

## Vibration-Electrospinning for High-concentration Poly (butylene succinate) / chloroform Solution

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**Abstract:** Electrospinning is one of the most popular methods to produce nanofibers. It has also genuine successes in numerous applications. However, some polymer with high viscosity can not be electrospun in a satisfactory way. Poly (butylene succinate) (PBS)/ chloroform (CF) solution is used to prepare for ultrafine fibers, as the concentration of PBS/CF increases, morphology evolves from beads to ultrafine continuous fibers, and when concentration exceeds 15%, traditional electrospinning does not work satisfactorily. An ultrasonic vibration with frequency of 400kHz is then added to the mixed solution, as a result, the solution behaves like polymers for electrospinning, ultrafine PBS fibers are obtained.

**Keywords:** nanofiber, electrospinning, vibration technology, entanglement, electrospinnability.

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### I. INTRODUCTION

This work is concerned with showing the possibility of producing ultrafine fibers from solutions with high viscosity or even in gel state, which is difficult to be spun by traditional electrospinning, by vibration technology. Electrospinning is a simple but powerful method for making very thin polymer fibers [1-20], but not every polymer can be prepared for electrospinning. Generally speaking solution of polymer with too low or too high molecule weight (dilute unentangled or concentrated entangled solutions) can not be electrospun into continuous fibers [21].

Chain entanglements are one of many parameters that can significantly influence fiber formation during polymer electrospinning [22]. At polymer concentrations higher than the critical concentration, above which polymer entanglement can occur, it was found polymer fibers could be electrospun, provided the spin-dope solution was sufficiently viscous [23].

Mathew *et al.* expanded the range of this technique by making fibers from small molecules, namely phospholipids[1]. Mathew *et al.* showed that at concentrations above the onset of entanglements of the wormlike micelles, electrospun fibers were fabricated with diameters on the order of 1 to 5 micrometers[1].

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In this paper we expand its application to macromolecules, high-concentration PBS/CF solution, which can not be electrospun by traditional electrospinning, by vibration technology. Vibration-electrospinning was first suggested theoretically in Ref. [24], the novel strategy produces finer nanofibers than those obtained without vibration[25], and this paper shows that the technology can produce nanofibers which can not be done by traditional electrospinning.

## II. THEORETICAL ANALYSIS

The influence of polymer rheological behavior, concentration, viscosity, and chain entanglement on the electrospinning process has been studied by many authors [17, 18, 22, 23, 26-30]. In our previous theoretical analysis, we have the following scaling relationships [21]:

$$d \propto \eta^a, \quad (1)$$

$$\eta \propto C^b \quad (2)$$

$$\eta \propto M^c \quad (3)$$

where  $d$  is the average diameter of the electrospun fibers,  $\eta$  viscosity,  $C$  concentration,  $M$  molecular weight, the scaling exponents  $a$ ,  $b$ , and  $c$  might differ between different polymers, for example  $d \propto \eta^{1/2}$  for acrylic solution [31],  $d \propto \eta^{0.71}$  and  $d \propto C^{3.1}$  for poly (methyl methacrylate)[26],  $d \propto C^{2.7}$  for PDMAEMA-HCL (0.1wt% APS) solution[27],  $d \propto \eta^{0.8}$  and  $d \propto C^{2.6}$  for linear and branched PET-co-PEI solutions [28]. For good solvents, de Gennes[32] suggested

$$\eta \propto C^{3/(3\gamma-1)} \quad (4)$$

where  $\gamma$  is the Flory exponent (0.5 for theta solvents and 0.66 for good solvents) [26]. Colby *et al.* [33,26] predicted experimentally an even stronger viscosity dependence on concentration  $\eta \propto C^{4.8}$ .

The scaling relationships between viscosity and concentration for polyelectrolyte solutions in the semidilute unentangled, semidilute entangled, and concentrated regimes are [27]

$$\eta \propto \begin{cases} C^{0.5}, & C^* < C < C_e \\ C^{1.5}, & C_e < C < C_D \\ C^{3.75}, & C > C_D \end{cases} \quad (5)$$

where  $C_e$  is the entanglement concentration,  $C_D$  marks the onset of the concentrated regime.

