The role of vinyl terminated silanes for producing highly concentrated polystyrene slurries in a single step process

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KEYWORDS: Single process, nano-slurry, polystyrene nanoparticles, sodium dodecyl
sulfate (SDS), vinyl terminate silanes, silica functionalization.

ABSTRACT

Slurries with low viscosity and polystyrene (PS) nanoparticles concentration up to 52 wt.% have been synthesized in one-step process with no waste generation, by suspension polymerization and optimizing the concentration of dispersants (sodium dodecylsulfate, SDS, and the cosurfactant, CS). The CS was manufactured *in situ* from tetraethyl orthosilicate (TEOS) and vinyltriethoxysilane (VTES). The incorporation of the CS on the PS polymer was confirmed by FT-IR, EDS and TGA; observing the functionalization of PS nanoparticles with SiOH. Morphology and particle size of the dispersed solid, together with viscosity and stability of the polystyrene slurries (PSSs) were analyzed, finding an abrupt reduction of the viscosity for PSSs by combining SDS and CS. Addition of SDS and CS (3.0 and 1.5 wt.%, respectively) allowed to produce PSSs with improved stability ($\zeta = -48.5$ mV after one year), low viscosity (20.5 mPa·s at 25 °C) and Newtonian behavior, containing up to 40.0 wt.% of single-spherical PS nanoparticles (< 100 nm).

1. INTRODUCTION

A slurry is a fluid formed by a stable dispersion of a solid into a liquid (commonly water or glycerol). Slurries are habitually made by dispersing either micro or nanoparticles in the media by means of dispersants and, commonly, with the help of mechanical stirring or sonication. This kind of material can flow not only under the effect of gravity, but can also be pumped. Therefore, slurries facilitate the manipulation of bulk solids and, depending on the nature of the dispersed particles, they can be applied in many different fields¹⁻³, such as mining⁴, excavation^{5, 6}, construction⁷, coating/plating⁸, sealing^{9, 10}, ceramics¹¹ and thermal energy storage¹²⁻¹⁴.

One of the key parameters, which determines the properties of a slurry, is the size of the dispersed solid particles. Polymer slurries formed by micro-particles have been more explored than nanoparticle-based ones, since obtaining micro-particle size is easier. For instance, Ugelstad *et al.*¹⁵ reported the first approach of a slurry made of polystyrene (PS) microparticles by emulsion polymerization using an emulsifier mixture of anionic emulsifier and fatty alcohol. Unfortunately, the average size of dispersed particles in that slurry was mainly over 1 micron, making the suspension poorly stable since the product began to separate after 2 weeks. More recently, several efforts have been done in order to develop and improve the properties of polymer slurries by reducing the particle size¹⁶⁻²⁰, producing mostly submicron particle-based slurries. In the case of PS, Yamamoto and Takahashi synthesized a slurry made of polystyrene-silica core-shell particles and silica hollow particles, where the N-vinylacetamide acts as stabilizer for the polymer dispersion¹⁷. Few approaches have been made to prepare colloidal suspensions of polymer nanoparticles in aqueous media. Using emulsion polymerization, Ishii *et al.* obtained monodisperse PS nanoparticles in water^{21, 22}, whereas Li *et al.*²³ reported poly(vinyl acetate) (PVAc)/silica nanocomposite particles. Nevertheless, most of those

procedures were focused on the production of nanoparticles, not paying attention to the final polymer suspension stability^{21, 22}. Furthermore, when the final liquid dispersions were obtained, they were prepared by drying and re-dispersing the polymer nanoparticles in another solvent, obtaining products with very low concentration¹⁹. Unlike micro-particle slurries, nanoparticle-based ones can potentially keep much larger stability over time, since nanoparticle aggregation and deposition issues can be avoided or, at least, significantly reduced. Both aggregate formation and phase separation are not easy to control, as even nanometer-sized particles often aggregate due to the combined effects of electrical double layer (EDL) and Vander Waals (VDW) interactions²⁴; *i.e.*, they coalesce together creating clusters, and then lead the stratification of those aggregates into immiscible phases. The nanoparticle aggregation and deposition issues involve an important drop in the stability of the slurry and, consequently, a deterioration of its properties^{25, 26}.

