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Computer simulation of electrospinning. Part I. Effect of solvent in electrospinning

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Abstract

Electrospinning technique has been recognized as an efficient method to manufacture nano-fiber. At present, research focuses on the structure and morphology of the fibers, a few investigations have been reported the mechanism of electrospinning. In our experiment, appropriate polymer EVOH (ethylene/vinyl alcohol copolymer) and different solvents were chosen, the energy change in the process of molecule orientation was analyzed by computer simulation, and the morphologies of the fiber were indicated by scanning electron microscope (SEM). Results indicate that: in the process of molecule orientation, some barriers should be overcome; the height of the barrier is determined by the relaxation times (τ) of the molecule. The relaxation times vary in different solutions, when the relaxation time is short, the orientation of molecule is easy, so jet instability will be fierce, and fibers with small diameter are obtained.

Keywords: Electrospinning; Computer simulation; Polymer

1. Introduction

Electrospinning is one of the most important techniques to manufacture nano-fibers. The theory is based on electrostatic force that acts on the polymer solution. When introduced into the electric field, solution will suffer from electrostatic force, accelerate, undergo jet instability and split into nano-fibers. At present, more that 100 different polymers have been electrospun into ultra fine fibers, with diameters ranging 40–2000 nm [1–9]. In spite of the surging interest in electrospinning, research focuses on structure and morphology of the fibers. A few investigations have been reported on the mechanism of electrospinning. Though the mechanism of electrospinning is not consummate, many researchers find that solution jet ejected from the capillary will undergo a rapid whipping instability, when travelling in the electric field. They call it jet instability. People believe that jet instability plays an important role in the formation of nano-fibers.

We study the influence of solvent on electrospinning, by choosing appropriate polymer EVOH (ethylene/vinyl alcohol copolymer) and different solvents. The influence of solvent on molecule energy and the orientation barrier of molecule chain are simulated.

2. Experiment

EVOH (ethylene/vinyl alcohol copolymer) (about 56–71 mol% poly (vinyl acetate) repeating units), the structure is indicated in Fig. 1 [10].

Two different solutions were prepared with the same concentration (10 wt%): (1) EVOH/isopropyl alcohol (70 wt%)/water (30 wt%) solution; (2) EVOH/DMAc (dimethylacetamide) solution.

2.1. Mechanism of electrospinning

The sketch of the electrospinning setup is show in Fig. 2. An electrode connected to the high voltage is immerged into the polymer solution contained with a capillary tube. The other is connected with the collector at a distance about 20 cm from the capillary tube. The solution is held by the surface tension in the form of a droplet, when no power is supplied. As the voltage is increased, the droplet will be elongated, when supplied voltage reaches certain voltage, a single solution jet will eject from the apex of a conical droplet (usually called Taylor cone) [11]. Before precipitate, solution jet will undergo jet instability

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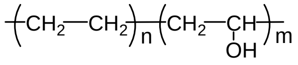


Fig. 1. Structure of EVOH.

(about several centimeters away from the capillary, as illustrate in Fig. 2), and split into small filaments collected on the collector in the form of non-woven.

Jet instability is due to the perturbations of the surface charge and the repulsive of the jet current [11–16]. Jet instability in electrospinning includes: Axisymmetric instability and bending instability [11] (indicate in Fig. 3).

Jet instability plays an important role in the formation of nano-fibers. In the process of jet instability, solution jet suffers from constant shear flow, elongate and split into smaller filaments. So how to increase jet instability is the core of gaining nano-fiber [17]. In polymer solution, flexible molecule orients easily, and jet instability is fierce, fibers with smaller diameters will be obtained [18].

