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MECHANICAL BEHAVIOR OF PIEZOELECTRIC NANOMEMBRANES DOPED WITH CARBON NANOTUBES

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Abstract. *Piezoelectric materials are attractive to industry due to its unique property of energy harvesting. However, a less explored characteristic is equally important, i.e. the possibility of being used as sensor/actuators. The limitations are frequently associated to the brittle behavior of such materials. Noticed that most of piezoelectric materials available into the market is based on ceramic compounds. In recent years, a new class of piezoelectric materials called piezo-polymers is gaining more attention. These polymers have semi-crystalline structures and the piezoelectric phase formation is, in general, induced by large deformations. This paper deals with three different piezo-polymers, i.e. PVDF (Poly vinylidene fluoride), PVDF-HFP), PVDF-HFP (Poly vinylidene fluoride-co-hexafluoropropylene) and PVDF-TrFE (polyvinyledene difluoride-trifluoroethylene). To be able to induce the beta phase formation, which is responsible to the piezoelectric behavior, the electrospinning technique was applied. Moreover, multi-walled carbon nanotubes were also added to these piezo-polymers during the nanofibers synthesis. The fiber diameters ranged from sub-micron (around 400 nm) to nanometers (approximately 100 nm). The PVDF-TrFE nanomembranes lead to a bead-less formation, while for PVDF and PVDF-HFP nanomembranes a large number of beads were observed. Furthermore, the beads morphology were also affected by the carbon nanotubes concentration and the usage or not of surfactants (in this case SDBS - Sodium dodecyl benzene sulfonate). Infrared Fourier Transform spectroscopy (FTIR) analysis spotted beta phase formation between 78% and 95%. Tensile test on these nanomembranes revealed a non-linear behavior and a correlation between piezoelectricity/beta phase formation and its mechanical response to loadings.*

Keywords: *piezoelectricity, nanomembranes, PVdF, carbon nanotubes, FTIR analysis.*

1. INTRODUCTION

From the thin films and nanomembranes perspective, the technology applied to polymers has being evolving continuously. From the large variety of polymeric matrices available now-a-days, one class is gain much attention. According to Kang and Cao (2014), Poly (vinylidene fluoride) (PVdF) and its co-polymers (PVdF-HFP and PVdF-TrFE) have high mechanical strength, good chemical and aging resistance and thermal stability. As discussed by Chen et al (2016), Poly (vinylidene fluoride) (PVDF) and its co-polymers Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) and Poly(vinylidene fluoride-trifluoroethylene (PVDF-TrFE) have been widely investigated due to their advantages, such as flexibility, low cost and long-term stability. These polymers form the basis for a new class of technology, the so called wearable devices. According to Hwang et al (2015), PVDF and its co-polymers thin films can be employed as sensors and energy harvesting for biomedical devices, such as a new generation of pacemakers. The limitation of such thin film is its mechanical strength. To solve this problem, Park et al (2016) enveloped these thin films using PDMS films. The flexible wearable “sandwich” device can be used as a sensor. To be able to improve even more these devices the phase change mechanism must be controlled accurately. The PVDF crystalline phase formation is due to different chain configurations is the key issue to understand the piezoelectric behavior. Among the five different phases formation (α, β, δ, γ and ε), the polar β phase is the only one with strong piezoelectric behavior. This phase formation can be induce by non-polar α phase, which is the most stable one, transformation by stretching or blending with nanofillers. According to Cauda et al (2015), piezoelectric polymeric nanofibers can also be obtained by electrospinning. The advantage of this technique is its simplicity and the possibility of make it scalable. The electric field, in general between 20-50 KV, applied to a cone containing the polymeric solution, generated an electric force which push the polymeric solution through the needle and deposited on a grounded substrate. The strong mechanical stretching and electrical poling during the electrospinning process align the dipoles of the nanofiber crystal. In the case of the PVDF polymer, as discussed by Cauda et al (2015), α phase has its dipoles oriented and it is transformed to β phase. Martins et al (2014), however, explained the increase on β phase by the electrospinning jet high stretching ratio, which can be compared to uniaxial mechanical stretching. Cui et al (2014) also commented that although the electrospinning technique can lead to polar phase formation, in special the β one, the "stretching effect" is dependent of operational parameters, i.e. applied voltage, gap needle-tip/target, polymeric solution concentration and its flow rate. To improve the piezoelectricity behavior of electrospun PVDF nanomembranes, some researchers, e.g. Dhakras et al (2012), Staudinger et al (2017), Yuan et al (2016) and Lee et al (2017), proposed the addition of nanoparticles to the polymeric solution before the electrospinning process. Dhakras et al (2012) suggested the usage of nickel chloride hexahydrate ($NiCl_2 .6H_2O$). They claimed to be able to improve non-polar β phase formation by 30%, but by reproducing their experiment we were not able to obtain the results reported. In fact, no improved was observed. Staudinger et al (2017) pointed out the excellent electrical properties of carbon nanotubes. Therefore, small quantities of CNT are required to change the solution electric conductivity, which affect the electrical pull-out force created. The same idea was proposed by Yuan et al (2016) but instead of using CNT they employed graphene. Moreover, according to them, the graphene addition to PVDF solution can act as nucleation sites making the crystallinity to increase. The PVDF crystallinity can also be affected by different nanoparticles. Lopes et al (2013), for example, investigated the effect of MMT on PVDF phase formation. They claimed that MMT were responsible to the decrease on crystallization time, however, the phase changed induce was from α phase to δ phase. Unfortunately, the piezoelectric behavior of δ phase is not enough to improve piezoelectricity behavior. The MMT addition, however, promoted an increase on mechanical properties as reported by He et al (2017). Lee et al (2017) demonstrated that although nanostructures/nanoparticles can be used to improved piezoelectric behavior of PVDF and its co-polymer, they also affect fibers' morphology and consequently density and surface tension. Therefore, wettability can be another parameter to evaluate these nanomembranes.

This paper investigates the effect of carbon nanotubes into piezoelectric behavior of PVDF based nanomembranes. A morphological analysis is made to correlate the β phase formation, the polymer crystallization and its mechanical properties.