The viscosity is related to molecular weight is called Mark-Houwink-Sakurada equation.

The viscosity scales allometrically with oscillation frequency [24,25]:

$$\eta \propto \omega^{-\beta} \quad (6)$$

where  $\beta$  is a scaling exponent that varies with the polymer's characteristics. For PMMA solution at 239 °C Ibar's experiment[34] showed  $\eta \propto \omega^{-2/5}$ . Our experiment [25] revealed  $\eta \propto \omega^{-7/10}$  for PAN/DMF solution, see Figs. 1 and 2.

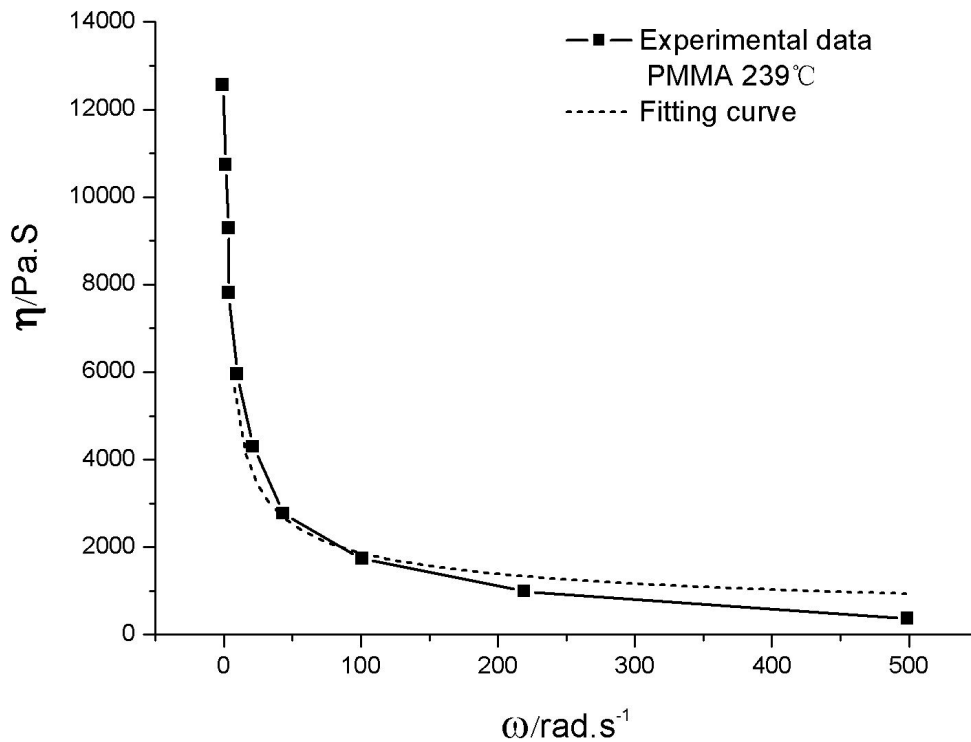


Fig.1 Solution viscosity ( $\eta$ ) of PMMA vs. the vibration frequency ( $\omega$ ) [34]

When an oscillatory shear was imposed on the polymer sample, the resulting chain orientation leads to a new environment in which the initially well-entangled chains manage to disentangle inhomogeneously[35], as a result dramatic reduction in viscosity occurs. So the oscillation leads to finer electrospun fibers than those electrospun without oscillation.