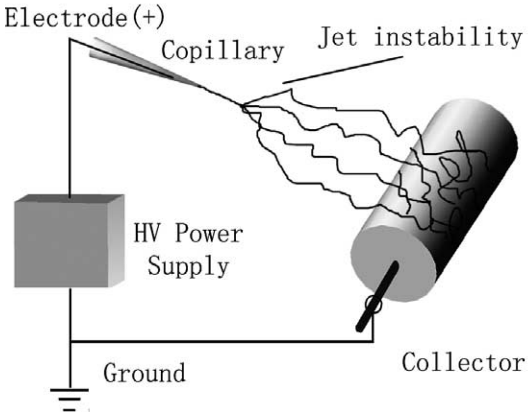


Fig. 2. The sketch of the electrospinning setup (capillary diameter: 0.20 mm; voltage supply: 15 and 20 kV; flow rate: 0.1 cm^3/min; capillary-collector distance (C-CD): 20 cm).

2.2. Morphology of the electrospun fibers and solution property

Morphology of the electrospun fibers were indicated by scanning electron microscope (SEM). Solution apparent viscosity was analyzed by rotational viscometer, at different temperature [19].

2.3. Computer simulation

2.3.1. Molecule model

In many computer simulations, off-lattice polymer model is considered as a simple and effective model. In our simulation, molecule chain is modeled by a succession of 50 spherical monomers (stands for CHOH monomer), joint together freely at arbitrary angles [20–26] (illustrate in Fig. 4).

Take the origin of coordinates as the center of a sphere ($r=1.52$), a point was taken randomly on the surface of the sphere as monomer 1, again take monomer 1 as the origin of a new coordinates, a second point was taken on the surface of the new sphere randomly as monomer 2. Create monomers successively according to this method, a polymer with different monomers (N) is obtained (in our simulation $N=50$).

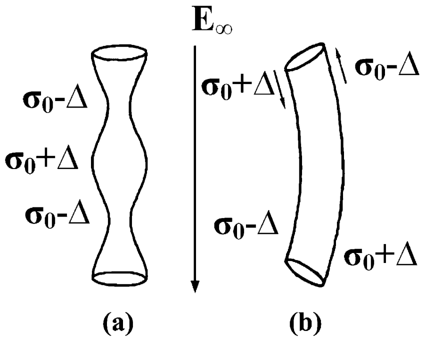


Fig. 3. (a) Axisymmetric instability. (b) Non-axisymmetric instability (bending instability), Δ denote perturbations of the surface charge density (σ) [reprinted from: Y.M. Shin, M.M. Hohman, M.P. Brenner. Experimental characterization of electrospinning: the electrically forced jet and instabilities. Polymer 2001;42:9955–67].

In polymer solution, the energy of the molecule includes: bond-stretching potential ($E_{\text{stretching } h}$), bond-bending potential (E_{bending}), non-bonded Lennard–Jone interactions (E_{segment}), and Lennard–Jone interactions between segment and solvent (E_{solvent}) (including van der Waals interaction (E_{v}) and hydrogen bonding interaction (E_{hydro})), The potential is defined as follow: (in our simulation molecule torsional potential is neglected).

$$E_{\text{stretching } h} = \frac{1}{2}K_l(L-L_0)^2 \tag{1}$$

$$E_{\text{bending}} = \frac{1}{2}K_\theta(\theta-\theta_0)^2 \tag{2}$$

$$E_{\text{segment}} = 4\varepsilon_{\text{segment}}\left[\left(\frac{\sigma}{d}\right)^{12} - 2\left(\frac{\sigma}{d}\right)^{6}\right] \tag{3}$$

$$E_{\text{v}} = 4\varepsilon_{\text{v}}\left[\left(\frac{\sigma}{d}\right)^{12} - 2\left(\frac{\sigma}{d}\right)^{6}\right] \tag{4}$$

$$E_{\text{hydor}} = 4\varepsilon_{\text{hydro}}\left[\frac{A}{d^{12}} - \frac{B}{d^{10}}\right] \tag{5}$$

K_l is the bond-stretching constant; K_θ is the bond-bending constant; $\varepsilon_{\text{segment}}$ is Lennard–Jone parameters between molecule segments; ε_{v} is Lennard–Jone parameters between chain

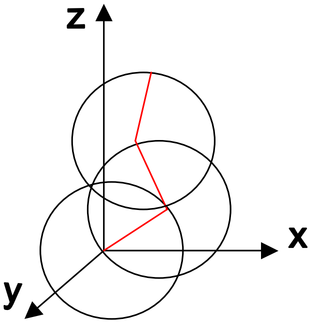


Fig. 4. Construction of random walk chain (RW).

