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## Water-based acrylic coatings reinforced by PISA-derived fibres

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Polymerization-induced self-assembly (PISA) is an efficient approach to synthesize self-assembled core-shell nanofibres in water, made of amphiphilic block copolymers. We demonstrate here for the first time that such anisotropic and high T<sub>g</sub> nanofibres can be used as reinforcing fillers for water-based acrylic materials. This strategy opens the way for strong all-organic aqueous coatings.

There is an increasing demand from the coating industry to reduce the amount of volatile organic compounds (VOC).<sup>1</sup> For instance, solvent-based paints are replaced by water-based latex paints, obtained through radical emulsion polymerization processes. However, most of the formulations still contain VOCs used to assist the film formation at low temperature by plasticizing the polymer in the latex particles. Alternatively, the latex particles can be softened by changing the composition to lower the glass transition temperature (T<sub>g</sub>). This provides good deformability as the films dry, but the resulting materials exhibit generally poor mechanical properties. A solution to obtaining stiffer rubbery materials without sacrificing deformability is the introduction of hard fillers, such as inorganic silica particles or carbon black. However reported disadvantages are loss of transparency, increase in density and the relatively high amount of filler necessary.<sup>2,3</sup> To reduce the amount of filler, the addition of anisotropic fillers such as glass fibres, carbon nanotubes<sup>4,5</sup> or natural fibres<sup>6</sup> has also been considered. Thanks to their high aspect ratio, percolation and thus an increase of the mechanical performance can be reached with very low amounts of these additives. However, these fillers are difficult to tune (in terms of composition and diameter) and to disperse. Alternatively, polymeric composite films have been proposed that are made of *latex blends*<sup>7</sup>, mainly mixtures of soft with hard spherical particles<sup>8,9</sup>, but also reactive blends<sup>10</sup> or structured core-shell latexes, to form

nanostructured films with suitable properties.<sup>11</sup> In particular, we reported recently how one can take advantage of the current developments in polymerization-induced self-assembly (PISA) to prepare nanostructured latex-based films combining high stiffness and high deformability, seemingly contradictory properties.<sup>12,13</sup> The materials were exclusively made of spherical soft-core/hard-shell particles, constituted of highly asymmetric poly(acrylic acid)-*b*-poly(*n*-butyl acrylate), PAA-*b*-PBA, block copolymers, synthesized in water thanks to a RAFT emulsion polymerization process.<sup>14</sup> The enhanced stiffness of the materials at low strain was attributed to the percolating network formed by the glassy PAA shells. Unfortunately, these formerly reported materials are entirely made of relatively costly PISA-derived particles which may be seen as a limitation of the approach.

In this work, we propose a new concept to design reinforced all-organic water-based soft coatings taking advantage of the most recent developments in PISA and existing latex blend strategies. It has been shown that the morphology of the amphiphilic copolymer self-assemblies can be reproducibly tuned from a spherical shape to anisotropic filamentary structures (also called worm-like) by subtle changes in the polymerization conditions, and that aqueous fibre dispersions can be obtained in high concentration and yields.<sup>15,16</sup> We propose here to use high T<sub>g</sub> nanofibres, in the form of self-stabilized aqueous dispersions, obtained by PISA, as reinforcing additives for water-based soft acrylic films. In this pioneering work, the materials are obtained from simple mixtures of a conventional low T<sub>g</sub> latex with limited quantities of PISA-derived polystyrene (PS) nanofibres. The mechanical properties of this new class of films made from latex blends were evaluated by tensile tests. Materials reinforced with the *spherical* counterparts were used as reference. The increased stiffness of the fibre-reinforced materials (while maintaining high extensibility) was explained by the high aspect ratio of the fillers which may form a reinforcing network of glassy nanofibres.

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Electronic Supplementary Information (ESI) available: Materials and methods section, scheme of the synthetic pathway, detailed Tables for the polymerizations including polymerization conditions and polymer/latex characterization, size exclusion chromatograms of the polymers, additional TEM and stress-strain plots, creep test.