2. MATERIALS AND EXPERIMENTS

The nanomembranes were prepared using electrospinning technique. As discussed by Avila et al (2014), the nanofibers morphology and spatial deposition is highly dependent of the electrospinning operational parameters. After a series of tests, based on a design of experiment matrix (Montgomery, 2014), the following parameters were obtained: the applied voltage was 25 KV, the flow rate was around 0.01 ml/h, the gap between needle tip and target was 20 cm, and the deposition time was around 3 hours. The solutions electrospun were listed in Table I. All nanomembranes were electrospun using the same electrospinning parameters. The CNT/SDBS ratio was $5x10^{-5}$(m/m).

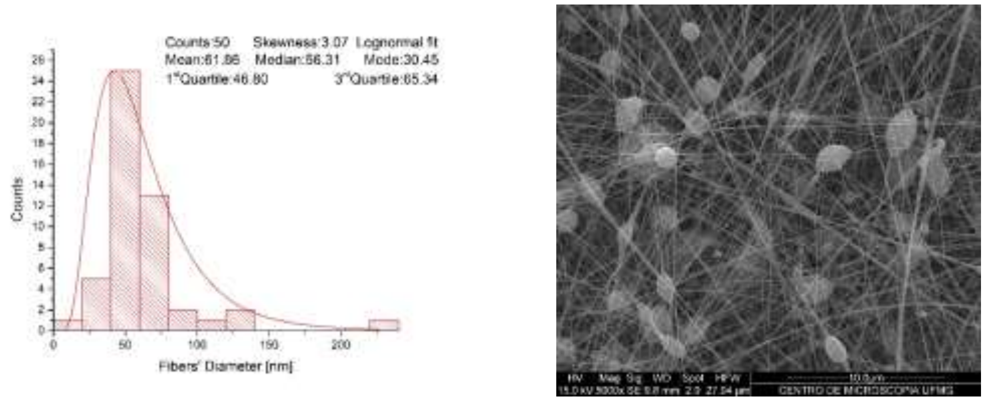
Table I. Summary of experiments

	Group ID		
	PVDF	***PVDF-HFP***	***PVDF-TrFE***
Baseline sample	*1*	*8*	*15*
0.15 % m/m CNT	*2*	*9*	*16*
0.15 % m/m CNT+SDBS	*3*	*10*	*17*
0.30 % m/m CNT	*4*	*11*	*18*
0.30 % m/m CNT+SDBS	*5*	*12*	*19*
0.60 % m/m CNT	*6*	*13*	*20*
0.60 % m/m CNT+SDBS	*7*	*14*	*21*

The morphology analysis was made using a high resolution scanning microscopy (HRSEM) Quanta 200 FEI. The water contact angle, fiber diameter and nanomembrane density were measured using ImageJ (Schindelin et al, 2015), a public domain code developed by NHI. As suggested by Baniasadi et al (2017), the β phase formation was evaluated by Fourier Transformed Infrared Analysis (FTIR) using a Shimadzu IRAffinity-1 spectrometer with resolution of 4 cm^{-1} and wavelength 600-4000 cm^{-1}. Finally, the tensile tests were performed following ASTM D882 (2012).

3. DATA ANALYSIS

Data analysis can be divided into two different levels. The first one is based on fiber morphology, while the second one is focuses on β phase formation. As it can observed in Figure 1A-G show the PVDF nanomembranes' morphology and diameter distribution. As it can be observed, the bead formation is in all groups from #1 to #7. The bead morphology is close to an ellipsoid that, can be an indication of a non-uniform traction force into the needle. Group #5 is virtually bead free, which as described by Ramakrishna et al [17], it is an indication of a uniform electric field and traction force. When a statistical analysis is performed into the fibers' diameter distribution, again the 0.30 group #5 is the only one with diameter statistically different (≈ 92 nm). All other diameters are around the 65 nm. The CNT addition seems to promote a decrease on bead formation, which can be translated into a stable and uniform electrical field.



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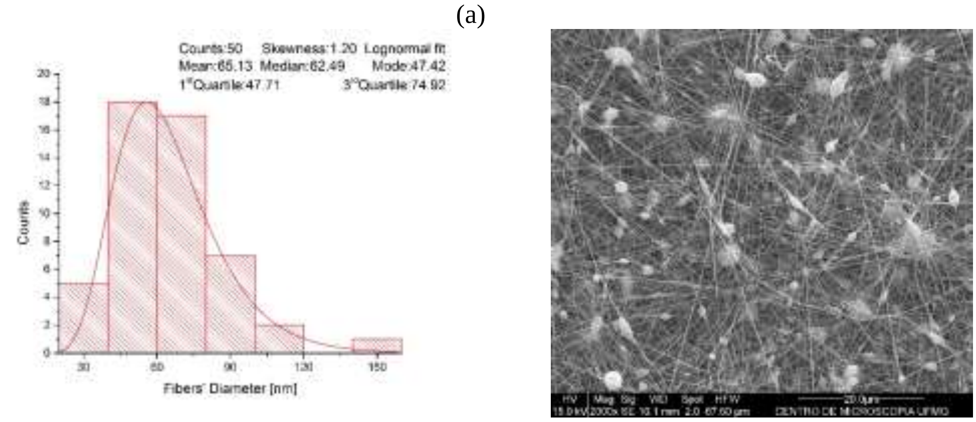

