispersions. POLYM. ENG. SCI., 54:396–403, 2014. ª2013 Society of Plastics Engineers

INTRODUCTION

Industrial interest in structured hollow particles has grown as technology advanced and fundamental insights on the synthesis of these materials were obtained [1]. A broad range of approaches can be found in literature: osmotic swelling [2, 3], incorporation of a blowing agent in emulsion polymerization [4, 5], interfacial polymerization [6, 7], seeded polymerization [8, 9], water-in-oil-in-water emulsion polymerization [10, 11], self-assembly [12, 13], and template-synthesis combined with core sacrifice [14, 15].

This study deals with a particular technique for production of multivesiculated particles (MVPs), based on crosslinking of a water-in-oil-in-water double emulsion [16–27]. It is different from other double emulsion processes in that it can be configured as a straightforward single-step emulsification procedure, and water-in-oil emulsifiers are not necessary, as will be discussed below. The final polymeric particles contain, after drying, a dense distribution of air-filled microvoids. The large refractive index difference between the polymer shell and entrapped air results in scattering of incident light, causing a thin film made of these micro-particles to have a white and highly opaque appearance. This has justified their industrial use as an economic alternative to the costly titanium dioxide opacifying pigment in paint formulations. MVPs are produced and used as a suspension in aqueous medium, and can therefore be readily incorporated in water-borne paints. The ability to vary the average particle sizes allows use in different types of coatings: 0.5 μm particles are used in gloss paints, 4–10 μm in matt paints, and up to 40 μm in paints with textured effects [28]. They can have other applications, namely opacifiers in paper coatings [26] and molding compositions [21].

Aside from patents, there is almost no information in the published literature considering the principles behind this MVPs synthesis procedure. The production methods can be divided in two-step [17, 19, 20, 22, 24–26] and one-step processes [16, 27]. In the first case, water is first dispersed in an organic solution of unsaturated polyester in styrene previously neutralized with an amine. This water-in-oil emulsion is then dispersed in an aqueous phase containing protective colloids [poly (vinyl alcohol)(PVA) and hydroxyl ethyl cellulose (HEC)], and a final water-in-oil-in-water double emulsion is obtained. The one-step process is a more interesting approach in terms of ease of industrial implementation. The polyester/styrene organic phase is directly emulsified in the aqueous solution of protective colloids (Fig. 1a). Water ends up diffusing into the organic droplets, forming the water-in-oil-in-water double emulsion (Fig. 1b). In both processes, the water droplets are stabilized in the organic phase due to the presence of highly hydrophilic sites, formed by the acid–base pairs involving the polyester terminal carboxyl groups and the added amine groups [29]. In a previous study, we have studied in detail how this phenomenon relates to the internal vesiculated structure of MVPs [30]. In another work, we have studied how relevant operation parameters of the organic phase emulsification step influence the properties of the resulting MVPs [31].

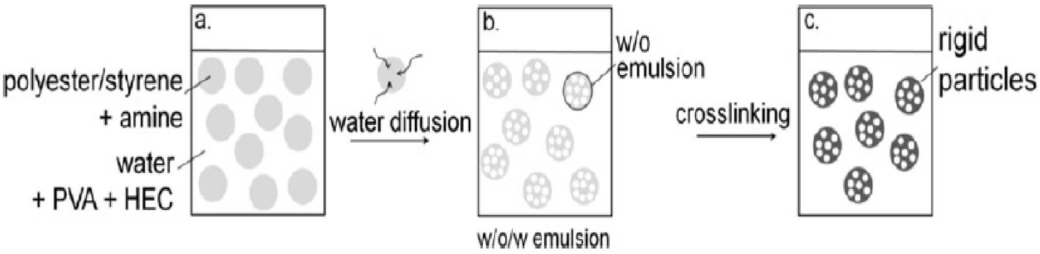


FIG. 1. Mechanism of a w/o/w emulsion preparation, by one-step process. (a) Organic droplets (polyester/ styrene and amine) emulsified in the aqueous medium (water, PVA, and HEC). (b) Double emulsion (w/o/w) after the external water diffusion into the organic droplets. (c) Final waterborne dispersion of crosslinked polyester/styrene particles, containing multiple water vesicles.

After crosslinking of the organic phase, the water drop-lets are retained within the hardened polymeric particles, forming a multivesiculated, or alveolar, structure (Fig. 1c). After drying, water evaporates and the vesicles become air-filled.

Independently of the process chosen, preparation of MVPs involves the final cure stage, which consists on the well-known process of reticulation of unsaturated polyester with styrene by free radical polymerization [32, 33]. Inthe present case, an organic peroxide (cumene hydroperoxide) is used as the free radical initiator, in combination with a metal redox activator (aqueous solution of ferrous sulfate and diethylenetriamine), in order to allow for polymerization at relatively low temperatures (below 80°C) [16, 27]. Razumovskii et al. [34] have described the radical formation mechanism in this system, which first involves formation of a complex between ferrous iron and the amine. This complex then reacts with the peroxide, forming organic radicals (Eq. 1).

$$ROOH + R'NH_2Fe^{2+} \longrightarrow RO\bullet + R'NH\bullet + Fe^{2+}\bullet + H_2O \qquad (1)$$

where R corresponds to $C_6H_5C(CH_3)_2$ and R0 corresponds to $NH_2CH_2NHCH_2$.

