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Enhanced oil removal from water in oil stable emulsions using electrospun nanocomposite fiber mats

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Supporting information

S.I-1 Mechanical properties of PMMA/PCL nanocomposite fibrous mats

Figure S.I-1 shows two representative stress-strain curves of PMMA/PCL mats at polycaprolactone concentrations of 30 wt.% and 70 wt.%. In both samples, when no stress is applied the fibers in the mats are randomly oriented (see inset). As the samples are strained, the fibers arrange their orientation along the direction of the external load. The elongation increases slowly with the applied load, indicating a high resistance of the fibrous mats to deformation. At this point, two different behaviors can be noticed. Specifically, in the curve of the mats with 70% PCL, the elongation increases rapidly with the increase of the load. In this region, the fibers become increasingly thinner with the stretching of the sample. After reaching the maximum tensile strength, a further increase in deformation leads to the gradual breaking of the fibers, corresponding to a gradual decrease in the curve. On the other hand, in the curves of sample with 30% PCL, the fiber thinning is not present. Thus, the fibers break after they are aligned along the direction of the load.

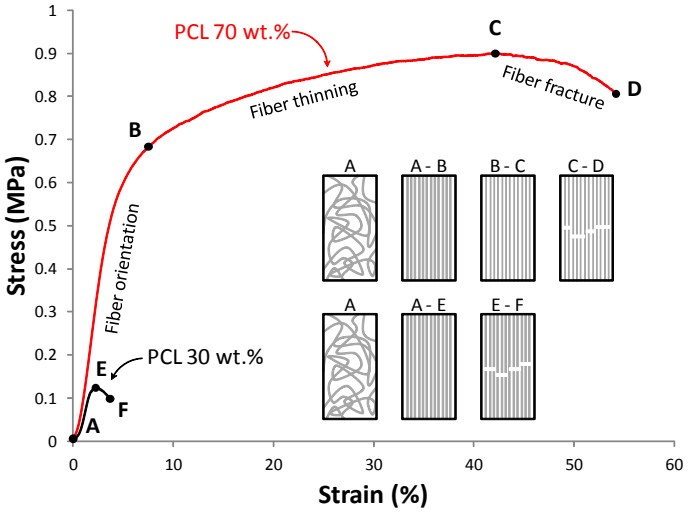

Figure S.I-1 Representative stress-strain curves of PMMA/PCL mats at polycaprolactone concentration of 30 wt.% and 70 wt.%. The inset depicts the response of the fibers in the mats at the external load.

S.I-2. Porosity of the fibrous mats

As shown in Table S.I-1, the porosity of the fiber mats presents no significant differences between the pure polymer fibers and the different blends formed (about 0.80), apart from the 30/70 PMMA/PCL which has a higher porosity (0.93) probably related to the non-homogenous size distribution of the fibers. It should be mentioned that the porosity of the PMMA was measured at the pressed mats since, as discussed in the experimental part, these were the ones utilized for the emulsions separation experiments. Porosity is an important characteristic of the material, indicative of the oil absorption capacity, as it is related to the space available for oil storage between fibers (assuming that the oil does not induce swelling of the individual fibers)[1], and therefore it should be expected that all the mats present similar oil absorption capacities.

Table S.I-1 Porosity of the fiber mats.

Fibers	Porosity (V_f)
PCL	0.81 ± 0.01
PMMA	0.80 ± 0.02
70/30 PMMA/PCL	0.79 ± 0.05
50/50 PMMA/PCL	0.80 ± 0.07
30/70 PMMA/PCL	0.93 ± 0.08
SNP/PMMA/PCL with 1wt.%	0.76 ± 0.02

In particular, the theoretical maximum oil absorption capacity (C^t_{max}) can be estimated from the porosity (V_f) and the densities of the oil (ρ_{oil}) and foam (ρ_{foam}) using Equation S.1[1].

$$C_{max}^{\ t} = V_f \cdot \frac{\rho_{oil}}{\rho_f} \qquad [S.1]$$

According to that, these fiber mats should present maximum oil absorption capacities between 2.5-6.0 g/g, much lower than those of most of the fiber mats presented in this work. Therefore, the achievement of most of the experimental oil absorption capacities obtained should be related to a modification of the three-dimensional structure of the fiber mats upon interaction with the oil during the absorption tests (Figure S.I-2).

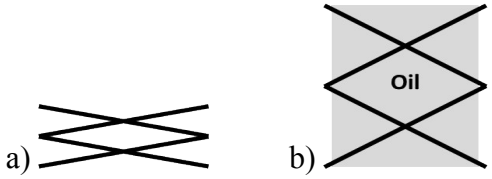

Figure S.I-2 Scheme of (a) the three-dimensional structure of the dry fiber mats, and (b) the three-dimensional structure of the wet fiber mats.

Then, with the aim to prove this hypothesis, the geometrical volume of the fiber mats samples before and after being dipped into the oil was measured and compared.