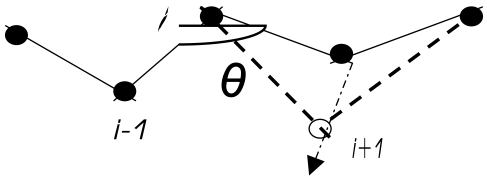


Fig. 5. Adjustment of the bond angle.

segment and solvent; $\varepsilon_{\text{hydro}}$ is Lennard–Jone parameters between chain segment and water molecule [27–29].

In EVOH/isopropyl alcohol/water solution, interactions of molecule segment and solution include van der Waals interaction (ε_v) and hydrogen bonding interaction ($\varepsilon_{\text{hydro}}$). In EVOH/DMAc solution, interaction of molecule segment and solution is van der Waals interaction (ε_v), hydrogen bonding interactions are not considered.

2.3.2. Energy adjustment

In ordinary off-lattice polymer model, bond angle and segment interaction potential is neglected. In order to obtain a stable molecule chain, we adjust the angle and the segment of the molecule, after molecule was constructed [30]. The method of bond angle and segment adjustment is described as following:

(1) Adjustment of the bond angle: calculate the angle of segments ($i-1$, i, $i+1$), if the angle is larger (or smaller) than 109°29′, angle strain will exist (Fig. 5). The direction of angle strain is along the tangent of the bond. The monomer will move along the direction, so bond angle will get close to 109°29′ (illustrate in Fig. 9).
(2) Adjustment of bond stretch: calculate the distance of two segments (i, $i+1$), and if the distance is larger (shorter) than L_0 (1.52 Å), bond-stretching potential will exist, and contract (repulsion) force will make the segments move close (or away) (illustrate in Fig. 6).
(3) Adjustment of Lennard–Jone interactions is similar to the adjustment of bond stretch. Distances between every pair of segments are calculated, when the distance is larger (or shorter) than σ, attracting (or repulsion) force will exist; it will make the segment move close (or away).

From Fig. 7, we can see that the energy of the molecule is decreasing as the adjust time elapses, from 4000 to about 1700 kJ/mol. After energy adjustment we obtain a stable molecule mode ($N=50$) (illustrated in Fig. 8).

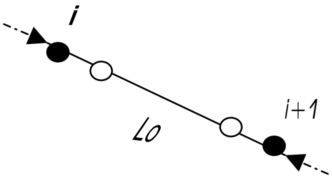


Fig. 6. Adjustment of bond stretch.

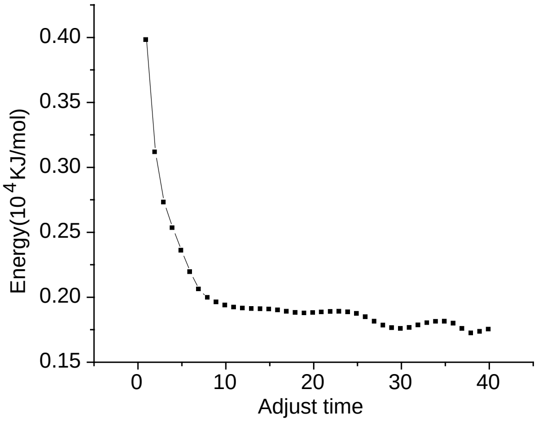
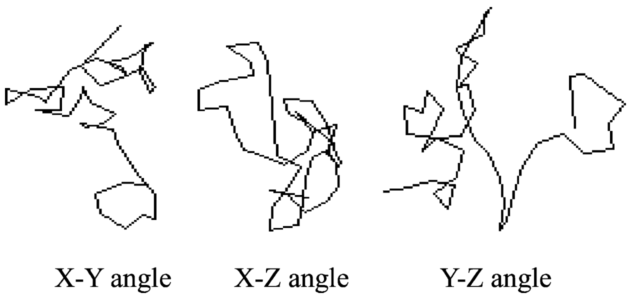


Fig. 7. Relationship between molecule energy and the adjust time.