Radical polymerization is thus initiated, involving styrene and double bonds of unsaturated polyester, and resulting in hardened polyester crosslinked by polystyrene chains (Fig. 2).

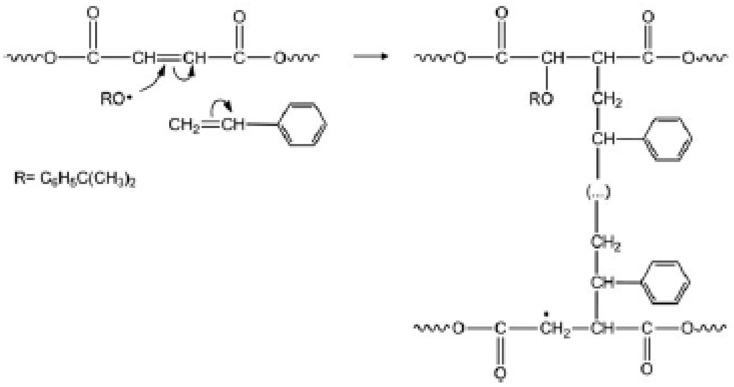


FIG. 2. Free-radical crosslinking of polyester/styrene by polystyrene chains.

The existing patent literature on MVPs production describes the curing conditions as room temperature, without agitation. The reaction time is only generically mentioned as being ‘‘overnight’’ [16, 17, 27]. This study evaluates the influence of different curing temperatures and times on final properties of MVPs, namely, dry film opacity, particle size distribution, viscosity, and stability.

EXPERIMENTAL

Materials

The unsaturated polyester (UP) is a solution of polyester in styrene (weight ratio of 70/30, acid value of 15–20 mg KOH/g, Brookfield viscosity of 1000–2000 cP and gel time of 40–50 min). It was provided and characterized by Resiquímica (Mem Martins, Portugal). Styrene (pure), poly (vinyl alcohol) (PVA, Mw > 205,000 g/mol, degree of hydrolysis = 88%), hydroxy ethyl cellulose (HEC) and ferrous sulfate (Fe_2SO_4) were provided by Resiquímica.

Diethylenetriamine (DETA, 98% purity), cumene hydroperoxide (CHP, technical grade 80%) were provided by Sigma–Aldrich.

All materials were used as received without further purification.

Multivesiculated Particles Preparation

The one-step process was adopted in this study, since it is a more straightforward approach to obtain the double emulsion. UP (diluted in 30 wt% styrene) was first neutralized with 2.1 wt% of DETA, at low speed. This mixture was diluted in 6.5 wt% of styrene and the resulting organic phase was then dispersed, by drop wise addition, in an aqueous solution of PVA and HEC (in concentrations of 2.3 and 0.4 wt%, respectively), and 0.06 wt% of DETA. This dispersion stage was carried in a jacketed glass reactor (250 mL) at room temperature, using a 40 mm impeller at 600 RPM. After gradual addition of the organic phase (10 min), stirring was maintained for 20 min and additional water was added. The cure reaction was then initiated by adding, in the same reactor, 0.1 wt% CHP and 0.01 wt%Fe_2SO_4 (previously dissolved in distilled water). The cure stage was performed at different temperatures, along a maximum time of 5 h, by circulating hot water from a temperature-controlled water bath in the reactor's jacket. In order to guarantee homogeneous temperature in the liquid medium, low agitation was implemented using an anchor-type impeller at 250 rpm. A refrigerated water condenser was used to avoid liquid evaporation during cure.

Characterization Methods

Optical Microscopy. Final double emulsions (before the curing stage) and cured MVPs' dry films were analyzed by optical microscopy, using an Olympus IX 51 inverted optical microscope. It allowed a qualitative data about the size and morphology of organic droplets.

Reflected Light Microscopy. Reflected light micros-copy images of MVPs' dry films were obtained with a Zeiss axiophot microscope, equipped with a Zeiss axiocam ICc 3. The specified spatial resolution is 370 nm.

Scanning Electron Microscopy. Dry films' morphology was observed by scanning electron microscopy (SEM), using a FEI Quanta 400FEG ESEM/EDAX Genesis X4M equipment. Thick MVPs films were applied on 1 cm2 of an opacity chart's black portion and dried in a vacuum desiccator, at room temperature. Before being analyzed, samples were sputtered with gold/platinum using a K575X Sputter Coater by Quorum Technologies.

To analyze internal vesiculation, thick MVPs films were applied on 1 cm2 glass slabs and left to dry at room temperature, for 24 h and then fractured in liquid nitro-gen, enabling the internal MVPs morphology evaluation. The same sputter treatment was done in this case, before their analysis by SEM.