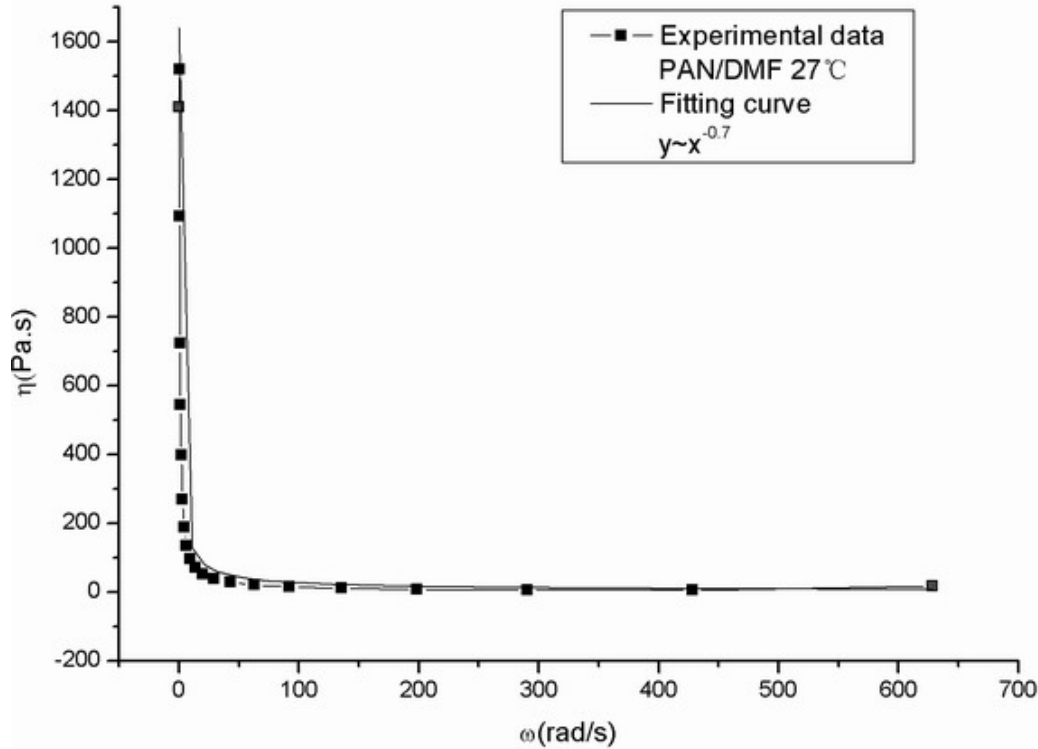


Fig.2 18%(Wt%)PAN/DMF solution viscosity via vibration frequency[25]

### III. EXPERIMENT

**Material:** Poly(butylene succinate) (PBS) with a molecular weight of 250,000 was supplied with Shanghai Institute of Organic Chemistry, CAS and chloroform was purchased from Shanghai Chemical Co..

**Instrumentation:** Ultrasonic generator SFSA-1 (Shenbo Ultrasonic Device Co. Ltd.) was used to apply ultrasonic vibration on solution at 400kHz. Electrospinning experiment was separately carried on with our set-ups shown in Fig. 3 (a and b).

PBS was dissolved in chloroform at concentration 15 wt%. The obtained solution was divided into 4 parts (solution A, solution B, solution C and solution D). Solution A was reserved under normal circumstance, solution B was taken to spin without ultrasonic vibration applied, solution C was vibrated by ultrasonic generator and then reserved under normal circumstance, solution D was taken to spin under ultrasonic vibration. After one day, solution C was turned out to be solution A.

Electrospun fiber diameter and morphology were analyzed using a JSM-5600LV Scanning Electron Microscopy (SEM). Fifty measurements on random fibers for each electrospinning condition were performed and average fiber diameters are reported.