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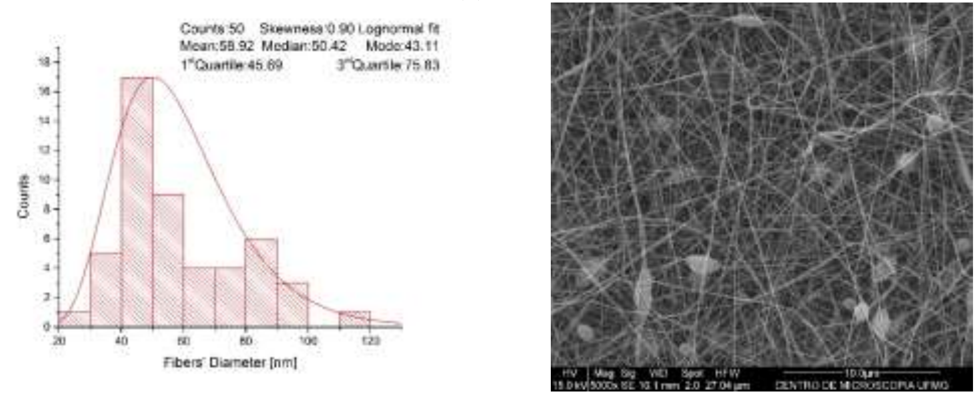
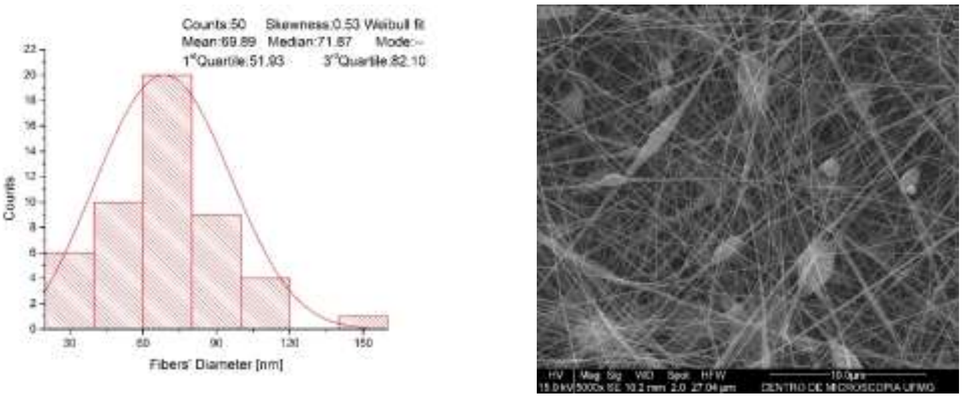
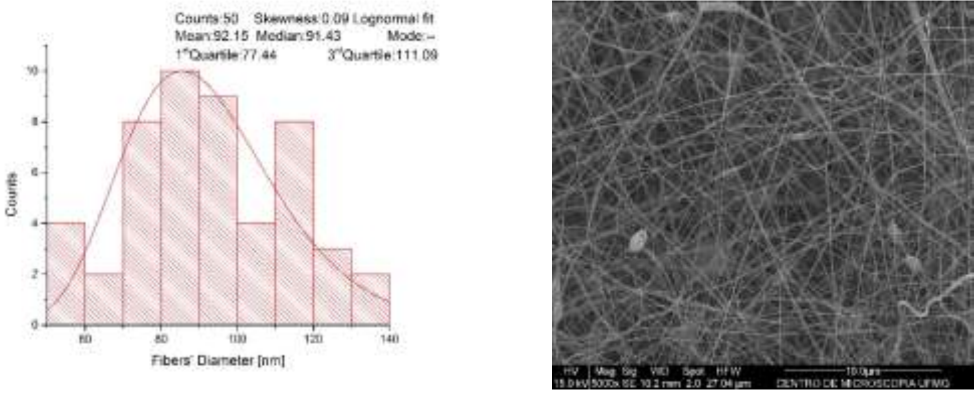


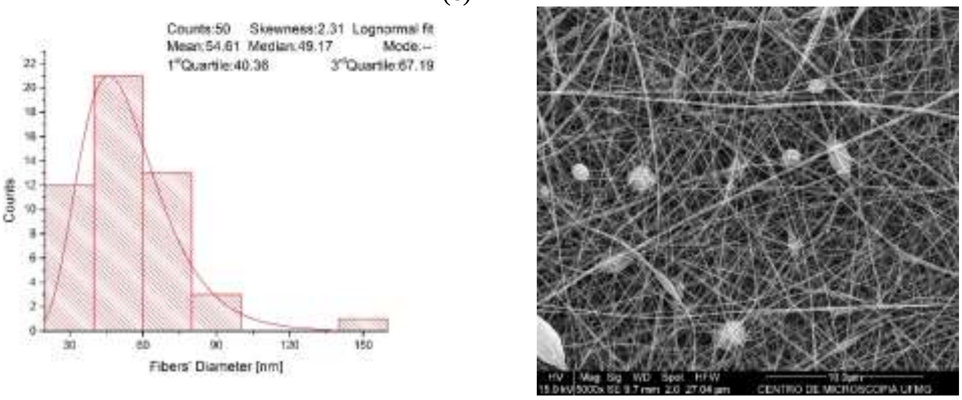
(c)



(d)



(e)



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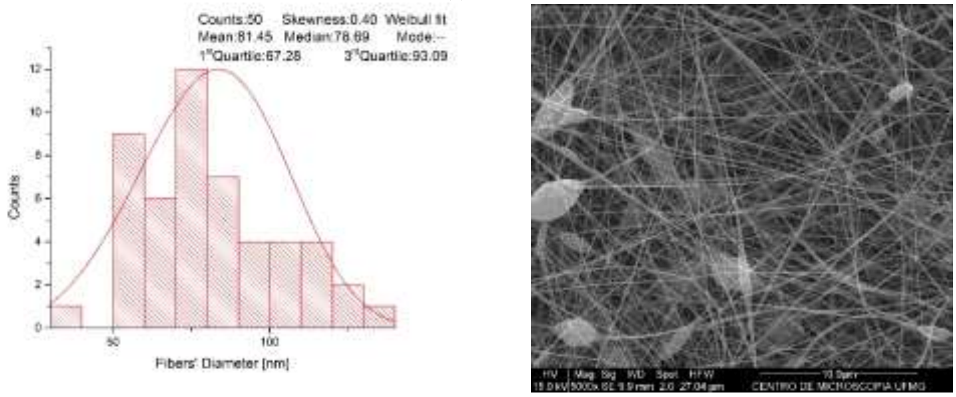
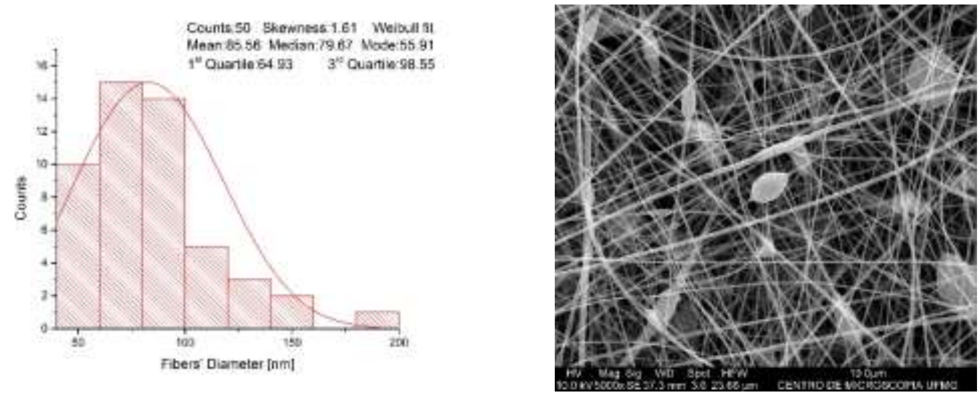