Contrast Ratio Measurements. The opacity of a film is a measure of the dry hiding power it possesses. It corresponds to the ratio between the reflectance achieved by a dry film applied to a black surface and the reflectance achieved by the same film applied to a white surface.

A thin film (100 μm) was applied on an opacity chart (Leneta 2A), consisting of a white and black surface. The film was left to dry for 24 h, at room temperature. The reflective indices of the white and black surfaces were measured, using a GretagMacbeth Coloreye 3100 spectrophotometer, at wavelengths between 400 and 700 nm, respectively. The equipment software computed the ratio between the two reflectance values, which corresponds to the Contrast Ratio (CR) value. A completely opaque film would have a CR of 100%.

Particle Size Distribution. The particle size distribution (PSD) of the MVPs dispersions was measured on a Beck-man Coulter LS230 light scattering system, with Polarization Intensity Differential Scattering (PIDS) assembly and an obscuration of 45%. The particle size distributions were computed by the equipment's software, based on Mie theory for light scattering. All cured dispersions were previously diluted and sonicated for 20 min, to avoid detection of agglomerates. Measurements with uncured dispersions were performed right after collection from the reactor.

Brookfield Viscosity Measurements. The viscosity of MVPs dispersions was determined using a Brookfield

LVDV-III Ultra rheometer, at 208C. For each curing time studied, 40 mL of sample were collected through the reactor's lid aperture using a graduated pipette. The sample container was immersed in a thermostated water bath at 208C. Brookfield viscosity was measured immediately after temperature stabilization. Spindle speed was 20 rpm and spindle type was chosen depending on measured torque percentage, which should preferentially be close to 50%. At these conditions, the maximum value given by the equipment is 20,000 cP. All readings were taken after 20 s stabilization time.

Residual Styrene Measurements. Measurements of the concentration of residual styrene in MVPs dispersions were performed in a Gas Chromatography (HP 5890, series II), equipped with headspace sampler (HP 7694) and a flame-ionization detector (FID). The injector temperature was 150^{o}C and detector temperature was 200^{o}C. Column (SGE) had an internal polar phase (BP 21) and dimensions 50 m (length) x 0.22 mm (internal diameter), 0.25 μm (thickness). Split ratio of injection was 1:93. Oven temperature was maintained at 908C (isothermic). Total run time was 30 min. Helium was used as a carrier gas (flow rate = 1.43 mL/min, P = 33 psi), ArK (P = 250 kPa), and Hydrogen (P = 130 kPa) as combustion gases and Nitrogen (P = 350 kPA) as auxiliary gas.

Relative to head-space (HS), the oven temperature was set at 70^{o}C, the loop temperature was set at 80^{o}C, the transfer line was set at 150^{o}C and the thermal equilibration time was 30 min. The injection time was 0.33 min and vial was pressurized to 1.2 bar in 0.33 min.

First, a reference solution of 0.30 mL of isobutanol (99.5%) in 1000 mL of water was rigorously prepared.

To prepare samples, 0.5000 g of MVPs dispersions was added to 10 mL of reference solution, in HS vials and mixed for 10 min.

A styrene calibration curve was already available for quantitative analysis. Results were computed in % (g of styrene/g of sample 3 100) by the equipment and then converted to ppm.

RESULTS AND DISCUSSION

The MVPs cure process involves crosslinking of an aqueous dispersion of unsaturated polyester dissolved in styrene. The dispersed medium is a double emulsion, with numerous water droplets being contained within the organic phase (Fig. 3a). Upon cure and drying, rigid and opaque particles are obtained (Fig. 3b).