The principal way to obtain slurries with an acceptable particle size and good stability is to add the adequate quantity of dispersants or surfactants. On this regard, sodium dodecyl sulfate (SDS) is a non-toxic material²⁷ that has been widely explored as anionic dispersant both for research and industrial applications²⁸⁻³². However, the typical concentration of SDS in commercial products varies from 0.01 to 50 wt.% in cosmetic products^{33, 34} and from 1 to 30 wt.% in cleaning products^{35, 36}, which could create an unnecessary increase in the cost of the final product. In the same way, a large amount of SDS in liquid does not ensure the production of a stable slurry and it could result undesirable for the environment³⁷. For this reason, the addition of cosurfactants has been addressed as an effective approach for reducing the total amount of surfactant material and improving the dispersion stability^{38, 39}. In fact, different cosurfactants have been already employed in combination with anionic SDS showing a synergistic effect, such as non-ionic surfactants:

Tween 80, Tween 20, Symperonic A7 or Triton X-100⁴⁰, cationic surfactants: cetyltrimethylammonium bromide (CTAB)^{40, 41}, alcohols: pentanol or hexanol⁴² or, more recently, caffeic acid⁴³.

Our research group has recently developed a non-aqueous dispersant (NAD) based on functionalized silica containing vinyl terminated groups, which can be anchored to hydrophilic surfaces by Si-OH bonding, whereas the hydrophobic vinyl terminated groups reacted with styrene monomer, favouring the PS particle dispersion in oily media⁴⁴. Utilizing this concept, silica materials could be exploited as surfactants of hydrophobic particles in watery media, since hydrophilic Si-OH bonds can be created outside the surface of a hydrophobic material, such as PS. Consequently, the use of vinyl precursor in the silica material synthesis could promote the nucleation step for the formation of new particles, decreasing the particle size and increasing the stability of the colloidal suspension, and thus reducing the slurry viscosity. CS can be created *in-situ* during the synthesis of the PS nanoparticles by suspension polymerization, facilitating the production of a stable PS slurry (PSS). Suspension polymerization process involves, basically, the preparation of a mixture containing monomer (or comonomers, in the case of copolymers) and an initiator to permit the growth of the polymer chain, together with a suitable and effective dispersing agent to maintain the stability of the dispersed organic phase in a continuous watery media. Contrary to the procedures reported in literature, in which the solid particles are firstly dried and further re-dispersed into the liquid media^{16, 38, 40}, the proposed method allows to produce the slurry in only one single fabrication step. The production of the slurry in one-step, where the entire reagent mass constitutes the final product, reduces significantly the consumption of raw materials, the generation of undesirable residues and additional purification processes. This goal can be achieved due to the great experience of our research group in heterogeneous phase polymerization⁴⁵⁻⁴⁹.

In summary, to the best of our knowledge, neither slurries having both highly concentration and low viscosity formed by nanosized particles, nor manufactured in just one step have been reported yet. Hence, in this work, the optimization of the slurry production was performed in two stages: earlier using only SDS in a moderate concentration (0.2 - 3.0 wt.%) and later, adding the additional CS (TEOS/VTES molar ratio of 0.5) within 0.5 - 2.5 wt.%, in order to improve the stability and rheological behavior of the slurries. The initial monomer concentration was varied from 20.0 to 55.0 wt.%. Finally, the produced slurries have been characterized by using several techniques as ζ , dynamic light scattering (DLS), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR) and rheology with a rotational viscometer.

2. EXPERIMENTAL

2.1. Materials

Styrene monomer (S, reagent grade, 99 wt.%, Sigma-Aldrich Chemical Co.) was purified by washing it three times with an aqueous sodium hydroxide solution (1.25 N prepared from NaOH pellets, Panreac), and subsequently with milli-Q water, with a final drying step to remove water using calcium chloride as desiccant; then, S was stored inside the refrigerator before use. The rest of chemicals were used as received, without any further purification. Hydrochloric acid (HCl, 2 N, Prolabo), sodium hydroxide (NaOH, 1 M, Panreac) were used for pH control during the reaction. Sodium dodecyl sulfate (SDS, $\geq$ 90 wt.%, Panreac Co.) was employed as dispersant. Tetraethyl orthosilicate (TEOS, 98 wt.%, Sigma-Aldrich Chemical Co.) and vinyltriethoxysilane (VTES, 97 wt.%, Sigma-Aldrich Chemical Co.) were used for producing the CS. 2,2'-azobis(2-methylpropionitrile), also known as azobisisobutyronitrile (AIBN, 98 wt.%, Fluka-

Analytical), was utilized as initiator. 1-dodecanethiol (NDDM, 98 wt.%, Sigma-Aldrich Chemical Co.) was selected as chain extender. Milli-Q water with a conductivity of $1\ \mu\text{S cm}^{-1}$ was produced in our laboratory by distillation followed by ion exchange deionization.

2.2. Synthesis of slurries

PSSs were synthesized by suspension polymerization technique, modifying previously reported methods developed in our group for the synthesis of microcapsules with PS shell⁵⁰⁻⁵³. Polymerization reactions were performed at atmospheric pressure and under N₂ inert conditions, in a 0.25 L jacketed glass reactor equipped with a reflux condenser, a Rushton turbine stirrer with six vertical blades and digital stirring control and a thermostatic bath to keep the reaction at the desired conditions.