**Table 1. Synthesis of aqueous fibre and sphere dispersions by PISA in two successive polymerization steps. ‡**

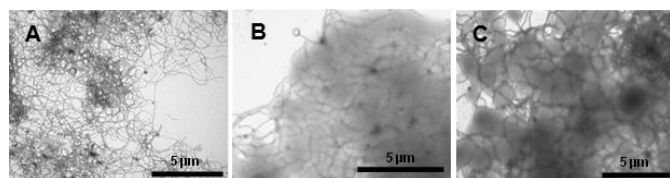
**1st step: Synthesis of macroRAFT agents in aqueous solution**

entry	[MAA] <sub>0</sub> /mol L <sup>-1</sup>	[PEOMA] <sub>0</sub> /mol L <sup>-1</sup>	[CTPPA] <sub>0</sub> /mol L <sup>-1</sup>	Conv. /%	M <sub>n,th</sub> /kg mol <sup>-1</sup>	M <sub>n,LS</sub> /kg mol <sup>-1</sup>	Đ <sup>PS</sup>
M-S1	0.20	0.20	0.013	97	16	25	1.12
M-F1	0.25	0.12	0.009	99	15	22	1.12
M-F2	0.40	0.20	0.014	97	16	25	1.11

**2nd step: Synthesis of aqueous fibre dispersions and spherical latexes via aqueous emulsion polymerization.**

entry	Morphology	[S] <sub>0</sub> /g mL <sup>-1</sup>	[S] <sub>0</sub> /[macro-RAFT] <sub>0</sub>	M <sub>n,th</sub> /kg mol <sup>-1</sup>	M <sub>n,LS</sub> /kg mol <sup>-1</sup>	Đ <sup>PS</sup>
S1	spheres	0.21	300	47	58	1.32
F1	fibres	0.13	300	46	53	1.15
F2	fibres	0.21	300	47	63	1.29

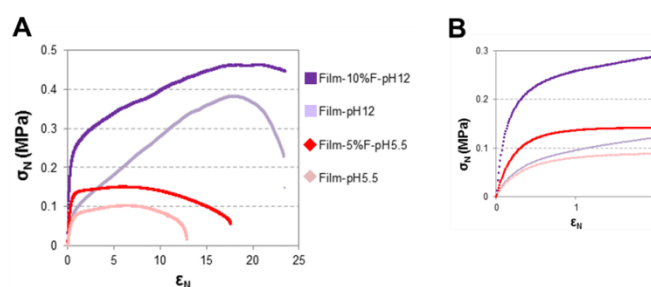
The core-shell fibre dispersions based on a hard polystyrene core and a stabilizing poly(methacrylic acid)-co-poly(methoxy(polyethylene oxide) methacrylate) P(MAA-co-PEOMA) (M<sub>n</sub> of PEOMA = 950 g mol<sup>-1</sup>) shell were prepared entirely in water, in two successive polymerization steps (Table 1). In a first step MAA and PEOMA (MAA/PEOMA = 67/33) were copolymerized in water in the presence of 4-cyano-4-thiopiropylsulfanylpentanoic acid (CTPPA) as a chain transfer agent, using 4,4-azobis(4-cyanopentanoic acid) (ACPA) as a radical initiator (see Scheme SI-1).<sup>17,18</sup> The polymerization reached full conversion within 2h yielding the water-soluble statistical macroRAFT agent P(MAA-co-PEOMA) (Đ = 1.1, M<sub>n,LS</sub> = 22 kg.mol<sup>-1</sup>) constituting *in fine* the stabilizing shell of the latex particles. The reaction medium was adjusted to pH 5 in order to ensure particle stabilization by the partially deprotonated carboxylic acid groups of MAA, and then styrene and a supplementary amount of initiator in water were added, and the polymerization was pursued in the same flask in emulsion conditions and under inert atmosphere. This second polymerization step was stopped after 3.5h and the aqueous fibre dispersion was recovered as a viscous liquid. Size exclusion chromatography (Figure SI-1) assessed the good control over the polymerization and the successful formation of P(MAA-co-PEOMA)-*b*-PS diblock copolymers with low molar mass dispersity (Đ < 1.2, M<sub>n,LS</sub> = 53 kg.mol<sup>-1</sup>, Table 1, fibres F1). TEM showed the formation of micrometres long nanofibres, with an average diameter about 50 nm (Figure 1A).



**Figure 1. TEM micrographs of dried fibres (A), and mixtures of the soft acrylic latex with 5 wt% (B) and 10 wt% (C) of fibres (pH = 12).**

For comparison *spherical* core-shell particles based on the same type of polymer were also prepared by PISA according to the same protocol, using a different MAA/PEOMA molar ratio