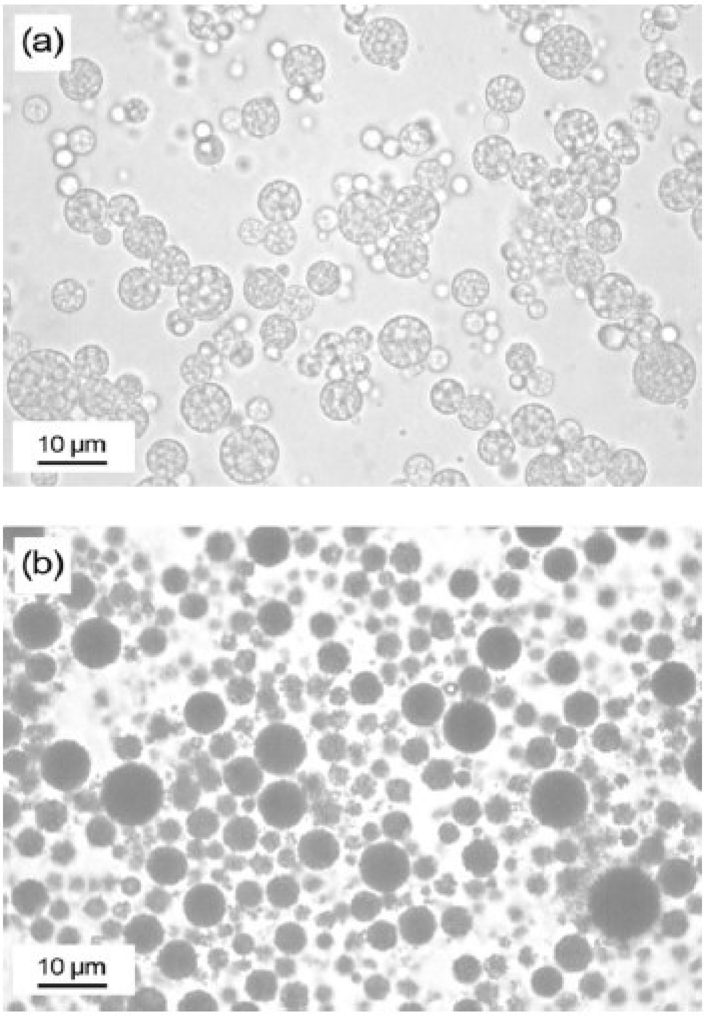


FIG. 3. Optical microscopy images (magnification 1000x) of MVPs. (a) Aqueous dispersion of polyester/styrene before cure—small water-in- oil droplets are distinctly visible within the organic phase. (b) Dry solid particles obtained after cure.

The opacity of dry MVP films results from the presence of multiple air pockets (vesicles) within the particles. If the dispersion is applied on a substrate prior to curing, a film of unvesiculated and transparent polyester is obtained (Fig. 4a and b). On the other hand, after curing the dispersion forms an opaque film of solid and well-individualized particles (Fig. 4c and d). The internal multivesiculated structure is visible in Fig. 4d, since this film was fractured under liquid nitrogen, causing the breakage of several particles. Uniformly distributed spherical vesicles, separated by thin polymer walls, are clearly visible in this case.

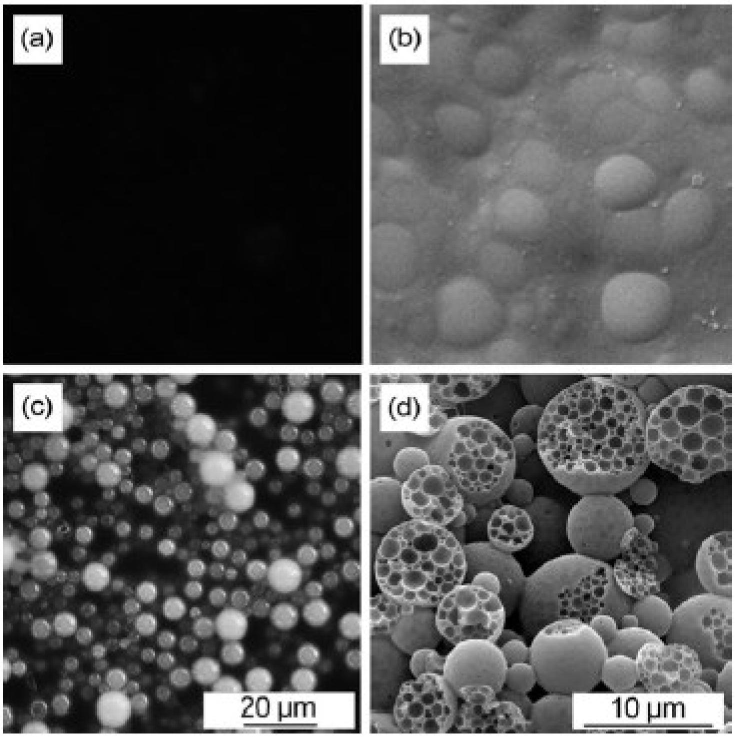


FIG. 4. Reflectance microscopy (magnification 500x, images a and c) and SEM images (magnification 6000x, images b and d) of dry films of MVPs applied on a black substrate. Images (a) and (b) show a transparent film obtained from an uncured dispersion. Images (c) and (d) show an opaque film obtained from a cured dispersion.

The curing temperatures tested in this work were 25, 40, 60, 70, and 80°C. The prior preparation of the double emulsion was performed identically in all cases, as already described in the ''Methods'' section. At the end of each hour of curing, a liquid sample was collected and cooled down to 20°C. Dry film opacity and viscosity measurements were then performed with these samples.

Dry Film Opacity

The opacification effect is only possible if the particles become sufficiently rigid to preserve the internal vesiculated structure and avoid inter-particle coalescence upon drying. Figure 5 shows representative SEM images of dry films obtained from dispersion samples collected along the curing reaction performed at 25°C. The films were left to dry at room temperature in a vacuum desiccator. Figure 5a presents the result obtained before addition of the curing initiation system, showing a coalesced polyester film. This film was completely transparent to the naked eye. Twenty minutes after adding the initiator (Fig. 5b), some vesiculated particles started to form, still embedded in a mass of coalesced polymer. Visually the film showed some opacity, but was still mostly translucid. More individualized particles are visible after 30 min curing (Fig. 5c). The holes in the surfaces correspond to collapses of the thin vesicle walls, probably occurring during the drying stage. Only after more than 1 h of curing the particles became completely individualized (Fig. 5d). The mass in the inter-particular regions now corresponds to dispersion stabilizers (PVA and HEC), and not to uncrosslinked polyester. The film was uniformly opaque.