In this study, the discontinuous phase was prepared by dissolving AIBN into the S and NDDM mixture at 50 °C. The continuous phase was formed by water, SDS and the cosurfactant (CS). The SDS was firstly dissolved in water and, when needed, CS was synthesized *in-situ* in the continuous phase under stirring (1180 rpm) at room temperature, by drop-wising the corresponding amount of the mixture ethanol/TEOS with a molar ratio of 4. Later, the pH of the continuous phase was controlled within 2 - 3 with hydrochloric acid solution (2 M). After one hour of reaction, the desire amount of the mixture ethanol/VTES (molar ratio of 4) was added drop by drop. The reaction was completed after half hour and the pH value was increased up to 8 - 9 with sodium hydroxide solution (1 M), producing a CS having a TEOS/VTES molar ratio of 0.5. After that, the SDS was added into the continuous phase. Once the continuous phase was generated, the reactor was heated up to 80 °C and the agitation was increased up to 1500 rpm. At that moment, the discontinues phase was fed on the continuous phase dropwise,

allowing the continuation of the polymerization reaction which is finished at 5 hours. After this time, the product was stored and cooled down without any further purification or post-treatment. A summary with all the studied recipes is shown in Table 1. The fabricated slurries are named as PSS_{S(wt.%)}-SDS (wt.%) -CS (wt.%).

Table 1. PSSs recipes

	Product	Content(wt.%)								
		PSS _{20-0.2-0}	PSS ₂₀₋₁₋₀	PSS ₂₀₋₃₋₀	PSS ₄₀₋₃₋₀	PSS _{20-3-0.5}	PSS _{20-3-1.5}	PSS _{20-3-2.5}	PSS _{40-3-1.5}	PSS _{55-3-1.5}
Continuous phase	Water (Mili-Q)	79.05	78.25	76.25	56.25	75.75	74.75	73.75	54.75	39.75
	SDS	0.2	1.0	3.0		3.0				
	CS	-	-	-	-	0.5	1.5	2.5	1.5	1.5
Discontinuous phase	S	20.0			40.0	20.0			40.0	55.0
	NDDM	0.5								
	AIBN	0.25								

2.3. Characterization

2.3.1. Stability

The stability of manufactured PSSs without dilution was analyzed by ζ measurements, using Doppler laser microelectrophoresis technique with fitting to Smoluchowski equation employing a Z-Sizer Nano ZS (from Malvern Instruments). This procedure allows to determine ζ of particle suspensions with a diameter comprised within 3.8 nm - 100 μm .

2.3.2. Particle size distribution

The particle size distribution in volume, number and their average particle size values ($dv_{0.5}$ and $dn_{0.5}$, respectively) of the solid particles were determined by Dynamic Light Scattering (DLS), utilizing a Z-Sizer Nano ZS from Malvern Instruments and

NanoApplication software to analyze the experimental data. The software calculates the polydispersity index (*PdI*) according to the ISO standard document 13321:1996 E⁵⁴ and ISO 22412:2008⁵⁵.

2.3.3. Transmission Electron Microscopy (TEM)

TEM studies were performed using a 2100 JEM (JEOL) electron microscope operating at 200 kV and equipped with an Energy Dispersive X-Ray Spectroscopy (EDS) detector (Oxford Link). Samples for TEM observation were prepared by depositing aqueous suspensions diluted of the samples onto a holey carbon grid (EMS). The size of the particles was measured by DigitalMicrograph software.

2.3.4. Thermogravimetric analysis (TGA)

Thermal stability and total solid content of the synthesized PSSs were obtained by TGA using an equipment from TA instruments (SDT Q600 Simultaneous DSC-TGA). Temperature was tuned from room temperature to 700 °C, using a heating rate of 10 °C min⁻¹ under nitrogen atmosphere. The yield of the reaction is calculated considering the synthesized PS and the initial amount of S, AIBN and NDDM as reactants:

$$Particle\ yield\ (\%) = \frac{PS\ particles\ content\ (wt.\%)}{S\ (wt.\%)+AIBN\ (wt.\%)+NDDM(wt.\%)} \cdot 100 \quad [1]$$

2.3.5. Fourier transform infrared spectroscopy (FT-IR)

Fourier transform infrared (FT-IR) spectroscopy analyses were carried out on a SPECTRUM TWO spectrometer (Perkin Elmer, Inc) and performed in transmission mode using ZnSe (550-4500 cm⁻¹), using at least 4 scan and a resolution of 1 cm⁻¹.