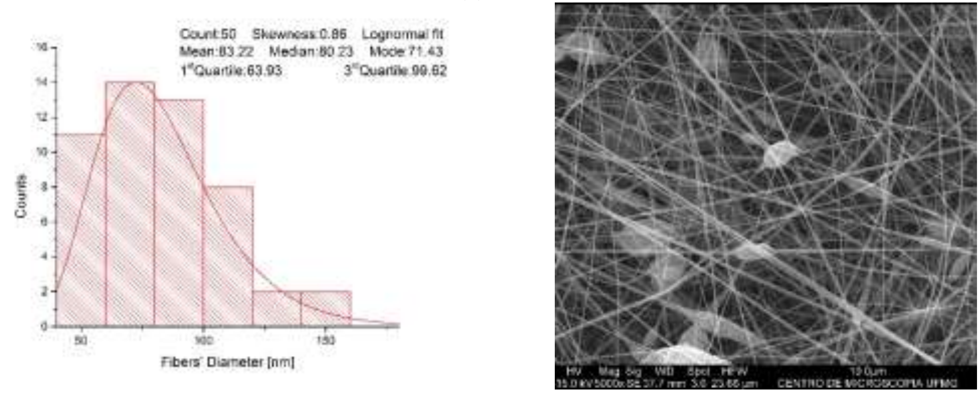
(g)

Figure 1. HRSEM observations and fiber diameter distributions for groups with PVDF: (a) #1, (b) #2, (c) #3, (d) #4, (e) #5, (f) #6, (g) #7

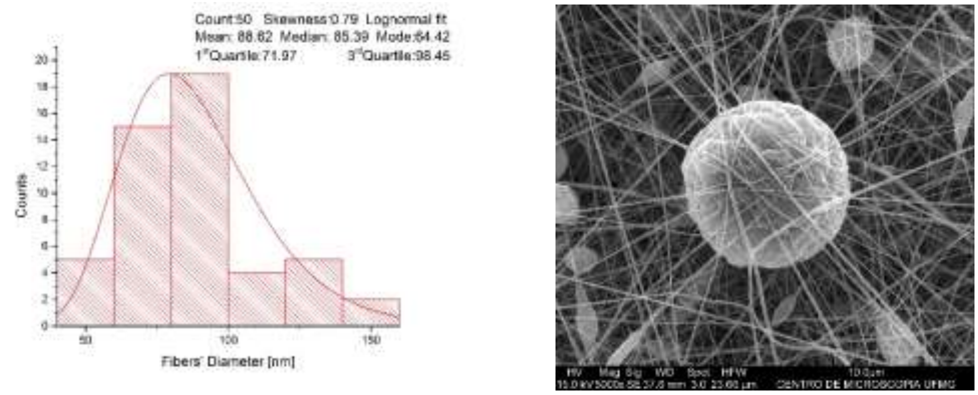
Figures 2A-G describe the fibres morphology and fibers' diameter distribution for the PVDF-HFP group.


Counts:50 Skewness:1.61 Weibull fit
Mean:85.56 Median:79.67 Mode:55.91
1st Quartile:64.93 3rd Quartile:98.55
Counts
Fibers' Diameter [nm]
0
2
4
6
8
10
12
14
16
50
100
150
200
HV Mag Sig WD Spot HFW
10.0µm
10.0 kV 5000x SE 37.3 mm 3.0 25.66 µm
CENTRO DE MICROSCOPIA UFMG

(a)


Count:50 Skewness:0.86 Lognormal fit
Mean:83.22 Median:80.23 Mode:71.43
1stQuartile:63.93 3rdQuartile:99.62
Counts
Fibers' Diameter [nm]
0
2
4
6
8
10
12
14
16
50
100
150
HV Mag Sig WD Spot HFW
10.0µm
CENTRO DE MICROSCOPIA UFMG