X-Y angle X-Z angle Y-Z angle

Fig. 8. Snapshots of polymer chain (view from different angles).

2.3.3. Influence of solvent on molecule

Based on the model described above, solvent molecules are added around the molecule. First, the head of the molecule (monomer 1) is fixed at the origin of the coordinate, then, in a cubic (length: 100, wide: 100, high: 100) center around the origin, 10^6 solvent molecules are filled randomly into the cubic (in EVOH/isopropyl alcohol/water solution include 30% water molecules). In the process of solvent adding, the Lennard–Jone interaction between segment and solvent are considered. When the interaction exceeds the range of Lennard–Jone potential the position of solvent is reconsidered.

After solvent construction, we select a segment randomly and let the segment rotate a random angle around the axis, illustrate in Fig. 9.

In the process of segment rotation, Lennard–Jone interactions between segment and solvents before and after rotation are compared. The configuration of the monomer can be carried out only if the possibility (P_i defined as follow) exceeds a random number random uniformly in the interval from zero to one [21].

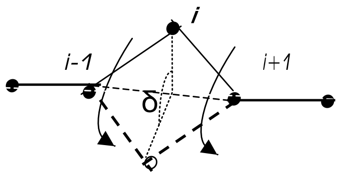


Fig. 9. Model of molecule chain: the new position of a monomer i. May be chosen by select a random angle δ from the interval [0–2π].

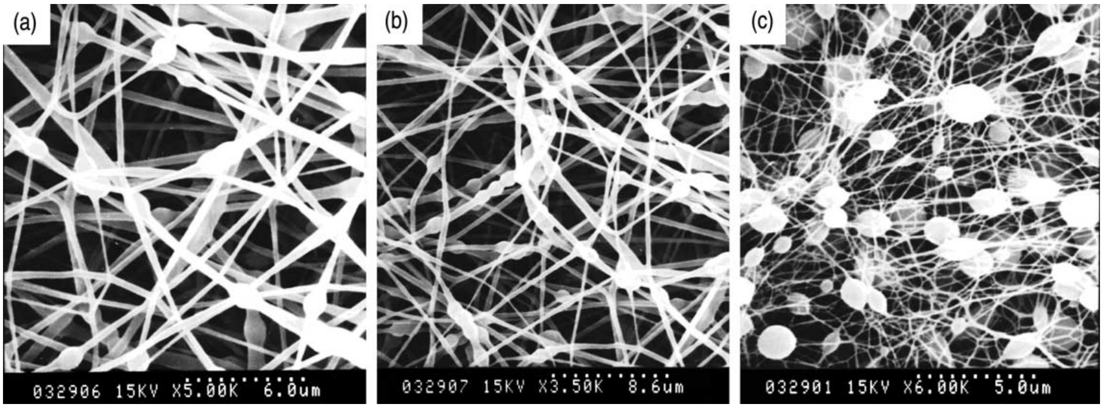


Fig. 10. SEM photographs of electrospun fibers. (a) Solvent: isopropyl alcohol/water; voltage: 15 kV; concentration: 10 wt%; C-CD: 20 cm, (b) Solvent: isopropyl alcohol/water; voltage: 20 kV; concentration: 10 wt%; C-CD: 20 cm, (c) Solvent: DMAc; voltage: 15 kV; concentration: 10 wt%; C-CD: 20 cm.

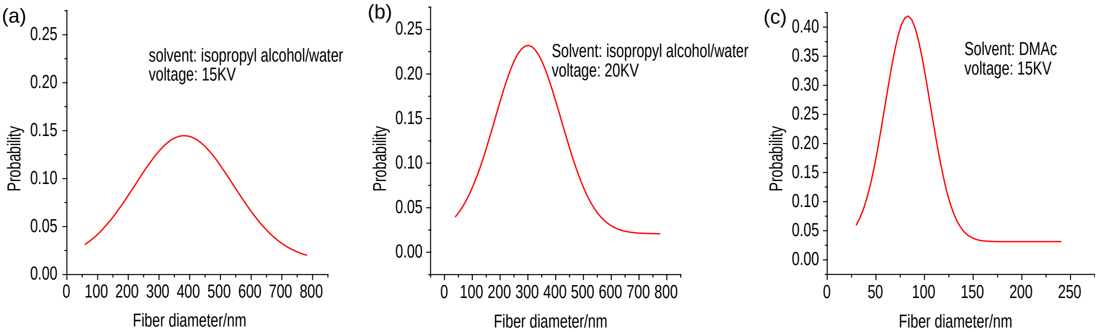


Fig. 11. Distribution of the fiber diameters.