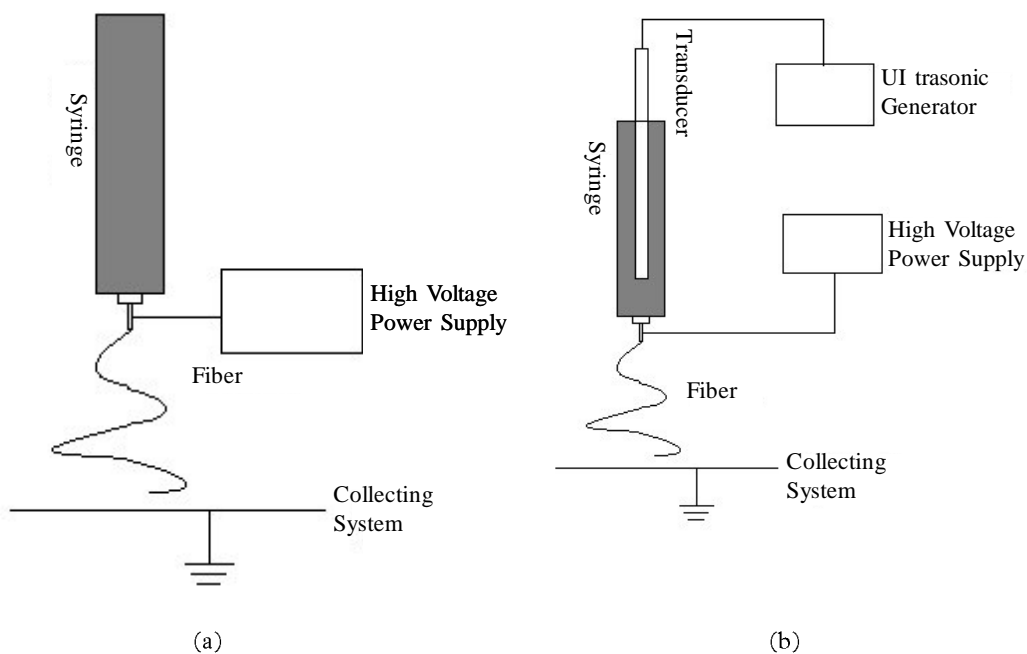


Fig. 3: Electrospinning set-up.

(a) Traditional electrospinning set-up without vibration

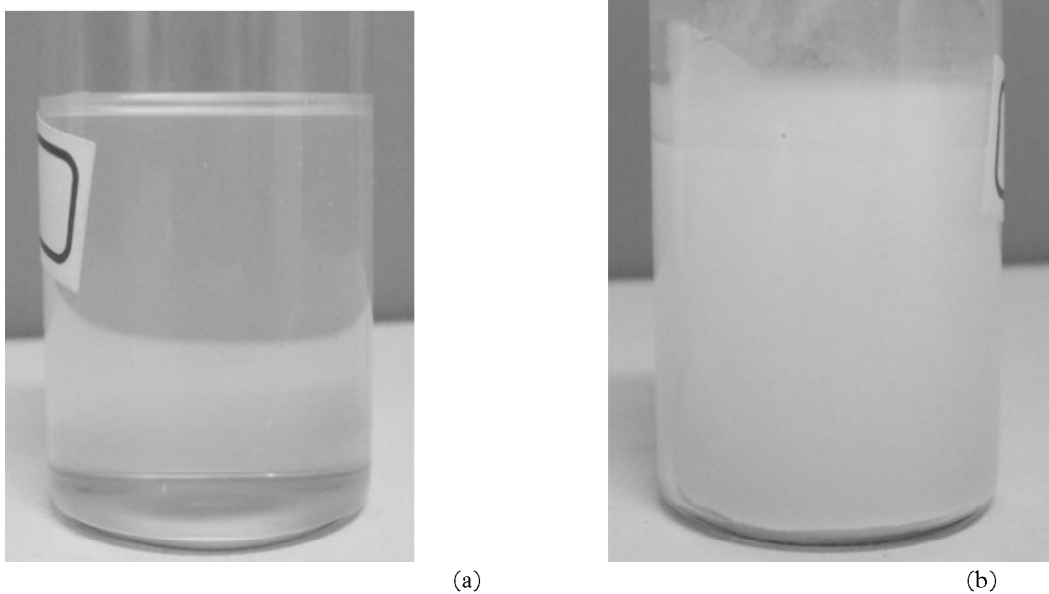
(b) vibration-electrospinning (this apparatus was patented: Wan, Y.Q., Zhang, J., He, J.H., Yu, J.Y., CHN Patent 200420020596.3, to use this principle to prepare electrospun fibers, transfer agreement must be made).