2.3.6. Rheological behavior

Rheological properties of slurries were measured with a rotational rheometer Anton Paar MCR302. Products were tested using a CP50 cone&plate system equipped with water trap, in order to avoid water evaporation. The cone has 50 mm of diameter and 1° of angle. The plate has a Peltier for temperature control. Each measurement was repeated three times with fresh samples, ensuring the reproducibility of the results. Shear rate was varied according to the cycle of 1 - 1000 s^{-1} and controlling the sample temperature at 25 °C.

3. RESULTS AND DISCUSSION

High concentrated PSSs were synthesized by suspension polymerization technique in one single step, changing SDS and CS contents in order to improve their particle size, stability and dynamic viscosity.

3.1. Influence of SDS

The influence of SDS amount on the PSS properties was studied. Firstly, varying its concentration from 0.2 to 3.0 wt.% for a S concentration of 20 wt.%. Once optimized the concentration of SDS, the maximum solid concentration was determined.

3.1.1. Stability

ζ analysis is one of the most important parameters to consider in order to analyze the stability of synthesized liquid suspensions²⁶. ζ values obtained for PSS₂₀₋₁₋₀ and PSS₂₀₋₃₋₀ were – 79.9 and – 62.8 mV, respectively. These values confirmed the outstanding stability of these products, since their absolute values were significantly higher than 30 mV, the limit commonly accepted to be considered as a stable particle suspension⁵⁶⁻⁵⁸. In fact, PSS₂₀₋₁₋₀ and PSS₂₀₋₃₋₀ products show an excellent stability according the state of the arte, presenting both $|\zeta| > 61 \text{ mV}$ ⁵⁹. As both ζ values are greater than 61 mV, the differences in the exact value of ζ can not be directly related with a real increase in the stability of such

PSS products since both present ζ values over the maximum stability category established by Kumar⁵⁹. Hence, it is possible to say that these products were stable slurries. On contrary, PSS_{20-0.2-0} resulted poorly stable due to the low concentration of dispersing agent (below its critical micelle concentration, CMC), being not possible to be measured by microelectrophoretic techniques using the ζ set up^{60, 61}. In the case of PSS₄₀₋₃₋₀, a ζ value of -36.80 mV was obtained, confirming the success in the production of stable concentrated PSSs ($|\zeta| > 30$ mV).

3.1.2. PS particle size

In order to know the PS particle size distribution of the different PSSs, dynamic light scattering (DLS) measurements were developed. Figure 1 shows the DLS results.

Figure 1. PS particle size distribution in number (ND) and volume (VD) for different PSSs; (a) for different SDS concentration (PSS₂₀₋₁₋₀ and PSS₂₀₋₃₋₀) and (b) varying S concentration (PSS₄₀₋₃₋₀ and PSS₂₀₋₃₋₀), being represented the value of $dn_{0.5}$ and $dv_{0.5}$ of PSS₂₀₋₃₋₀ by the dashed vertical lines for comparison purposes.

In Figure 1, it can be distinguished that the particle size distributions followed monomodal distribution and the average values of the particle size decreased with the increase of SDS concentration. The observed median particle diameters in number ($dn_{0.5}$)

for the PSS₂₀₋₁₋₀ and PSS₂₀₋₃₋₀ were quite similar, being 51.3 and 44.2 nm, whereas $d_{v0.5}$ were 84.3 and 53.9 nm, respectively, due to the presence of bigger particles. Moreover, in both cases, the particle size distribution was narrow, with *PdI* values of 0.195 for PSS₂₀₋₁₋₀ and 0.095 for PSS₂₀₋₃₋₀. The lower *PdI* of PSS₂₀₋₃₋₀ can be attributed to the fact that more nucleation points remain active when SDS amount increases, permitting the formation of a greater number of PS particles with lower particle size. For the concentrated PSS₄₀₋₃₋₀, the increment of S triggered a moderate decrease in the median PS particle size ($d_{v0.5}$ = 44.3 and $d_{n0.5}$ = 30.9 nm), but at the expense of a broader particle size distribution (*PdI* = 0.199). Anyway, all PSSs presented a particle size lower than 100 nm, satisfying the criterion to be considered as a nanomaterial, where more than the 50 % of the particles must have a size comprised between 1-100 nm^{62, 63}. Furthermore, the obtained PS particle size was placed in the range or even smaller than similar products reported in literature^{17, 64-67}.

Figure 2 shows TEM images of the PS nanoparticles present in the produced slurries.

Figure 2. TEM images of the PS particles contained in the PSSs, (a) PSS₂₀₋₁₋₀, (b) PSS₂₀₋₃₋₀ and (c) PSS₄₀₋₃₋₀.