For MVPs cured at 70°C, on the other hand, the SEM images of films obtained 10 min after addition of the initiator system (data not shown) already showed well-formed and individualized vesiculated particles.

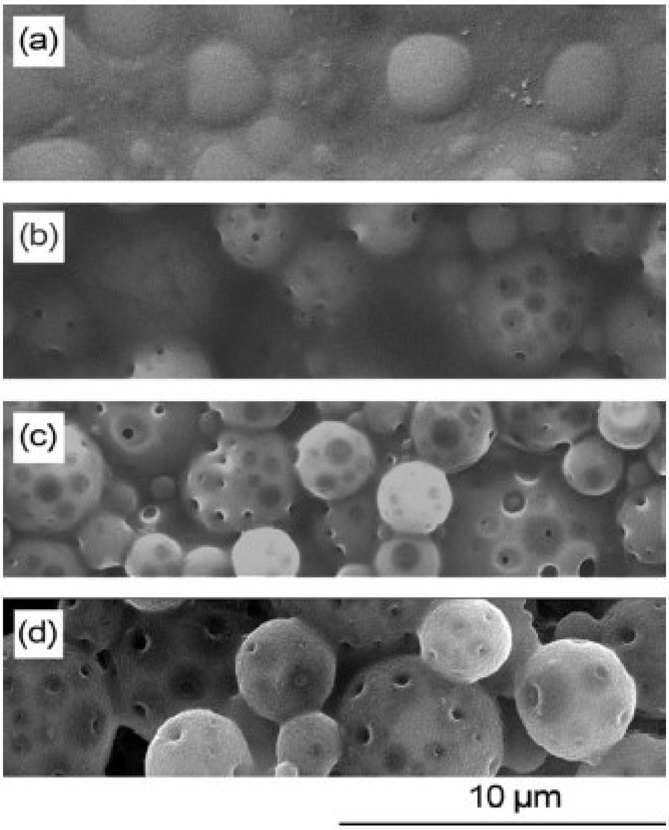


FIG. 5. SEM images of MVP films (magnification 6000x), cured at 25°C, for different curing times: (a) before cure; (b) 20 min; (c) 30 min; and (d) 2h

Figure 6 presents the dry film opacities measured on samples cured at different temperatures, and collected for curing times higher than 1 h. For the MVPs cured at 25 and 408C (Fig. 6a) the opacities show an irregular trend and large dispersion along curing time. The average contrast ratio values obtained are between 81 and 86%. On the other hand, MVPs cured at higher temperatures (Fig. 6b) yielded consistently higher opacities, immediately after 1 h reaction time. The maximum values measured were about 88%, at least 5% points higher than for the previous set. Note that this difference in contrast ratios can be detected by the naked eye. The scattering in the measurements shown in Fig. 6b is lower than before. This is consistent with the fact that the dry films were visually more homogeneous in this case.

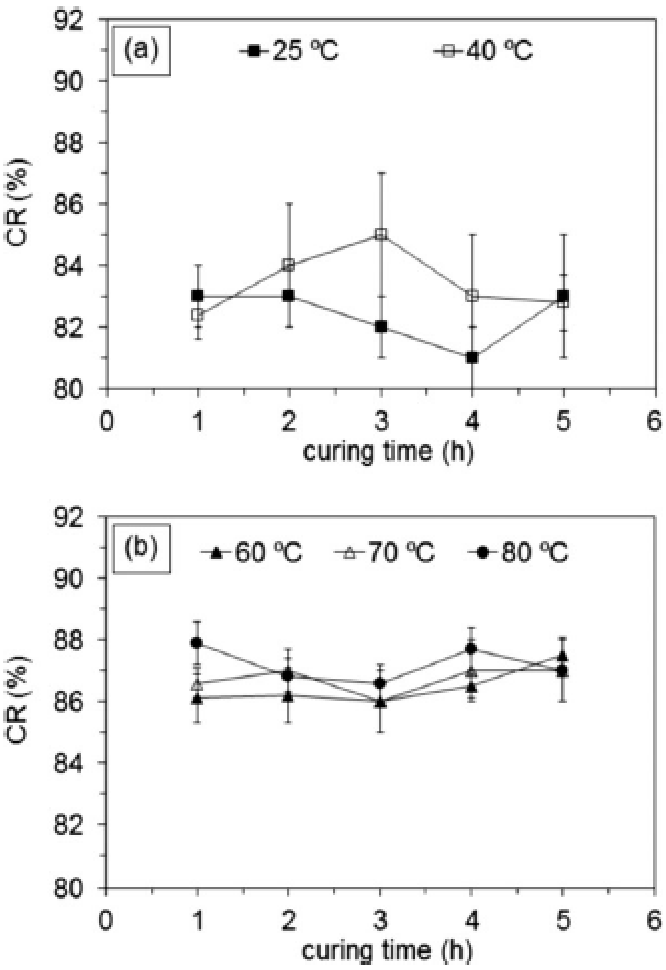
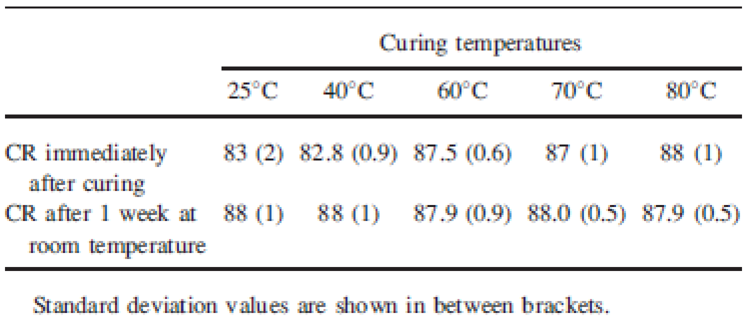