(b)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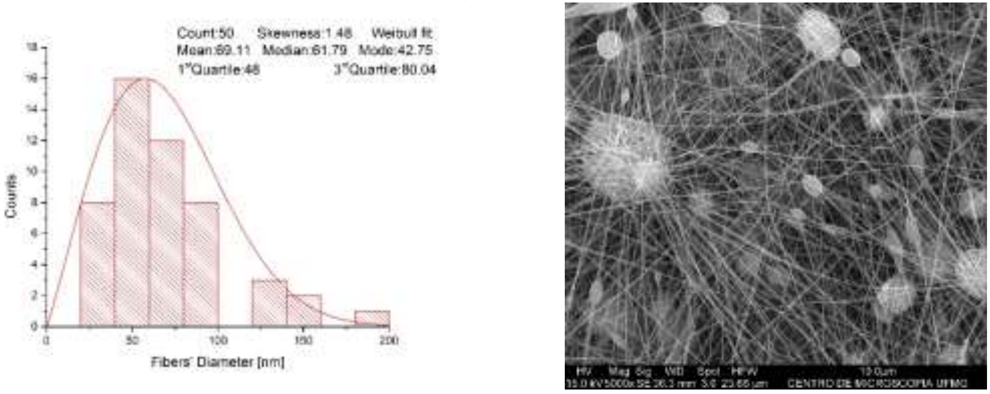
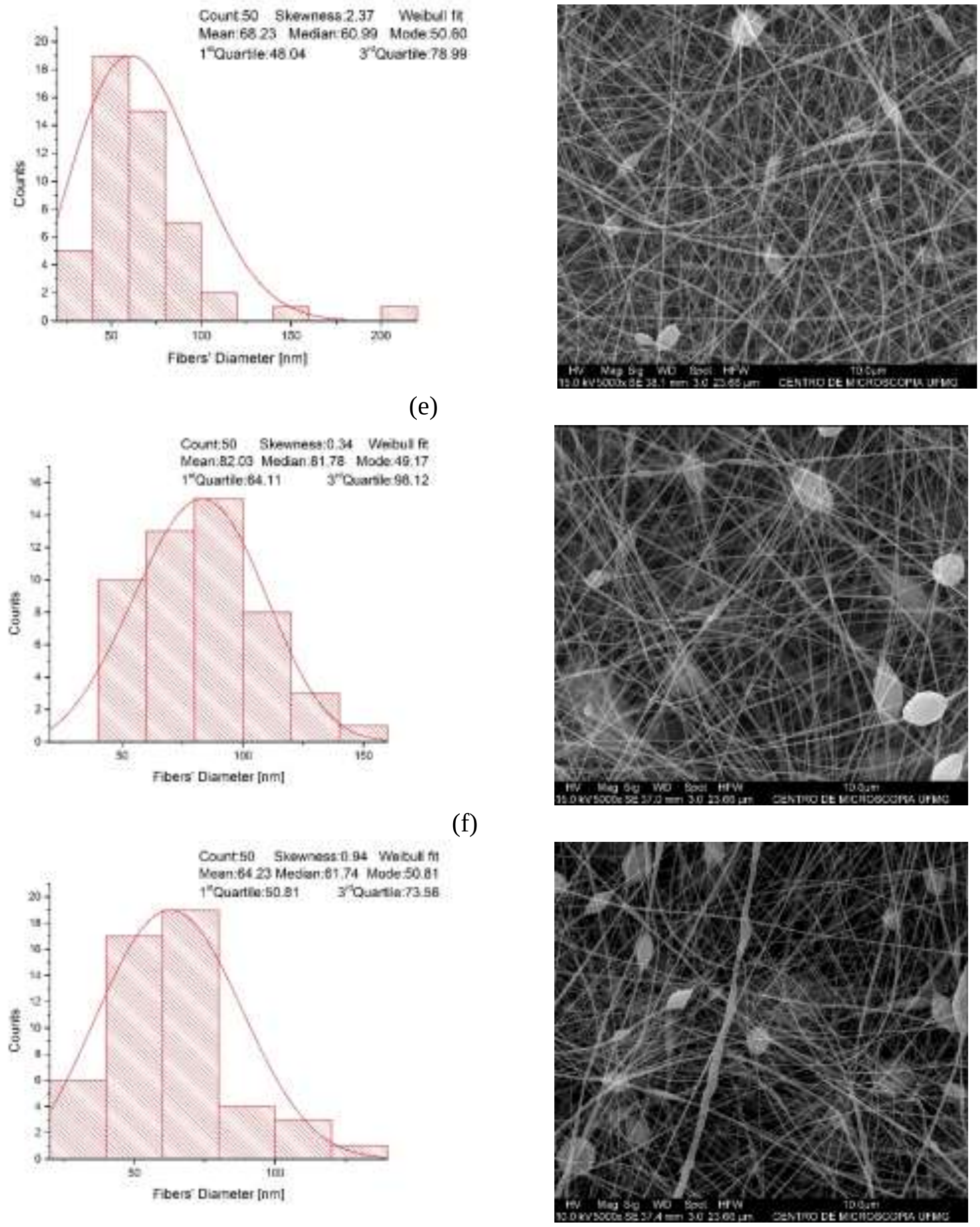
Mean: 88.62 Median: 85.39 Mode:64.42
1stQuartile:71.97 3rdQuartile:98.45
Counts
Fibers' Diameter [nm]
0
2
4
6
8
10
12
14
16
18
20
50
100
150
HV Mag Sig WD Spot HFW
10.0µm
CENTRO DE MICROSCOPIA UFMG

(c)


Count:50 Skewness:1.48 Weibull fit
Mean:69.11 Median:61.79 Mode:42.75
1stQuartile:48 3rdQuartile:80.04
Counts
Fibers' Diameter [nm]
0
2
4
6
8
10
12
14
16
18
0
50
100
150
200
HV Mag Sig WD Spot HFW
10.0µm
CENTRO DE MICROSCOPIA UFMG

(d)



(e)

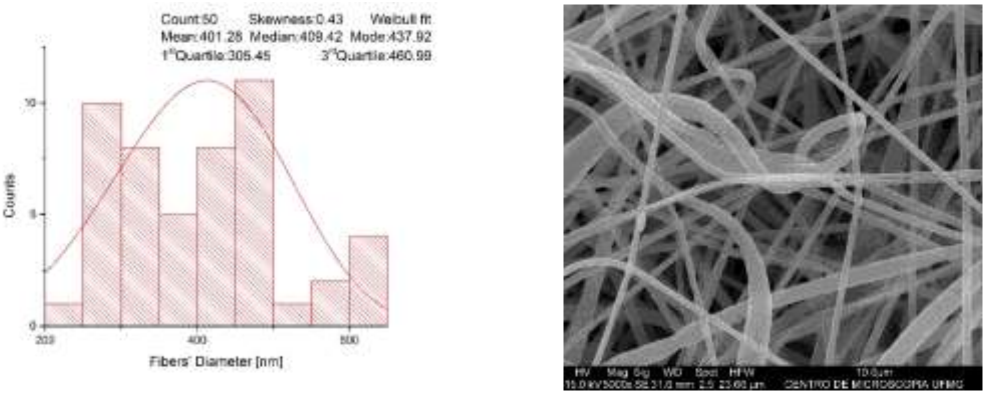
(f)

(g)