According TEM images the PS particles presented spherical and smooth shape. The agglomerates observed in the figures are clearly promoted by the solvent evaporation, since the particles preserve an independent morphology (without sharing walls between each other) morphology. Particles presented average diameters of 72, 54 and 43 nm for PSS₂₀₋₁₋₀, PSS₂₀₋₃₋₀ and PSS₄₀₋₃₋₀, respectively, in good agreement with DLS results.

3.1.3. Solid concentration and thermal stability

The solid concentrations of these PSSs were calculated by thermogravimetric analyses (Figure 3).

Figure 3. Thermogravimetric analyses of PSS₂₀₋₁₋₀, PSS₂₀₋₃₋₀, PSS₄₀₋₃₋₀, SDS and PS from bulk polymerization.

Three weight losses can be seen in the synthesized PSSs. The first one, between 20 and 100 °C, corresponds to water evaporation. The second one represents the degradation of the SDS, with a maximum degradation temperature *ca.* 220 °C, corresponding with the TGA decay of SDS. The last weight loss is *ca.* 400 °C and it corresponds with the PS

degradation⁶⁸. Regarding the PS particles content of the slurries (expressed as weight percentage of the prepared slurry), the experimental solid concentration obtained by TGA were 17.1, 18.9 and 39.0 wt.% for PSS₂₀₋₁₋₀, PSS₂₀₋₃₋₀ and PSS₄₀₋₃₋₀, respectively. Considering these PS particles contents, the particle yields were 82.4, 91.0 and 97.5 % for PSS₂₀₋₁₋₀, PSS₂₀₋₃₋₀ and PSS₄₀₋₃₋₀, respectively. Therefore, the particle yield was importantly enhanced when the SDS concentration was raised from 1.0 to 3.0 wt.% and also with the S increase.

3.1.4. Viscosity

Other key property of the slurries is their viscosity since they are usually designed to be pumped. The dynamic viscosity of PSS₂₀₋₁₋₀, PSS₂₀₋₃₋₀ and PSS₄₀₋₃₋₀ was measured with a rotational rheometer. In detail, the viscosities of PSSs were 2.3 and 2.6 mPa·s for PSS₂₀₋₁₋₀ and PSS₂₀₋₃₋₀, respectively; whereas for PSS₄₀₋₃₋₀, the viscosity was within 3733-56.1 mPa·s at low, 1-10 s⁻¹, and high, 100 – 1000 s⁻¹, shear rates, respectively. As expected, PSSs showed greater viscosity than the water used as base fluid, which is 0.89 mPa·s at 25 °C. On the one hand, the viscosity of PSS₂₀₋₁₋₀, and PSS₂₀₋₃₋₀ did not present any variation with shear rate, *i.e.* both ones behaved as Newtonian fluids. Moreover, the viscosity of these two PSSs remained always low, not being significantly changed by the SDS content added in the fabrication step. PSS₂₀₋₃₋₀ presented lower viscosity than PSS₂₀₋₁₋₀ (2.3 and 2.6 mPa·s, respectively), even though it exhibited higher particle concentration and particle yield. On the other hand, comparing the rheological behavior of PSS₂₀₋₃₋₀ and PSS₄₀₋₃₋₀, the abrupt rise in solid concentration from 18.9 to 39.0 wt.% pushed an excessive increase of viscosity, turning the Newtonian fluid into a non-Newtonian one, with pseudoplastic character. To wrap up, a 3.0 wt.% concentration of SDS was unquestionably the most adequate condition between the ones investigated. However, taking into account the viscosity-boosting problems observed in the PSS₄₀₋₃₋₀

and that its ζ was not very high, it was proposed the addition of a cosurfactant prepared *in-situ* and based on VTES/TEOS.

3.2 Influence of CS

As commented before, to increase the affinity between hydrophobic PS and hydrophilic watery media, the addition of a CS, that allows the PS functionalization, is proposed. The CS was synthesized *in-situ* from VTES and TEOS. The specific objective is the synthesis of vinyl-terminated particles that react with the styrene monomer in order to create a PS polymer chain terminated with siloxanes groups. These hydrophilic terminations (-OH) would increase the PS polymer stability and its dispersibility in the aqueous media. According to previously reported works, this type of dispersant has been demonstrated to be effective for stabilizing PS particles in polyol media due to the creation of hydrophilic silanol groups^{44, 69}. Therefore, three reactions were carried out modifying the amount of CS, from 0.5 to 2.5 wt.%, keeping the 3.0 wt.% of SDS as ideal concentration of dispersing agent. Three fluid products were successfully obtained (PSS_{20-3-0.5}, PSS_{20-3-1.5} and PSS_{20-3-2.5}).