FIG. 6. Dry film opacity (contrast ratio) as a function of curing time, for different curing temperatures: (a) T = 25 and 45°C; (b) T = 60, 70, and 80°C. Error bars represent standard deviations computed from measurements on, three opacity charts, with at least three measurements per- formed on each chart.

The opacities were also measured after letting the cured dispersions rest for 1 week at room temperature. Table 1 shows the results obtained. Note that particle size distribution measurements (data not shown), have con-firmed that the particle sizes have remained unchanged during this period, for all dispersions. For the MVPs cured at 25 and 40°C, the contrast ratios increased from 83 ± 2% to 88 ± 1% after the resting period, becoming similar to the values obtained immediately after curing with the MVPs cured above 60°C. This indicates that when curing was performed at 25 or 40°C, 5 h reaction time was not sufficient for complete crosslinking of the organic phase. After drying, the not fully hardened particles have probably undergone some degree of interparticle coalescence and/or deterioration of internal vesiculated structure, limiting the opacification effect. During the 1 week resting period, polymer crosslinking proceeded, and the MVP films equaled the performance of the ones cured at higher temperatures.

TABLE 1. Influence of curing temperature on dry film opacity (contrast ratio [CR]), for films applied after curing and after 1 week at room temperature.



	Curing temperatures				
	25°C	40°C	60°C	70°C	80°C
CR immediately after curing	83 (2)	82.8 (0.9)	87.5 (0.6)	87 (1)	88 (1)
CR after 1 week at room temperature	88 (1)	88 (1)	87.9 (0.9)	88.0 (0.5)	87.9 (0.5)

Standard deviation values are shown in between brackets.

Particle Size Distribution

The particle size distribution (PSD) of the MVPs produced at each curing temperature is shown in Fig. 7. The superposition of all measured curves shows that curing temperature does not affect particle size. Figure 8 presents the PSD evolution along curing time (at 25°C). The PSD is seen to remain essentially constant along the cure reaction. There is no significant difference between the PSD of the original organic phase dispersion (''0 h'' curve in Fig. 8) and the final suspension of crosslinked particles.

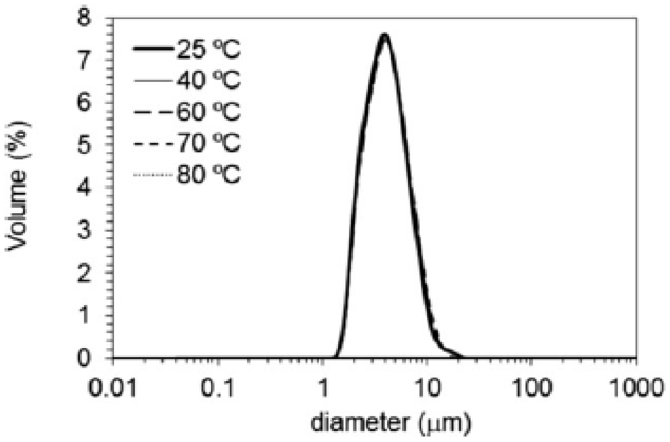


FIG. 7. Influence of curing temperature on particle size distribution (μm).

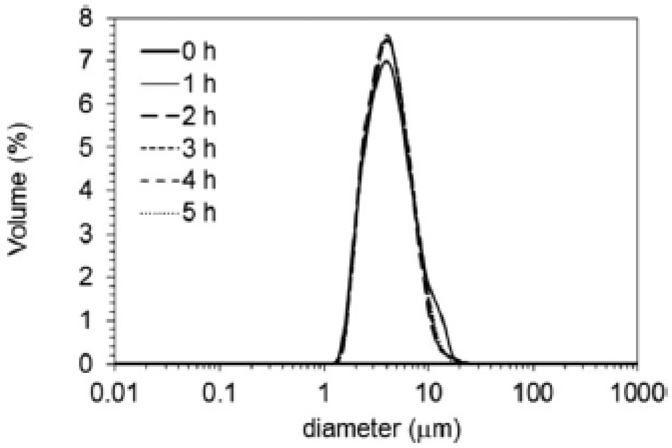


FIG. 8. Influence of curing time on particle size distribution (μm). Curing temperature of 25°C.