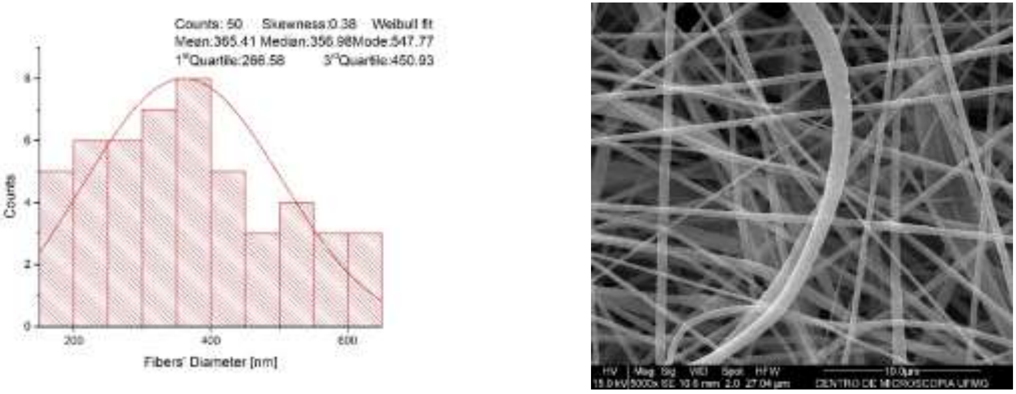
Figure 2. HRSEM observations and fiber diameter distributions for groups with PVDF-HFP: (a) #8, (b) #9, (c) #10, (d) #11, (e) #12, (f) #13, (g) #14

The nanofibers' morphology were not affected by the CNT addition. However, the CNT 0.30 % m/m lead to smaller fiber diameters around 68 nm. This is an indication of a stronger electric field influenced by the CNT electrical properties. An adverse result was observed, i.e. an increase on fiber diameter when the CNT concentration reached the 0.60 % m/m. This phenomenon can be explained by cluster formation, which lead to a non-uniform electrical field and consequently an irregular traction force. This hypothesis can be confirmed by the ellipsoidal beads formed. In all cases the fiber distributions was non-normal, which is an evidence of the fiber deposition randomness.

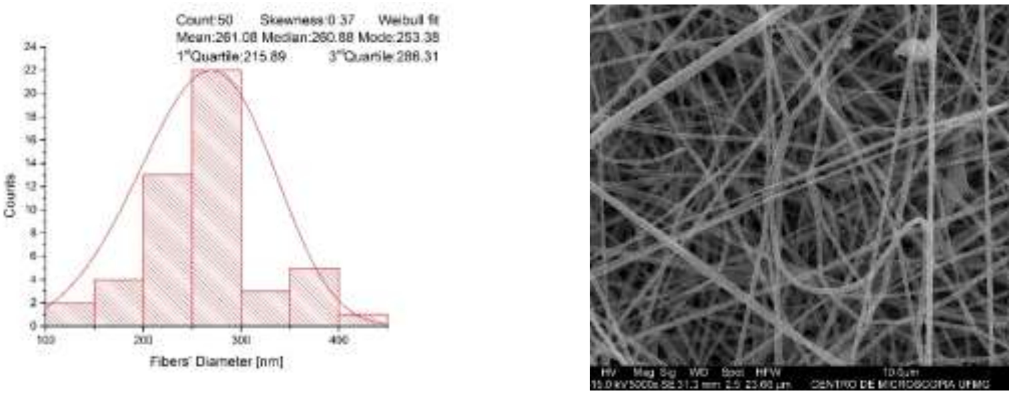
Figures 3A-G represent a summary of the most representative samples of groups made of PVDF-TrFE,


Count:50 Skewness:0.43 Weibull fit
Mean:401.28 Median:409.42 Mode:437.92
1stQuartile:305.45 3rdQuartile:460.99
Counts
Fibers' Diameter [nm]
CENTRO DE MICROSCOPIA UFMG

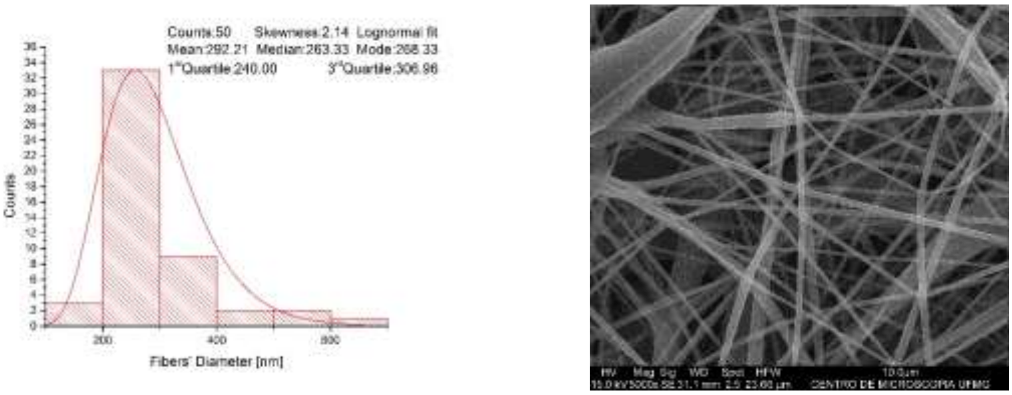
(a)


Counts: 50 Skewness:0.38 Weibull fit
Mean:365.41 Median:356.98 Mode:547.77
1stQuartile:266.58 3rdQuartile:450.93
Counts
Fibers' Diameter [nm]
CENTRO DE MICROSCOPIA UFMG