$$P_i = \exp\left(\frac{-\Delta E}{RT}\right)$$

When $\Delta E < 0$ the configuration change will become easy; otherwise the change will be difficult. After every $n(50)$ selections (usually called a Monte Carlo time (MC)), Lennard–Jone interaction potential between monomer and solvents is calculated.

2.3.4. Simulation of shear flow

When jet instability takes place, molecules will suffer from shear flow and orient. In our simulation, the influence of relaxation time on the change of the energy is analyzed as molecule travels in shear flow. Energy adjustment adopts the method described above (influence of solvent on molecule energy is not considered).

$$E_{\text{total}} = E_{\text{stretching } h} + E_{\text{bending}} + E_{\text{segment}}$$

We assume that the jet current is along the z axis, and the shear rate is the function of the coordinate(x, y).

$$\Delta v(x, y) = v\left[1 - \left(\frac{x^2 + y^2}{R^2}\right)\right]$$

Relaxation time (τ) in our simulation is represented by energy adjust times (n) in a unit time:

$$\tau \propto \frac{1}{n}$$

n is energy adjust time in a unit time (in our simulation $n = 10$, 30, 50).

After energy is adjusted n times, the position of each monomer are updated, and the energy of the molecule (E_{total}) is calculated.

3. Result and discussion

3.1. Morphology of the electrospun fibers

Morphology of the electrospun fibers were indicated by scanning electron microscope (SEM) (Fig. 10).

From Figs. 10 and 11, we can see fiber diameters electrospun from EVOH/isopropyl alcohol/water solution ranging 100–800 nm; while fibers electrospun from EVOH/DMAc solution range 50–60 nm and diameter distribution is much smaller than that in EVOH/isopropyl alcohol/water solution. Besides, from Fig. 10(a) and (b) we can see that fiber diameter and diameter distribution decrease as the electric-field strength increases. This finding is in accordance with our previous research [18].

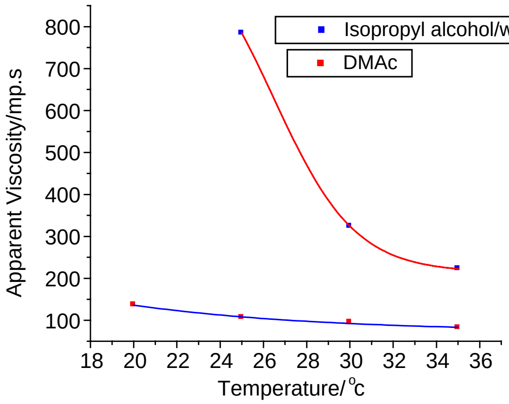


Fig. 12. Apparent viscosity–temperature curve of the two solutions.

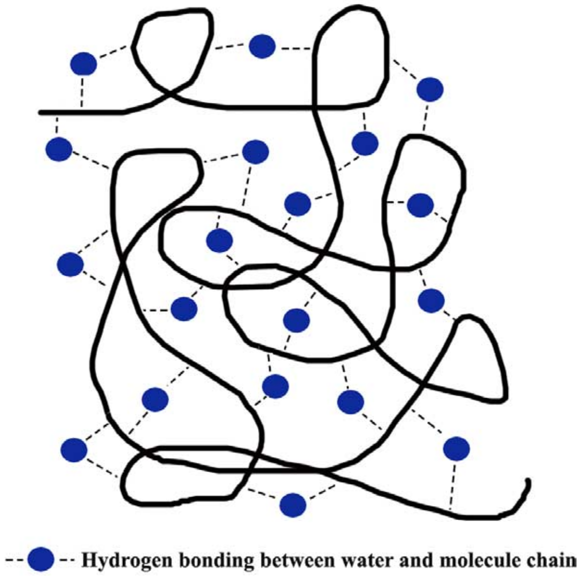


Fig. 13. EVOH chain in the solution of EVOH/isopropyl alcohol/water.