(50/50) in order to promote the formation of spheres instead of fibres.<sup>18</sup> Again, SEC confirmed the formation of amphiphilic diblock copolymers with good control (Đ = 1.3, M<sub>n,LS</sub> = 58 kg.mol<sup>-1</sup>). Like in the fibre synthesis, a small amount of residual macroRAFT agent was detected, that is to say both samples contain some free P(MAA-co-PEOMA) chains. Moreover, the average molar mass of each block was comparable for both systems (Table 1 and Table SI-1). However, TEM assessed that spheres instead of fibres (with similar diameter, 45 nm, Figure SI-2) were obtained, simply by changing the molar ratio of the hydrophilic comonomers. As illustrated in Scheme SI-2, acrylic films were then prepared from a typical soft acrylic latex (statistical copolymer P(*n*BA-co-AA), 1.9 wt% AA, see SI) used for pressure-sensitive-adhesives<sup>19</sup> to which 5 wt% of glassy fibre (F1) or sphere (S1) latex were added as a reinforcing filler. A reference film without filler was also formed in the same drying conditions (see Series I, Film-pH5.5, Film5%F-pH5.5 and Film5%S-pH5.5 in Table 2). Standard tensile tests were then performed to evaluate the impact of the incorporation of the glassy filler in the soft acrylic polymer matrix. For strains below 10% the films presented a linear behaviour, but for larger strains all films underwent a progressive softening, before break-up only beyond 1000% extension (see Figure 2 and Figure SI-3), as typically observed for soft PBA films. As summarized in Table 2, the addition of 5 wt% fibres increased the Young's modulus by a factor of 2, whereas the corresponding spherical particles showed only a slight increase of modulus. This first series (I) was prepared from mixtures of the acrylic matrix latex without pH adjustment, *i.e.* at pH 5.5.



**Figure 2. (A) Nominal stress (σ)–strain (ε) curve for pristine films and films containing fibres at pH = 5.5 or 12 (strain rate = 0.1 s<sup>-1</sup>), (B) Enlargement of the low strain region.**

For the next series of films, the latex blends were prepared in alkaline conditions in order to more efficiently deprotonate the carboxylic acid groups of the MAA units which should decrease inter-fibre interaction via H-bonding (by MAA dimerization or interaction of MAA with PEO) and thus promote a better dispersion of the fibres in the acrylic latex. Various amounts of spherical or fibre additive (5 or 10 wt%) were tested (Figure SI-4) and a reference film was also cast at the same pH. The comparison of the reference films formed at pH 5.5 or 12, in Figure 2, shows that the film made at pH 12 was much stiffer, in the medium strain region, and more extensible, while maintaining a similar Young's modulus as the film formed at pH 5.5. The observed stiffening through pH increase is a known phenomenon in acrylic acid (AA) containing formulations<sup>7,20</sup> and it is usually explained by the formation of long lived ionic clusters. It must therefore be

taken into account in the interpretation of the films incorporating the glassy additives.

**Table 2. Film composition and results of the tensile tests.**

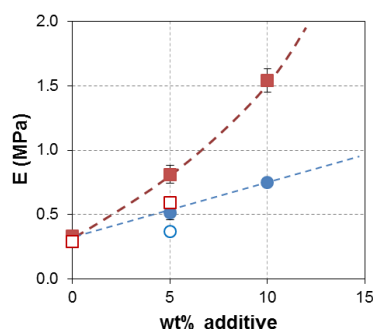
#	Film	Additive	wt% additive	$\sigma_{\max}^b$ /MPa	$\epsilon_B^b$	$E^c$ /MPa	$E/E_0^c$
<i>Series I prepared from P(nBA-co-AA) latex 1 at pH 5.5<sup>a</sup></i>							
1	Film-pH5.5	-	-	0.10 $\pm 0.01^e$	12 $\pm 1^e$	0.29 $\pm 0.03^e$	1.0
2	Film5%S-pH5.5	S1	5	0.13 $\pm 0.01$	10 $\pm 1$	0.37 $\pm 0.03$	1.3
3	Film5%F-pH5.5	F1	5	0.15 $\pm 0.01$	16 $\pm 2$	0.59 $\pm 0.04$	2.0
<i>Series II prepared from P(nBA-co-AA) latex 1 at pH 12<sup>a</sup></i>							
4	Film-pH12	-	-	0.41 $\pm 0.08$	26 $\pm 3$	0.33 $\pm 0.05$	1.0
5	Film5%S-pH12	S1	5	0.25 $\pm 0.02$	> 25 <sup>d</sup>	0.51 $\pm 0.03$	1.5
6	Film10%S-pH12	S1	10	0.27 $\pm 0.02$	> 25 <sup>d</sup>	0.79 $\pm 0.05$	2.4
7	Film5%F-pH12	F1	5	0.34 $\pm 0.02$	> 29 <sup>d</sup>	0.89 $\pm 0.07$	2.7
8	Film10%F-pH12	F1	10	0.44 $\pm 0.04$	> 25 <sup>d</sup>	1.54 $\pm 0.09$	4.7

<sup>a</sup> pH of the latex or the latex mixture before film formation, <sup>b</sup>  $\sigma_{\max}$  = maximum stress,  $\epsilon_B$  = strain at break =  $(L_B - L_0)/L_0$ , <sup>c</sup> E = Young's modulus,  $E_0$  = Young's modulus of the reference film prepared at the same pH without additive, <sup>d</sup> in the experimental set-up the film was extended without failure, <sup>e</sup> standard deviations on at least 3 samples.