It was found that both PCL and 30/70 PMMA/PCL fiber mats present a negligible or quite small volume change, which corresponds to the rather good agreement between the oil absorption theoretical and experimental values (PCL: C^t_{max} = 3.1 g/g, C_{max} = 3.8 g/g; 30/70 PMMA/PCL: C^t_{max} = 6.8 g/g, C_{max} = 10.0 g/g). On the contrary, PMMA, 70/30 and 50/50 PMMA/PCL, and SPN/PMMA/PCL 1 wt.% present a volume increase of at least 3 times (during the manipulation and measuring these samples lost a significant amount of oil, and therefore the measured volume expansion should be considered just as a lower limit). Therefore, it was proved that the fiber mats presenting the highest oil absorption capacities present a modification of their three-dimensional structure during the oil absorption (i.e., volume of the wet fiber mats > volume of the dry fiber mats).

S.I-3 Emulsion stability

The performance of the oil removal using PMMA/PCL and SNP/PMMA/PCL fibers were realized from stable emulsions. Initially, different water in oil emulsions were formed (10-30-50-80 v.% of oil) using Span80 as an emulsifier. The absorption capacity was calculated after the fibers were 15 minutes dipped into the stable emulsions, but the emulsion stability was analyzed during 60 min.

In the previous work stability until 30 v.% was proved[2]. As shown in Figure S.I-3, presented 50 v.% water in oil emulsions, there are no significant changes in the diameter or number of the formed droplets at different times after the emulsion preparation. Moreover, by the direct observation of the emulsion micrographs provided in Figure S.I-3, it can be confirmed that the emulsions show an excellent stability up to 60 minutes. On the contrary, it was found that without Span80 the demulsification starts after 10 min, being possible to observe the phase separation in a macroscopic scale. Figure S.I-4 shows the evolution of 80 v.% emulsion, but in this case, the micrographs present a completely different aspect. It was not possible to identify the individual drops, but also not significant changes or demulsification was found after 60 minutes. Therefore, it was proved that all the emulsions stabilized using Span80 present no changes or phase separation after 60 minutes.

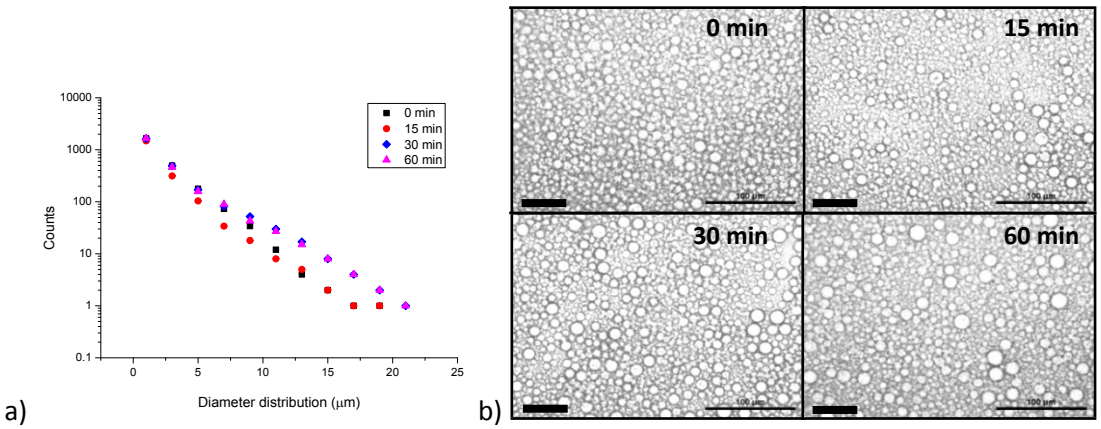

Figure S.I-3 (a) Drop diameter distribution evolution of 50 v.% water in oil emulsion, (b) sequence of optical micrographs of the emulsion at times from 0 to 60 minutes after the emulsion preparation (scale bar corresponds to 100 μm for all the micrographs).

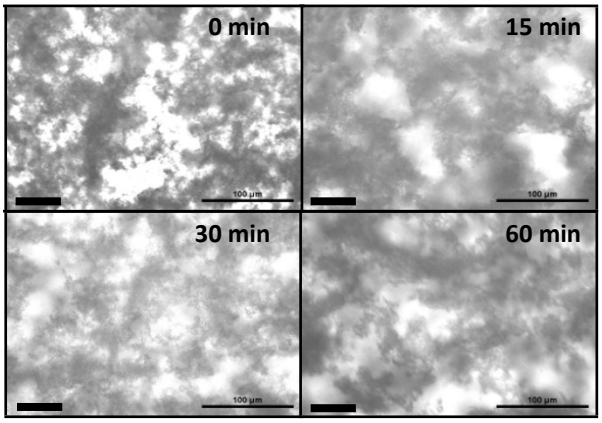

Figure S.I-4. Sequence of optical micrographs of the 80 v.% water in oil emulsion at times from 0 to 60 minutes after the emulsion preparation emulsion, (scale bar corresponds to 100 μm for all the micrographs).