**Electrospinning Process:** The mixed solutions were placed in a 20 mL syringe. The positive lead of a high voltage power supply (F180-L; Shanghai Fudan Middle School Affiliated Factory) was connected to the 7-gauge syringe needle via an alligator clip. A grounded metal target was placed 8 cm from the needle tip. The polymer solution flowed by its gravity without an original flow rate given, and the voltage was maintained at 15 kV.

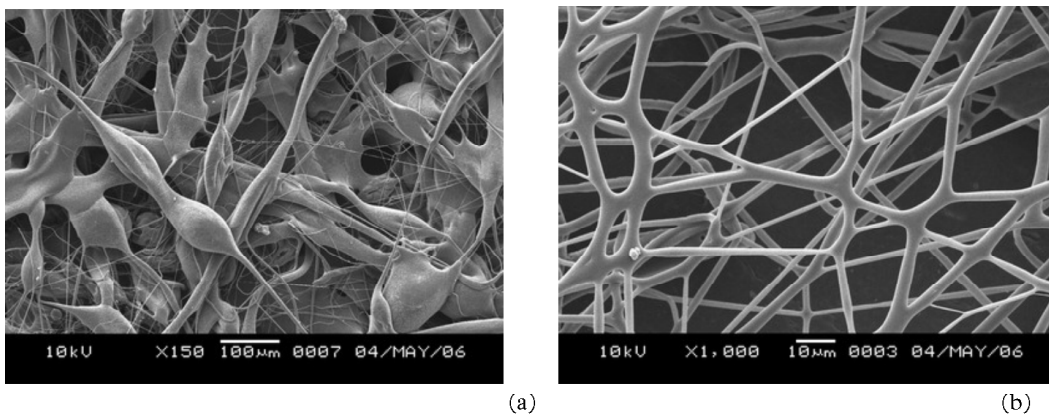
#### IV. RESULTS AND DISCUSSION

Solution A evolved from transparent solution (see Fig. 4(a)) to coagulated solution and finally became white colloid after one day's reservation (see Fig. 4(b)). Due to the vibration effect, solution C became diluter than solution A. Solution B was spun without ultrasonic generator, see Fig. 3(a). Solution B could not flow fluently and quickly coagulated at the needle tip, as a result fibers with beads are produced, see Fig. 5 (a).

Solution D was spun with an ultrasonic generator, see Fig. 3(b). Solution D could flow fluently through the needle tip under the vibration. Uniform ultrafine threads of polymers were emitted from jet by vibration-electrospinning process, see Fig. 5(b).