To confirm the real and effective functionalization of the PS nanoparticles with the selected CS silica materials, FT-IR spectroscopy and EDS analyses were performed, employing pristine PS particles as blank. Then, the positive signal observed in silica-functionalized PS nanoparticles was mainly caused by Si-OH and Si-R bonding. Additionally, for pure CS, air was used as blank. These results are shown in Figure 4.

Figure 4. a) FT-IR analyses of nanoparticles obtained from PSSs using different CS contents and pure CS b) EDS analysis of a single particle synthesized of the PSS_{20-3-1.5}.

The FT-IR spectra showed the characteristic bands of Si-alkoxy compounds in the 1110 - 1000 cm^{-1} range, which rose as the CS concentration was increased, and the characteristic bands of Si-OH groups in the range 920 - 850 cm^{-1} .⁷⁰ FT-IR spectra (Figure 4a) demonstrated, undoubtedly, the functionalization of PS by the Si atoms from the CS. Moreover, in all the three slurries the presence of Si atoms on the particles surface was confirmed by EDS. As an example, the EDS analysis of PSS_{20-3-1.5} is shown in Figure 4b.

3.2.1. Thermal stability of PS particles and PSSs solid content

Figure 5 shows the TG analyses of the solid from PSS_{20-3-0.5}, PSS_{20-3-1.5} and PSS_{20-3-2.5}.

Figure 5. Thermogravimetric analyses of the PS nanoparticles contained in the PSS_{20-3-0.5}, PSS_{20-3-1.5} and PSS_{20-3-2.5}. The main degradation temperatures of SDS and PS from bulk polymerization are shown as light grey stripes.

As expected, TG analyses revealed that the main weight loss of the nanoparticles was around 400 °C, due to thermal decomposition of PS. There was another weight loss *ca.* 220 °C that corresponded to the thermal degradation of organic part SDS (about 8.5 - 10 wt.%) which agreed well with the expected value (8.6 - 9.3 wt.%) attending to the initial amount of SDS in the formulation respect to the solid content. Indicating that the SDS remained in the solid material after the drying process. After the complete degradation of PS, the residue was attributed to the unburned SDS and the new formation of the highly thermal stable copolymer PS linkage with silicon groups⁴⁴.

The total PS nanoparticles contents obtained by TGA for the PSS_{20-3-0.5}, PSS_{20-3-1.5} and PSS_{20-3-2.5} are 19.0, 20.0 and 18.6 wt.%, respectively; and the particle yields from S were 91.4, 96.4 and 89.6 % for each PSS. An increase up to 1.5 wt.% of CS, helps to enlarge

the formation of solid polymeric nanoparticles into the final PSS, reaching a particle yield of 96.4 %, and confirming that the addition of CS exhibits a cooperative effect with the dispersant material (SDS) for the incorporation of solid nanoparticles. This effect could be due to the water affinity promoted by the incorporation of Si-OH groups in PS nanoparticles. On contrary, a 2.5 wt.% of CS resulted counterproductive from a particle yield point of view. This can be attributed to an excess of positive charges, that starts to destabilize the system⁷¹.

3.2.2. Particle size

Particle size distributions of PSSs produced with different concentrations of CS are shown in Figure 6.

Figure 6. Particle size distribution in number (ND) and in volume (VD) (a) PSS_{20-3-0.5} and PSS_{20-3-1.5} and (b) PSS_{20-3-2.5}, being represented the value of $dn_{0.5}$ and $dv_{0.5}$ of PSS₂₀₋₃₋₀ by the dashed vertical lines for comparison purposes.

Results shown in Figure 6a indicated that a 0.5 wt.% of CS (PSS_{20-3-0.5}) did not play a remarkable role in the variation of particle size, since quite similar values of mean diameter ($dv_{0.5} = 50.4$ nm and $dn_{0.5} = 44.2$ nm) were obtained in comparison with the

particles dispersed in the PSS₂₀₋₃₋₀. The use of a 1.5 wt.% of CS material (PSS_{20-3-1.5}) promoted the smallest particle size, being also smaller than that obtained in the PSS₂₀₋₃₋₀ ($d_{v0.5}$: $40.0 < 53.9$ nm and $d_{n0.5}$: $32.1 < 44.2$ nm, respectively). Furthermore, the particle size distribution of PSS_{20-3-1.5} in number and volume were quite similar, indicating a low polydispersity. This was coherent with the considered synergic effect of CS, since not only more particles, but also smaller ones were obtained after adding the CS materials. Furthermore, up to our knowledge, these are the smallest particles ever reported in literature for a nanoparticle slurry^{17, 64-67}. When the CS material concentration was further augmented (from 1.5 to 2.5 wt.%), the particle size increased a little bit (Figure 6b: $d_{v0.5}$ = 60.9 and $d_{n0.5}$ = 52.1). Anyway, the particle sizes of all the synthesized PSSs containing the CS were lower than 100 nm, therefore these slurries can be also classified as nanomaterials^{62, 6362, 6361, 62}.