S.I-4 Mechanical properties of fibrous mats

Nanocomposite fibers (SPN/PMMA/PCL) were fabricated by electrospinning, a well-known and effective technique for the production of fibers with diameters ranging from micrometers to nanometers with controllable compositions and structures[3] [4]. Two different concentrations 1 and 2 wt.% (with respect to the polymer) of AEROSIL® R 812 nanoparticles (SNPs) were incorporated into the 50/50 wt.% PMMA/PCL (Poly(methyl methacrylate/Polycaprolactone) solution.

Young's modulus of the 50/50 PMMA/PCL and SPN/PMMA/PCL at different SNPs concentration is shown in Figure S.I-5. It was found a decrease of the modulus with the increase of the amount of SNPs.

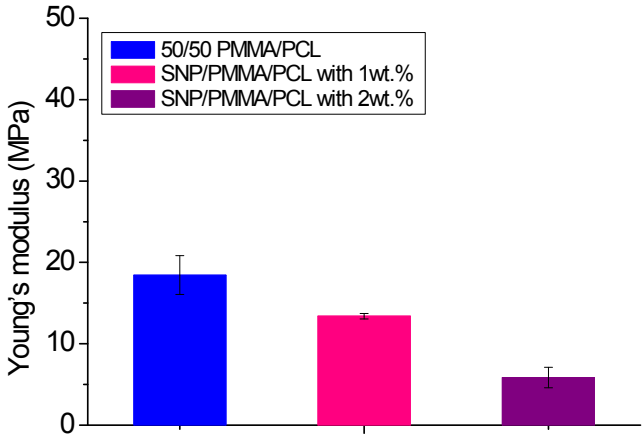

Figure S.I-5 Young's modulus of 50/50 PMMA/PCL and SNP/PMMA/PCL.

The mechanical properties of SPPFbs are summarized in Table S.I-4.1 Nonetheless the similar morphology, the mechanical properties of the nanocomposite fibers are affected by the SNPs, decreasing Young's modulus when increasing the content of SNPs, in about 5 and 13 MPa with respect to the 50/50 PMMA/PCL for 1 and 2 wt.% contents of SNPs, respectively. It should be noticed that in the case of the SPPFbs with 2 wt.% of SNPs the Young's modulus reaches similar values than the initial PMMA fibers. On the other hand, SPN/PMMA/PCL with 1 wt.% of SNPs present an enhancement of the UTS (0.51 instead of 0.26 MPa), and similar elongation at maximum load, which makes these fibers still suitable for their application in the oil removal from emulsions with high oil contents. However, further increase of the amount of SNPs (SPN/PMMA/PCL with 2 wt.% of SNPs) present no increase of the UTS and leads to a decrease of elongation at maximum load (Table S.I-2). As a consequence of the overall reduction of the mechanical properties due to the addition of the 2 wt.% of SNPs it was found that the SPN/PMMA/PCL with 2 wt.% of SNPs showed some fibers breakage/dispersion during the oil absorption tests, being discarded for further study about their use in the water in oil emulsions.

Table S.I-2 Mechanical properties of SNP/PMMA/PCL.

Material	Young's modulus (MPa)	UTS (MPa)	Elongation at maximum load (%)
SNP/PMMA/PCL with 1 wt.%	13.39±1.83	0.51±0.09	27.40±6.50
SNP/PMMA/PCL with 2 wt.%	5.84±1.26	0.24±0.03	13.00±3.20

S.I-5 Reusability of Fibers

The fibrous mats can be used 3 to 4 times, after which their oil absorption capacity is reduced to about one third with respect to the initial one. The water absorption capacity remains stable and always very low as it can be seen in the figure below. After each absorption cycle the fibers were recovered by a two-step procedure. First, the fibers were mechanically squeezed to remove the absorbed oil between them.

Secondly, the fibers were washed with ethanol to remove the remaining oil on the surface of the fibers. Once the fibers were dry, they were employed on a new absorption test.

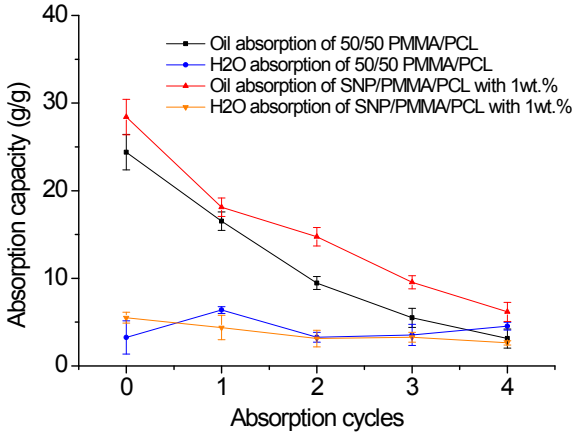

Figure S.I-6 Absorption cycles of 50/50 PMMA/PCL and SNP/PMMA/PCL with 1 wt.%.

It should be noted that most of the absorbed oil can be recovered by simple mechanical squeezing, but this mechanical compression can be responsible for the loss in the absorption capacity of the mats in the subsequent cycles, since the mats cannot recover to their initial configuration. This behavior is expected since the Young modulus of the prepared mats is very low, varying from 5 to 30 MPa.

References

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