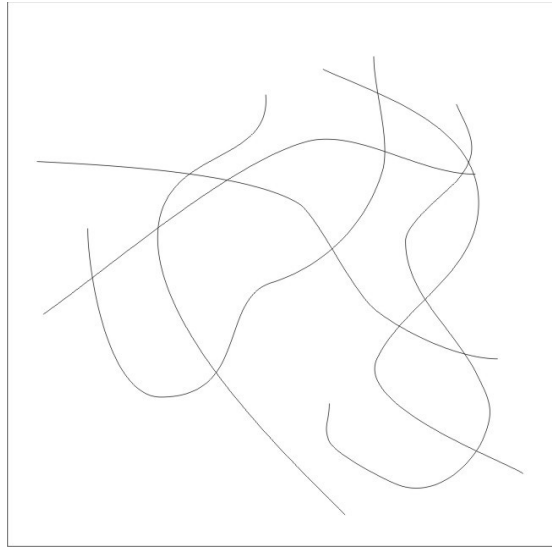


**Fig. 4: PBS/CF solution A (a) transparent solution; (b) coagulated solution**

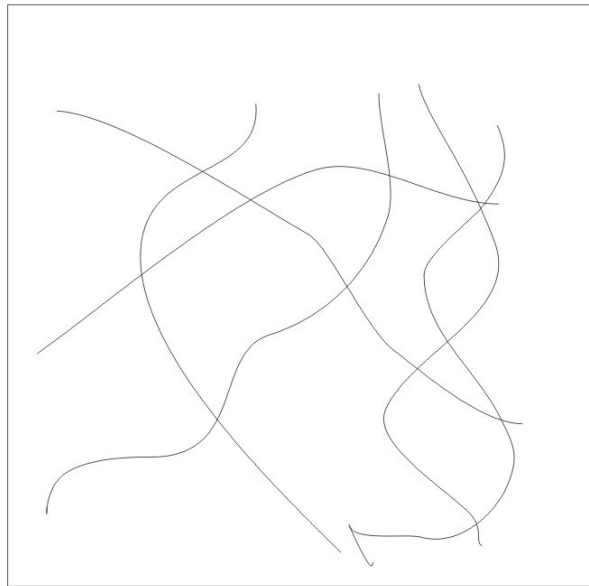


**Fig.5: 15% PBS/CF electrospun nanofibers. (a) without vibration; (b) with ultrasonic vibration**

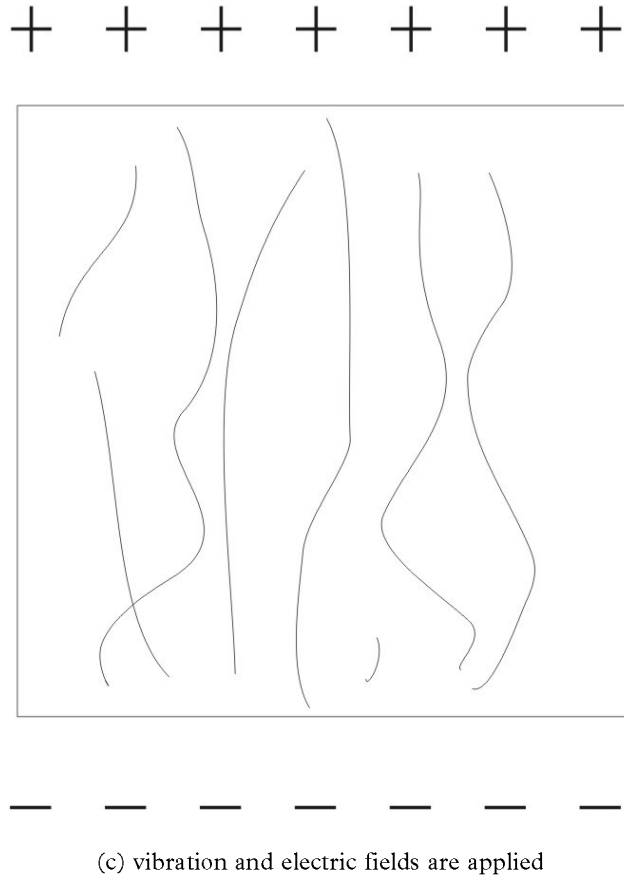
When an oscillatory shear was imposed on the polymer solutions, the resulting chain orientation leads to disentangle inhomogeneously in space. When a voltage is applied to the oscillating solutions, the disentangled chains become homogeneous in space, see Fig. 6. As a result dramatic reduce in viscosity occurs, and much smaller fibers are electrospun.



(a) Entangled macromolecules



(b) voltage is applied



**Fig.6 Physical Representation of the Entangled Macromolecules under Vibration and Electric Fields**

In absence of oscillation, the solutions can not be electrospun when the concentration reaches higher than 15%. As the concentration of PBS/CF solution decreases, morphology evolves from bead-like spheres linked with few fibers to ultrafine continuous fibers, to continuous fibers with beads, and finally to beads only when the solution become dilute unentangled, see Fig. 7

In presence of oscillation, the concentrated entangled regime is converted into concentrated regime, so that continuous fibers can be electrospun. The oscillation can, of course, converts the coagulated regime into concentrated entangled regime. So the oscillation enlarges electrospinnability.