Figure 7 presents TEM images for the PSSs synthesized with different contents of CS.

Figure 7. TEM images of the PS nanoparticles contained in the PSS_{20-3-0.5} (a) and PSS_{20-3-1.5} (b).

In Figure 7, it can be seen that PSSs were formed by independent nanoparticles with spherical structure. Nanoparticles had 60 nm and 52 nm of diameter, for PSS_{20-3-0.5} and PSS_{20-3-1.5}, respectively, which agrees with DLS findings.

3.2.3. Stability

The ζ of synthesized slurries was measured in order to study their stability. Notable absolute values of ζ were obtained for all the slurries, specifically -60.2 mV, -70.5 mV and -31.8 mV for PSS_{20-3-0.5}, PSS_{20-3-1.5} and PSS_{20-3-2.5}, respectively. These results indicated that all the PSSs synthesized with the CS were stable, having the highest stability PSS_{20-3-1.5}. Compared to the slurry without CS, the addition of only 0.5 wt.% of CS material did not improve its stability, since ζ values were practically the same (-62.8 mV for PSS₂₀₋₃₋₀, whereas -60.2 mV for PSS_{20-3-0.5}). On contrary, an addition of 1.5 wt.% of CS resulted in an interesting improvement of stability, growing the absolute values of ζ from 62.8 to 70.5 mV. The low value of ζ (-31.8 mV) for the PSS_{20-3-2.5} confirmed the counter-productive effect of using a 2.5 wt.% of CS, reducing the final stability of the slurry. It could be due to the positive charge contribution of an excess of CS⁷¹. On contrary, a moderate addition up to 1.5 wt.% of CS in the PSS, clearly enhanced the stability, the particle yield and the production of a monodisperse slurry.

3.2.4. Viscosity

The viscosity of the synthesized PSSs containing CS materials was studied at 25 °C, showing 2.7, 2.5 and 2.6 mPa·s, for PSS_{20-3-0.5}, PSS_{20-3-1.5} and PSS_{20-3-2.5}, respectively. As can be observed, although PSS_{20-3-1.5} showed the lowest viscosity, rheological changes related to the CS concentration were not significant for this solid content, obtaining low viscous Newtonian fluids for any studied CS amount.

3.3. Increase of the solid content of the PSSs synthesized with the best conditions

The feasibility of synthesizing more concentrated PSSs were performed by using 3.0 and 1.5 wt.% of SDS and CS, respectively. At this point, the main goal is to find the highest

PSS solid content that allows to produce a pumpable slurry. For that purpose, PSSs from S contents with 40.0 and 55.0 wt.% were prepared. The solid content and particle yield were obtained by TGA (Figure 8).

Figure 8. Thermogravimetric analyses of the PSS_{40-3-1.5}, the PSS_{55-3-1.5}. Light grey stripes represent the main degradation temperatures of SDS and PS from bulk polymerization.

As shown in Figure 8, similar weight losses than those ones observed for the PSSs from 20.0 wt.% of S were obtained. Attending to these results, solid contents of 40.0 wt.% for PSS_{40-3-1.5} and 52.0 wt.% in the case of PSS_{55-3-1.5} were attained, which corresponds with particle yields of 98.8 and 89.6 %, respectively. These values indicated that an increment of the S amount up to 40.0 wt.%, did not affect the PS particle yield.

The particle size distributions obtained by DLS and the TEM images from the concentrated PSSs are shown in Figure 9.

Figure 9. (a) Particle size distribution in number (ND) and in volume (VD) of PSS_{40-3-1.5} and PSS_{55-3-1.5}, being represented the value of $dn_{0.5}$ and $dv_{0.5}$ of PSS₂₀₋₃₋₀ by the dashed vertical lines for comparison purposes; and TEM (a) images of the PS nanoparticles contained in PSS_{40-3-1.5} and (b) PSS_{55-3-1.5}.

As illustrated in Figure 9.a, both PSSs exhibited a monomodal distribution in volume and number. In spite of the increase in the initial monomer amount from 20.0 to 40.0 wt.%, their respectively average particle sizes in volume ($dv_{0.5}$: 40.0 $\cong$ 42.5 nm) and in number ($dn_{0.5}$: 32.1 $\cong$ 30.8 nm) are practically the same. Nevertheless, for PSS_{55-3-1.5}, an increase in the particle size was detected ($dv_{0.5}$ = 78.6 nm and $dn_{0.5}$ = 65.8 nm).