As summarized in Table 2, upon addition of either 5 or 10 wt% of additive, all films of series II remained highly extensible (extension  $\geq 2500\%$ )<sup>5</sup> indicating that the glassy additives were *a priori* well-dispersed in the soft acrylic matrix. The successful dispersion of the fibres was confirmed by TEM images of thin films made from the corresponding mixtures (Figure 1B and C). Clearly, the desired stiffening of the materials was observed in the low strain region (Figure 2B). As for series I, the addition of the glassy fibres **F1** led to a clear increase in stiffness revealed by an increase of the Young's modulus by a factor of 2.7 (with 5 wt% **F1**) or 4.7 (with 10 wt% **F1**), respectively (Table 2,  $E/E_0$ ). Again, the values obtained for the fibre-containing films outperformed by far the effect of the corresponding spherical filler, which enhanced the Young's modulus by a factor of 2.4 at most (using 10 wt% of **S1**). The effect of the filler morphology on the modulus at the different pH is summarized in Figure 3. The strong influence of the filler morphology means that the possible presence of carboxylate clusters is not the main reason for the observed results.<sup>#</sup> The results may rather be explained by the high aspect ratio of the fibre latex **F1**, which suggests the formation of a quasi-percolating network of glassy PS fibres, which would be in turn responsible for the observed amplification of the modulus increase.

In order to test the robustness and versatility of the approach, we prepared a third series of films in alkaline conditions using a home-made soft acrylic latex (matrix latex 2 in the SI). Compared to the first soft latex, this latex possessed a slightly higher AA content (2.9 wt%, compared to 1.9 wt% in latex 1), and a gel fraction of 55%. The resulting blanc film was thus much less extensible ( $\epsilon_B < 7$ ) than the blanc films prepared with latex 1. The results of the mechanical tests are summarized in Table SI-2 in the Supporting Information. Again, the use of fibres instead of spheres increased the Young's modulus by a factor of 2.3 and 5.2 (instead of 1.4 and 2.8, for 5

and 10 wt% additive respectively). This amplification of the reinforcement suggests again the formation of a network by the fibres and demonstrates the robustness of the approach.



**Figure 3. Evolution of the films' Young's modulus with increasing amount of additive, at pH 12 (■ = fibres, ● = spheres) and pH 5.5 (□ = fibres, ○ = spheres).**

Finally, to further illustrate the potential of this new class of latex blend materials, a creep resistance experiment was performed (using a constant load of 10 g) with sample Film5%F-pH5.5 containing only 5 wt% of fibres and compared to the reference sample (Film-pH5.5) without additive and prepared at the same pH (pH = 5.5). As demonstrated in Figure SI-5, the film containing the fibres was hardly extended and broke only after 5h 30 min whereas the reference film failed after 1h in the same conditions.

## Conclusions

PISA is nowadays recognized as an efficient and valuable approach to synthesize nanofibres made of amphiphilic block copolymers, in high solids contents, in water. In this communication, we demonstrated for the first time the potential of as-prepared high Tg nanofibres as reinforcing fillers for soft acrylic water-based coatings. The composite materials were prepared from simple mixtures of a soft standard acrylic latex to which high Tg fibres were simply added as an aqueous dispersion. Comparison with a reference material reinforced with the spherical counterparts suggests that the high aspect ratio of the fibre-type fillers allows the formation of a reinforcing network of glassy nanofibres, which is responsible for the observed increased stiffness of the materials, while maintaining a high extensibility. This new approach is expected to pave the way to a new class of water-based coatings, that are environmental friendly (synthesis is exclusively water-based, no VOC additives) and simple to prepare (simple mixing process). In a future systematic study we will investigate the influence of the fibre length and diameter, as well as the nature of the core and shell polymer, in order to reduce the amount of additive.

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## Notes and references

‡ For further details see Table SI-1

§ If there is failure, it occurs at the clamp.

# In addition, Figure 3 shows that the relative increase of the modulus from spherical filler to filamentary filler is similar at pH 12 and at pH 5.5, although the proportion of carboxylate groups is much lower at the lower pH.<sup>21</sup>

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