Viscosity

The viscosity of the cured dispersions is an important property, considering the interest in subsequent incorporation in waterborne coating formulations. The viscosity was measured at the end of each hour of curing time, for all studied temperatures (Fig. 9). In all cases, the collected samples were previously cooled down to 20ºC. The initial viscosity of the dispersions, before initiating the cure process, was about 450 ± 24 cP at 20ºC.

The viscosity after 1 h of reaction was about 500 cP at 25ºC, close to the initial value. But, for higher curing temperatures, the viscosity increased significantly, being close to 2000 cP at 80ºC. For 25 and 40ºC the viscosity tended to increase as curing time progressed. This effect was more evident for 40ºC. For 60ºC, after a slight initial increase, the viscosity remained essentially constant past 2 h. For 70 and 808C the viscosity ended up decreasing significantly after 4 and 2 h of reaction, respectively. Two peculiar behaviors were therefore observed in this system:(1) increase of the dispersion viscosity with temperature after 1 h curing and (2) sharp decrease in viscosity after a certain curing time at the higher temperatures. The interpretation of these observations is not evident and will be discussed in some detail.

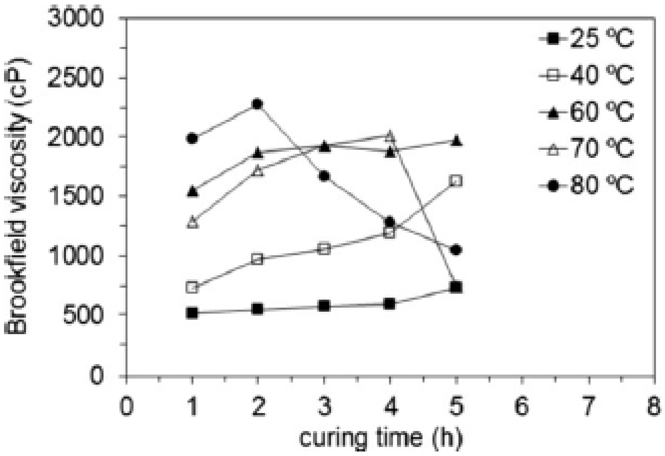


FIG. 9. Influence of curing temperature on Brookfield viscosity of the dispersions along curing time. Viscosities were measured at 20ºC.

The viscosity of the continuous phase of an aqueous dispersion of organic droplets, at low to moderate concentrations, can be influenced by factors like temperature, volume fraction of dispersed phase, average size and size distribution of droplets, ionic strength, inter-droplet inter-action, and concentration of water-soluble polymers in the continuous phase and at the adsorbed surface layer [35, 36]. The viscosity of the dispersed organic phase should not be a determinant factor, since the shear conditions used in viscosity measurements are not sufficient to cause momentum transfer inside the droplets, and these may therefore be approached as hard spheres [36].

It was shown above that the droplet size distribution is not changed by the curing process, whichever the temperature. Therefore, this cannot be considered a cause for the observed changes in viscosity. Another possible factor would be a modification in the thickness of the surface layer of adsorbed water-soluble polymers (protective col-loids) with increasing temperature. This would increase the effective volume fraction of the dispersed phase, thus increasing viscosity [35]. PVA is known to have higher sur-face adsorption and form thicker adsorbed layers as temperature is raised [37]. This is due to elongation of chain con-formations at the adsorbed layer, assuming a more linear orientation towards the bulk solution. However, the viscosities presented in Fig. 9 were all measured at 20°C, which would reverse this possible adsorbed layer thickness effect. In addition, the observed increase in viscosities along reaction time, and the final decrease for curing temperatures of 70 and 80°C, could not be explained by this hypothesis. Temperature-induced dissolution of unsaturated polyester into the aqueous phase may originate viscosity increase, but, as with the previous hypothesis, the observed evolution of viscosities along time is not properly explained.

Inter-particle interaction prompted by the curing reaction seems to be the most reasonable interpretation for the viscosity results. The curing reaction rate increases with temperature. As cure starts, the droplets become a sticky mass of crosslinking polymer swollen by styrene monomer. Despite the presence of the protective colloids at the surface, droplet collisions originate temporary agglomeration. This leads to viscosity increase, both because inter-particle water retention increases the effective volume fraction of the dispersed phase, and because energy is dissipated as the agglomerates are broken [35]. Droplet coalescence does not actually occur because the viscosity of the partially cross-linked organic phase is increasing. For a sufficiently high crosslinking extent, this sticky stage ends and the viscosity of the continuous phase decreases, as collisions between the now sufficiently hardened particles become mostly elastic. This hypothesis implies that when curing was performed at 25 or 40°C the sticky stage had not yet ended after 5 h reaction time, and thus the dispersion viscosity was still increasing with time. This is consistent with the opacity results presented before. The MVPs cured at these lower temperatures yielded lower film opacities, probably due to incomplete cure, as discussed.