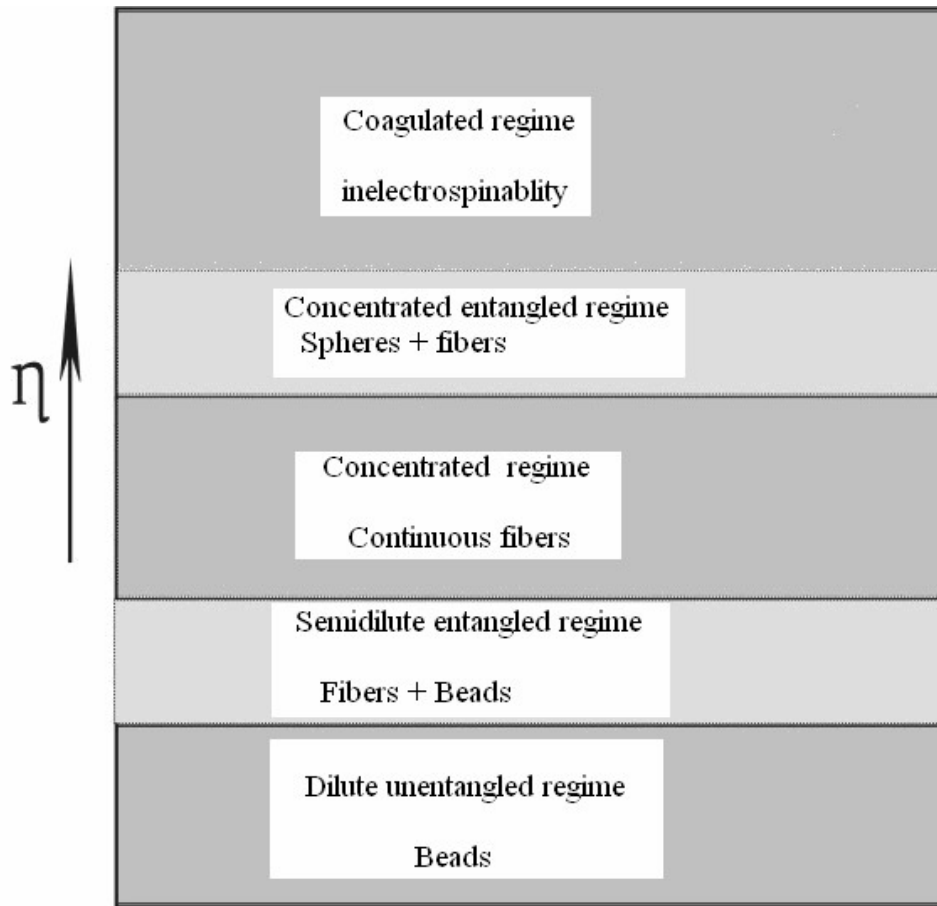


Fig.7: Electrospinnability of Different Concentrations

## CONCLUSIONS

Vibration-electrospinning can produce much smaller fibers than those obtained without vibration, furthermore, the obtained fibers are more uniform without any beads, see Fig. 5.

The theoretical prediction in Ref.[24] agrees excellently with experiments, which amounts to a strong evidence of the physical reality of vibration-electrospinning theory. Based on this theory the electrospinning can be applied to various polymers. Far-reaching implications of this technology are emerging for applications including medical implants, cell supports, and materials that can be used as instructive three-dimensional environments for tissue regeneration.

Our aim of vibration-electrospinning is to prepare for electrospun nanofibers with diameter of less than 100 nanometer. At such a scale many fascinating quantum-like phenomena occur[36]. How to control morphology of electrospun nanofibers at the

scale of 100 nm or less is the forefront topic in electrospinning, which is a technology applied in the grey area between classical mechanics and quantum mechanics [37].

In nano-scale (<100nm), nano-effect arises similar to that in quantum world [36]. For example, unusual current conduction properties arise when the size of wires are reduced below certain critical thickness (nano-scale), smaller wires may conduct more current. This nano-effect is very much similar to Arnold diffusion, the higher the dimensionality the stronger Arnold diffusion is [38].

Similar to the Hall-Petch relationship, the fiber strength depends upon fiber diameter in nano-scale (from few nanometers to tens of nanometers) [39]:

$$\tau = \tau_0 + \frac{k}{d^{1/2}} \quad (7)$$

where k is the fitting parameter (a material constant),  $\tau_0$  is the strength for bulk material, d is the fiber diameter,  $0 < d < 100nm$ .

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