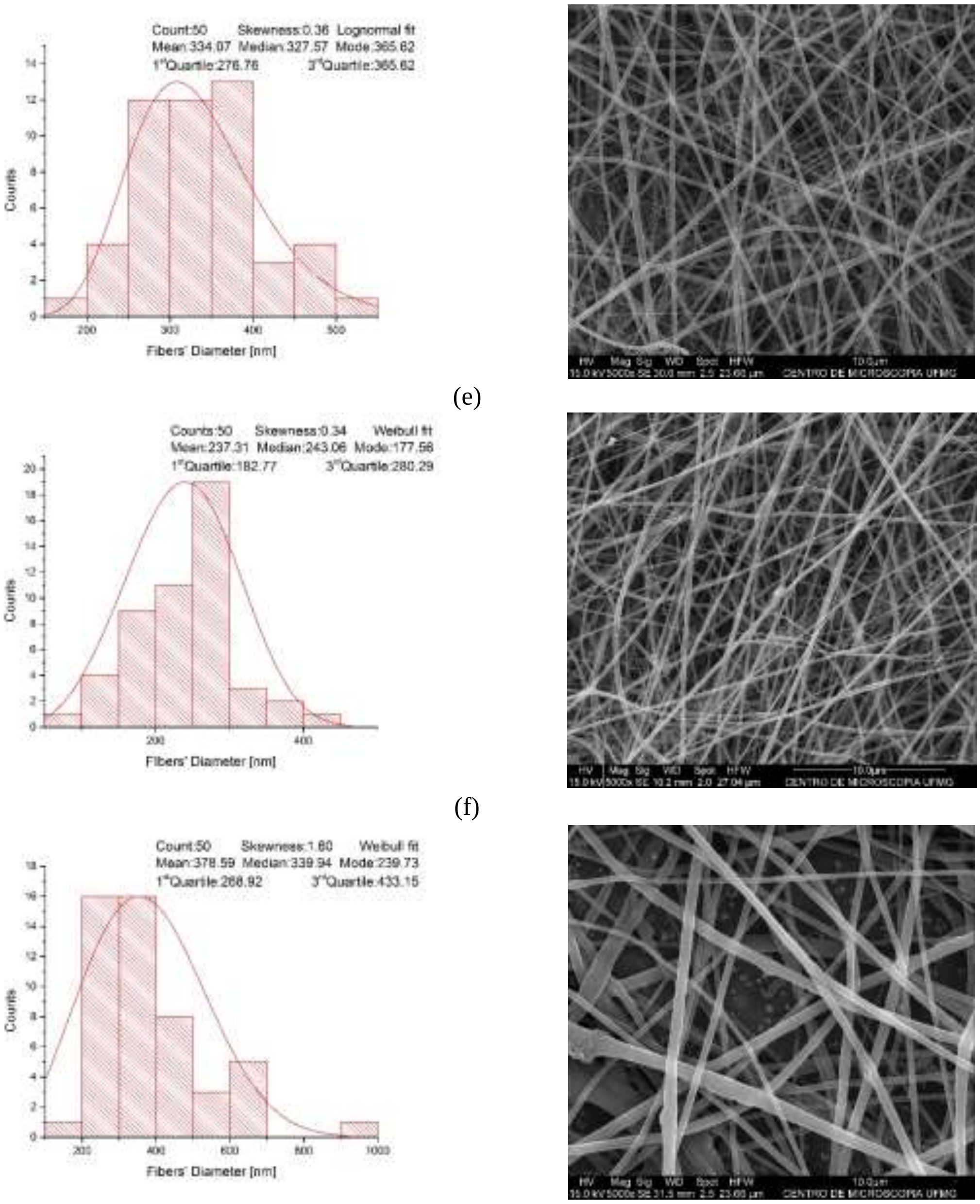
(b)


Count:50 Skewness:0.37 Weibull fit
Mean:261.08 Median:260.88 Mode:253.38
1stQuartile:215.89 3rdQuartile:286.31
Counts
Fibers' Diameter [nm]
CENTRO DE MICROSCOPIA UFMG

(c)


Counts:50 Skewness:2.14 Lognormal fit
Mean:292.21 Median:263.33 Mode:268.33
1stQuartile 240.00 3rdQuartile:306.96
Counts
Fibers' Diameter [nm]
CENTRO DE MICROSCOPIA UFMG

(d)



(e)

(f)

(g)

Figure 3. HRSEM observations and fiber diameter distributions for groups with PVDF-TrFE: (a) #15, (b) #16, (c) #17, (d) #18, (e) #19, (f) #20, (g) #21

As these groups are virtually bead free, it is possible to infer a stronger interaction between the polymer and the CNTs dispersed. However, Avila et al [13] discussed, the increase on fiber dimension seems to be an indication of a smaller traction force due to electric field. The overall conclusion is that fibers' dimension and morphology are affected by the amount of CNT dispersed. Moreover, the bead formation, shape and intensity can be related to the polymer/CNT with and without surfactant (SDBS) interactions. The SDBS may act as a bridge between the CNT and the PVDF, leading to a more stable pulling electric force and thus an increase on stretching and β phase formation. To prove this hypothesis a series of FTIR analysis were performed. The FTIR results are summarized into Table II.

As it can be noticed in Table II, to phenomena can be identified. The first one is the effect of CNT content on piezoelectric β phase crystal formation. As discussed by Kim et al (2009), the increase on this polar phase can be attributed to the rapid crystallization rate offered by the nucleating action of CNT. The second phenomenon is the saturation limit and the consequent decrease on β phase formation. This limit seems to be around 0.15% m/m. The usage of surfactant (SDBS), however somehow reversed this trend to high concentrations (0.60% m/m). This could be due to a more effective interaction CNT/SDBS and a uniform electrical field generated. Another important issue is the PVDF-TrFE behavior. As discussed by Baniasadi et al (2017), regardless of processing methods, in this co-polymer higher percentage of β phase forms because of extra TrFE co-polymer. In this case, the low β phase formation can be attributed to the insufficient stretching. This hypothesis can be confirmed when the average fiber diameter of PVDF-TrFE (≈300 nm) are compared against the PVDF (≈60 nm) and PVDF-HFP (≈ 80 nm). To solve this problem two approaches can be applied, the first one is the increase on gap and the second one the decrease on flow rate. As this research fixed the electrospinning parameters, these results are inevitable. Keeping constant all electrospinning parameters, the optimal piezoelectric nanomembrane is still an open question. As it is dependent on electrospinning operational parameters. However, the addition of CNT at concentrations of 0.15% m/m seems to serve as nucleation sites and make the β phase formation easier. However, when the CNT concentration increases the saturation limit is reached, which lead to a decrease on β phase formation. An important observation must be made, the usage of surfactants, in this case the SDBS, reverts the saturation limit allowing an increase on β phase formation. This phenomenon can be due to the interaction CNT/SDBS which reduces the cluster formations and allows a more uniform electric pulling out force throughout the needle-tip/target gap.