An additional blank run was performed in which the curing procedure was repeated at 70°C, but the organic phase was not added to the aqueous phase. The purpose was to verify whether some interaction between the catalyst system, the added amine, and the protective colloids could be contributing to the observed viscosity changes. Viscosity remained constant at a low value (about 10 cP) during the 5 h reaction time.

The viscosity of all dispersions was measured again, after resting for 1 week at room temperature. The measurements were made at 20°C, before and after mechanical agitation (10 min at 500 rpm) and are presented in Table 2.

After this 1 week period, the dispersions that were cured at 25 and 40°C presented very high viscosities and had gel-like consistencies. Agitation made the dispersions more fluid, but still highly viscous. On the other hand, dispersions cured at 60, 70, and 80°C presented viscosity values similar to those obtained immediately after curing, both before and after agitation. This reinforces the idea that curing reaction was not completed at the lower temperatures and progressed during the post-cure resting period. Consequently, gelation of the particle dispersion occurred, with negative consequences in terms of processing and incorporation in coating formulations.

Styrene Content

The concentration of residual styrene was quantified along time for curing at 70°C (Fig. 10).

A 98% decrease in styrene concentration, relative to the initial concentration, is attained after 2 h reaction time. Higher reaction times do not contribute to a measurable decrease in styrene content. This could eventually be achieved by adding a more active initiator system, in a post-curing step.

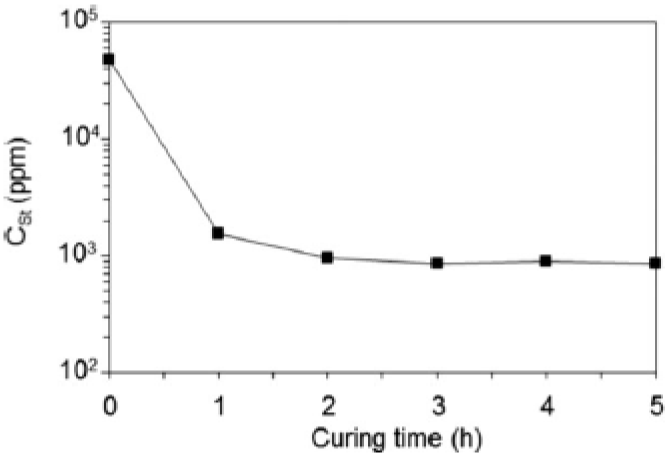


FIG. 10. Residual styrene present in MVPs dispersion as a function of curing time, at 70ºC.

TABLE 2. Influence of curing temperature on Brookfield viscosity (cP) of MVPs dispersions, 1 week after curing.

	Curing temperatures				
Brookfield viscosity	25°C	40°C	60°C	70°C	80°C
Before agitation	>20,000	12,850	2760	550	950
After agitation	>20,000	8970	2170	610	1120

CONCLUSIONS

The effect of reaction temperature and duration on the cure of polyester/styrene double emulsions was studied. Higher curing temperatures (60, 70, and 80ºC) led to higher dry film opacities (CR ≈ 88%), after just 1 h of cure. On the other hand, at 25ºC or 40ºC the measured contrast ratios were significantly lower (CR ≈ 83%), indicating that the particles were incompletely hardened, leading to inter-particle coalescence and/or damage of internal vesiculated structure during drying. When these latter dispersions were allowed to rest for 1 week, dry film contrast ratios of about 88% were obtained, due to progression of cure along the resting time.

Droplet/particle size distributions were the same before and after the cure process, independently of the curing temperature.

When the dispersions were cured at the lower temperatures, viscosity tended to increase as cure progressed. After 1 week post-cure resting at room temperature, these dispersions presented gel-like consistency. On the other hand, for curing temperatures of 70 and 80ºC, the viscosity was initially high but then decreased significantly after 4 and 2 h of reaction, respectively. The final viscosity values remained stable for the 1 week resting period, without gel formation. These results were interpreted in terms of time-dependent interaction/agglomeration of re-active particles during cure.

A 98% decrease in styrene concentration, was attained after 2 h reaction time at 70°C. Higher reaction times did not contribute to significantly decrease styrene concentration.

ACKNOWLEDGMENTS

Funding for this work was provided by FEDER, through Programa Operacional Factores de Competitividade – COMPETE, and by national funding through FCT – Fundação para a Ciência e a Tecnologia, in the frame-work of project PTDC/EQU-EQU/112151/2009. Ângela Dias thanks CIN – Corporação Industrial do Norte, S.A., Resiquímica – Resinas Químicas, S.A., and FCT for PhD grant SFRH/BDE/33432/2008.

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