The size and spherical morphology of the nanoparticles were similar than those ones prepared under the same conditions but with less concentrated PSS, concluding that the

morphology of nanoparticles was not affected by the initial monomer concentration. In detail, according to these images (Figure 9.b and 9.c) PSS_{40-3-1.5} and PSS_{55-3-1.5} presented particles sizes of 51 and 75 nm, respectively. These values agreed well with the results obtained by DLS, permitting to classify these products as nanomaterials.

Stability of concentrated PSSs was characterized by ζ experiments. When the amount of used S increased from 20.0 to 40.0 wt.%, the stability of the slurry was even improved, since ζ changes from -70.5 mV (PSS_{20-3-1.5}) to -76.7 mV (PSS_{40-3-1.5}). In contrast, PSS_{55-3-1.5} resulted a gelled fluid product, not being possible to evaluate its stability by ζ analysis. Pictures of fresh and one year aged PSS_{40-3-1.5} are shown in Figure 10, for studying their long-term stability. In these pictures, there are not perceptible aspect changes, neither evidences of sedimentation nor stratification. Besides, the ζ value of the aged slurry (-48.5 mV) demonstrated its great long-term stability.

Figure 10. Pictures of: (a) Fresh PSS_{40-3-1.5} and (b) Aged PSS_{40-3-1.5}.

Rheology analyses of these synthesized PSSs were obtained by using the rotational rheometer under shear rates of $1 - 1000 - 1 \text{ s}^{-1}$ at 25°C , reaching Newtonian slurries with dynamic viscosities of 2.5 and $20.5 \text{ mPa}\cdot\text{s}$ for the PSS_{20-3-1.5} and PSS_{40-3-1.5}, respectively. In contrast, in the case of the gelled PSS_{55-3-1.5}, it showed a Herschel-Bulkley rheological

behavior, exhibiting viscosity values of 37050 and 131.5 mPa·s at low ($1-10 \text{ s}^{-1}$) and high ($100 - 1000 \text{ s}^{-1}$) shear rates, respectively. Finally, analyzing the characteristics of the PSS₄₀₋₃₋₀ and PSS_{40-3-1.5}, it is possible to affirm that the CS addition had a positive effect on the ζ , the final particle yield and the rheological behavior, changing from -36.80 mV , 97.5% and non-Newtonian fluid, to -76.7 mV , 98.8% and Newtonian behavior, respectively. Hence, the addition of the cosurfactant containing Si has permitted an abruptly reduction of the final viscosity of the slurry. This behavior is explained by the fact that, at nanometric scale when Si-materials are used, an increment of solid concentration is not directly traduced into a significant viscosity increase⁷². As it was observed, only the average particle size of the PSS₄₀₋₃₋₀ ($d_p = 43 \text{ nm}$) was lower than the corresponding particle size of the PSS_{40-3-1.5} ($d_p = 51 \text{ nm}$). Hence, by combining the SDS and CS, it is possible to produce concentrated PS slurries having the desired physical, chemical and rheological characteristics and having long-term stability. Moreover, the total amount of dispersants (SDS-CS) used in the optimal product resulted much lower than in other commercial ones³³⁻³⁶. These findings can set a route for the commercially profitable manufacturing of polymer nanoslurries and their launch to market in applications as sealant, base product for expanded PS, filler and plasticizer additive.

4. CONCLUSIONS

The fabrication of slurries with a remarkable high concentration of PS nanoparticles and low viscosity has been achieved. The process consisted in a suspension polymerization reaction, without any further post-treatment and only using mechanical agitation. The optimization of the dispersant quantities indicated that a 3.0 wt.% of SDS and 1.5 wt.% of CS (silica-containing mixture of VTES/TEOS) were found as the ideal conditions for manufacturing a low-viscous Newtonian PSS (20.5 mPa·s) having a PS concentration up to 40 wt.% in nanoparticles ($d_{n0.5} = 30.8 \text{ nm}$). The use of the CS not only improved the

rheological properties but also the PS particle yield and the long-term stability of the final slurry. Moreover, CS introduction made feasible the fabrication of extremely concentrated slurries up to 52.0 wt.%.

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ACKNOWLEDGEMENTS

Authors gratefully acknowledge the financial support from the Spanish Ministry of Science, Innovation and Universities due to the project TRANSENERGY (RTI2018-100745-B-I00) and the fellowship for PhD studies (FPU16/02345) of D. López-Pedrajas; F.J. Ramos also thanks JCCM and FEDER due to the financial support for the research project GTSOL (Ref. SBPLY/17/180501/000554). The authors state that they have not conflict of interest with any public or private body.

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