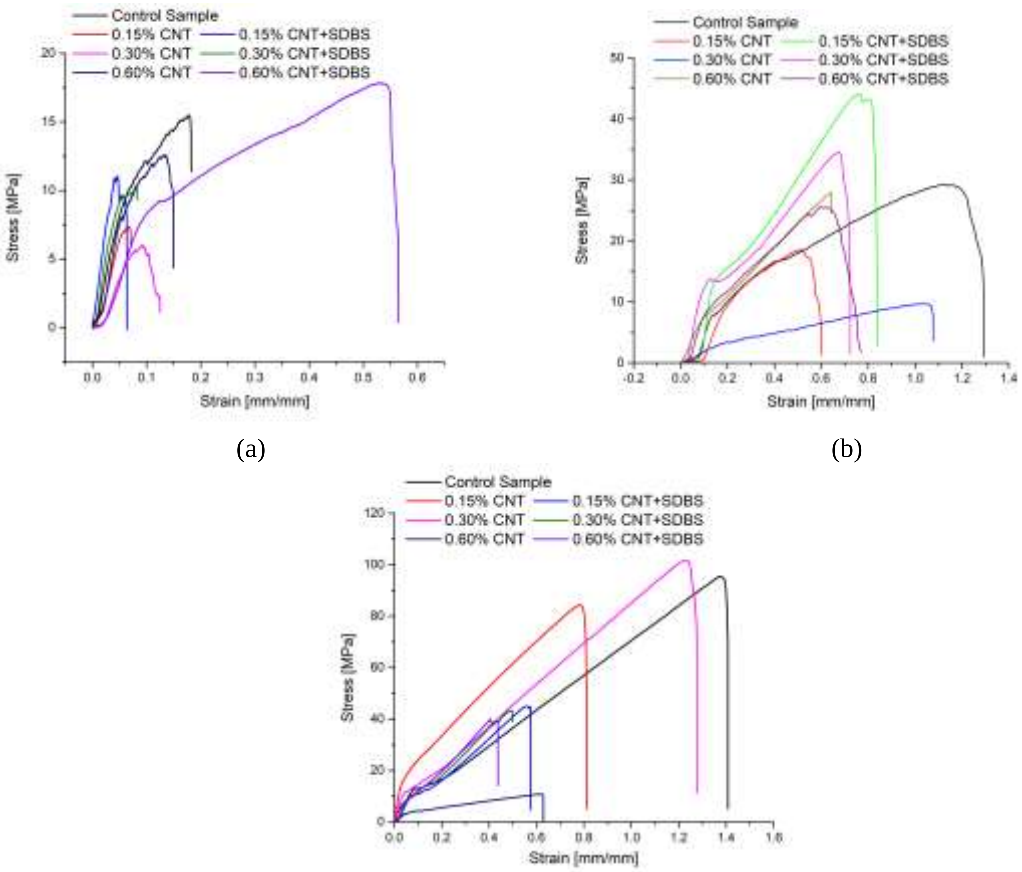
Table II. FTIR summary

	β phase formation [%]		
	PVDF	***PVDF-HFP***	***PVDF-TrFE***
Baseline sample	*0.955*	*0.833*	*0.968*
0.15 % m/m CNT	*0.959*	*0.920*	*0.743*
0.15 % m/m CNT+SDBS	*0.872*	*0.927*	*0.551*
0.30 % m/m CNT	*0.718*	*0.787*	*0.554*
0.30 % m/m CNT+SDBS	*0.848*	*0.717*	*0.838*
0.60 % m/m CNT	*0.752*	*0.734*	*0.642*
0.60 % m/m CNT+SDBS	*0.948*	*0.817*	*0.872*

The tensile tests revealed a direct influence into stiffness and strength with the addition to the CNT with and without surfactant. As discussed by Avila et al (2014) and Ramakrishna et al (2005), the addition of carbon nanotubes to the polymeric solution increase the solution overall electrical conductivity and thus the membranes' morphology. Another issue that must be addressed is the addition of co-polymers, i.e. HFP and TrFE. The interactions between these co-polymers and the polymer backbone (PVdF) lead to an increase on strength in all cases, see Figures 4A-C. For the backbone polymer (PVdF) the best mechanical results based on ultimate strength was obtained with large concentration of CNT+SDBS, while for the co-polymer (HFP) the highest ultimate strength was obtained for the 0.15% CNT. Finally, for the co-polymer with iron (TrFE) the peak stress was obtained for the 0.30% CNT. For the PVdF and PVdF-HFP, the peak stress samples were also the ones with highest β phase, which can indicated a larger capacity of sustain damage without break. For the PVdF-TrFE, however, the results were not conclusive and more tests were required.

4. CONCLUSIONS

Three piezoelectric polymers, i.e. Poly (vinylidene fluoride) (PVdF) and its co-polymers (PVdF-HFP and PVdF-TrFE), were used to investigate how the electrospinning process affects its piezoelectric behavior. To be able to improve, even more, the β phase formation, which is the phase responsible to the piezoelectric behavior, multi-walled carbon nanotubes functionalized by surfactants (SDBS) were introduced to the polymeric solution. Fiber morphology and spatial dispersion plays an important role into β phase formation. Moreover, the CNT addition to polymeric solution lead to a decrease on fiber diameter around 34% and an increase 24% into β phase formation. The SDBS effect was more effective at CNTs high concentrations (0.6% m/m), which somehow deactivate the saturation limit (≈0.15% m/m). Finally, the optimal nanomembrane configuration is highly dependent of the electrospinning operational parameters, but the CNT concentration of 0.15% m/m seems to serve as a nucleation site. The optimal piezoelectric nanomembrane is still an open question. As it is dependent on electrospinning operational parameters. However, the addition of CNT at concentrations of 0.15% m/m seems to serve as nucleation sites and make the β phase formation easier. However, when the CNT concentration increases the saturation limit is reached, which lead to a decrease on β phase formation. An important observation must be made, the usage of surfactants, in this case the SDBS, reverts the saturation limit allowing an increase on β phase formation. This phenomenon can be due to the interaction CNT/SDBS which reduces the cluster formations and allows a more uniform electric pulling out force throughout the needle-tip/target gap.



(a) (b)

(c)

Figure 4. Tensile tests. (a) PVdF; (b) PVdF-HFP; (c) PVdF-TrFE

5. ACKNOWLEDGMENTS

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