3.2. Solution property

From the SEM of the fibers, we can see that different solvents have a dominant effect on fiber diameter. Both solvents are good solvents of EVOH, and the difference is that there are a lot of water molecules around EVOH molecule in EVOH /isopropyl alcohol/water solution, and the apparent viscosity of the solutions is different (illustrate in Fig. 12).

From apparent viscosity–temperature curve (Fig. 6), we can see the apparent viscosity of EVOH /isopropyl alcohol/water is much higher than in EVOH/DMAc solution at each temperature. This indicates that molecule interactions in isopropyl alcohol/water solvent is larger than that of in EVOH/DMAc solution, besides the interaction of the molecule and solvent is strongly affected by temperature. So we deduce the interaction of the molecule and solvent in EVOH /isopropyl alcohol/water is hydrogen bonding interaction [31]. Papers reported that in poly (vinyl alcohol)/NaCl/water solution, hydrogen bonding is formed through the interaction of hydroxy connected on the poly (vinyl alcohol) chain and water molecule. As a result, a helix-structure molecule chain is formed, and molecule chain becomes rigid [32–37]. EVOH has a similar structure as PVA, so hydrogen bonding can be found in EVOH/isopropyl alcohol/water solution (illustrated in Fig. 13).

3.3. Computer simulation

3.3.1. Influence of solvent on molecule

From Fig. 14(a) and (b), we can see: the energy of molecule system decreases by 60 kJ/mol, due to the formation of hydrogen bonding in molecule system, while in DMAc solution energy reduces 15 kJ/mol. So in EVOH/isopropyl alcohol/water solution the configuration of the molecule is stable and molecule is rigid.

Flexibility of the molecule indicates the oriental ability of the molecule, and it can be described by chain relaxation time, defined as following:

$$\tau = A\exp\left(\frac{\Delta E}{RT}\right)$$

τ, relaxation time of the molecule chain; A, constant; ΔE, rearrange energy; R, gas constant; T, Kelvin temperature.

As intra/intermolecular interaction via hydrogen bonding in EVOH/isopropyl alcohol/water solution, orientation of the molecule chain has to overcome the hydrogen bonding

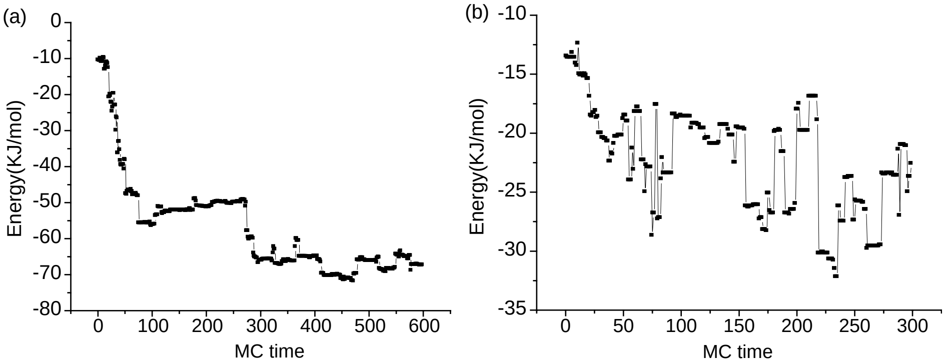


Fig. 14. Influence of solvent on molecule energy. (a) Solution with hydrogen bonding interaction (containing 30% water). (b) Solution without hydrogen bonding interaction.

interaction between molecule and solvents, so the rearrange energy (ΔE) is bigger than that in EVOH/DMAc solution, as a result relaxation time (τ) in isopropyl alcohol/water solution is longer.

3.3.2. Simulation of shear flow

As indicated in Fig. 15 molecules will stretch in shear flow, from a random coil configuration to an extending configuration. From Fig. 16, we can see that the energy is changing as molecule traveling in shear flow. The trend of the energy changing increases first and reduces afterwards. In the process of orientation, molecules have to overcome a transform barrier. The height of the barrier is determined by the relaxation time (τ), the barrier is low when the relaxation time is short, when n is 10, 30, 50 the configuration transform barriers is 0.9, 0.5, 0.39 (10^4 kJ/mol). Besides, from Fig. 16, we can see that the presence of the configuration transform barrier appears early when relaxation time is short; the presence of the configuration transform barrier will be late when the relaxation time is longer. This indicated that the orientation of flexible molecule is easy, so whipping instability is fierce, and fibers with smaller diameters are obtained.

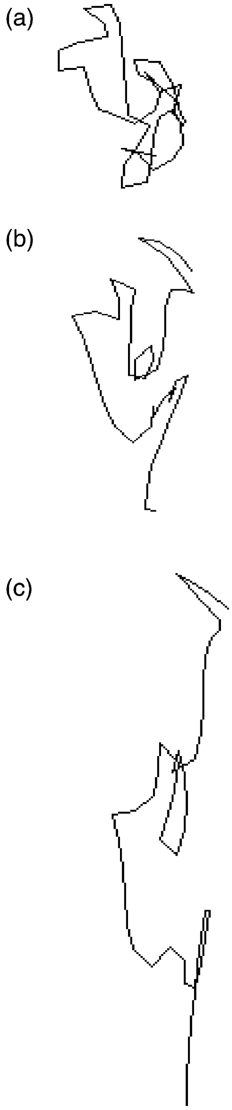


Fig. 15. Configuration of molecule in shear flow. (a) Original molecular. (b) Travel 8-unit time. (c) Travel 16-unit time.

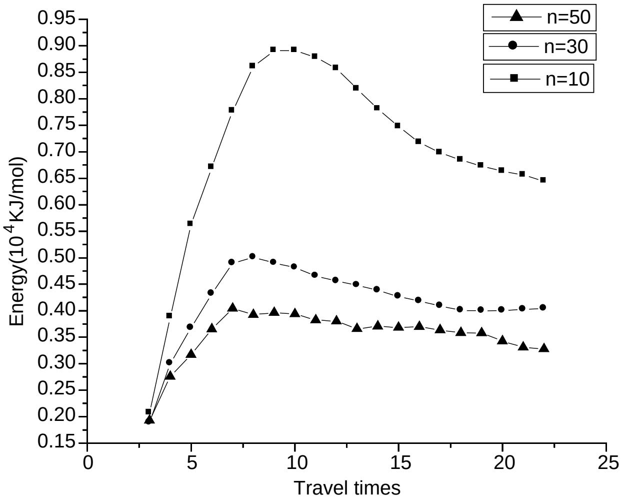


Fig. 16. Energy change as molecule travel in shear flow.

4. Conclusion

Electrospinning experiment results indicate that: diameters of fibers electrospun from different solvents are different: fibers diameter electrospun from EVOH/isopropyl alcohol/water solution is 100–800 nm; while from EVOH/DMAc solution is 50–60 nm.

The analysis of the two different EVOH solutions indicate: interaction of molecule and solvents in EVOH/isopropyl alcohol/water solution is stronger than in EVOH/DMAc solution.

The results of the computer simulation indicate: (1) molecule energy varies in different solutions. In water solution, due to hydrogen bonding interaction between monomer and water molecule, the energy is lower, and molecule is rigid. (2) Flexibility of the molecule chain is a crucial factor in electrospinning, in the process of jet instability molecule will suffer from shear flow, and the energy of the molecule is changing as molecule travels in shear flow. The energy-changing trend increases first and reduces afterwards; in the process of molecule orientation a configuration transform barrier is overcome. The height of the configuration transform barrier is determined by molecule relaxation time (τ). When molecule is flexible, the orientation of the molecule is easy, and jet instability is fierce, fibers with smaller diameters are obtained.

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