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A study of the effect of solution degradation due to aging on the electrospun cellulose acetate nanofibers

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ABSTRACT

Cellulose acetate (CA) electrospinning solution was left in sealed glass containers for about two weeks without performing any experiment due to equipment breakdown. The electrospinnability of the solution was found to have reduced. This led to this study which determined the effect solution degradation due to aging on the morphology of electrospun CA nanofibers and the maximum aging period (shelf life) of the spinning solution, before loss of nanofiber properties can be observed. CA solution electrospun after aging for 5 days produced finer fibers with an average fiber diameter of 100-110nm than the CA solution electrospun immediately (0 days of aging) which exhibited an average diameter of 160-180nm. CA electrospun immediately however, had a more uniform fiber distribution. CA solution aged for over 10 days produced non-uniform fibers with beads. Aging CA solution beyond 20 days resulted in fiber breakage during electrospinning. FTIR quantitative analysis confirmed degradation of CA solution with aging as the cause of deterioration of the electrospinnability. The color of the CA solution spinning solution also recorded a significant change due to aging.

KEYWORDS

Cellulose acetate (CA);
Electrospinning;
Aging;
Nanofibers.

INTRODUCTION

Electrospinning is a method that uses electrical potential to draw nano-scale fibers from a polymer solution. It occurs when the surface tension of a polymer droplet is overcome by electrical force; thereby a charged jet is ejected. The jet elongates and stretches and is collected on a target screen after it dries for melt solution or solvent evaporation for dissolved polymers. It is an effective way of producing polymeric nanofibers. Electrospinning can be used for a wide range of polymers and polymer blends[1,2]. Electrospinning was patented by Formhals in 1934 and it outlined the experimental set up for production of polymer nanofibers using electrostatic force[3]. Electrospun polymer nanofibers are versatile and have found applications in composite reinforcement, filtration, electrical and optical applications, tissue engineering scaffolds, drug delivery systems, cosmetics, protective clothing, nano-sensors, biomedical applications among others[4].

Of interest to this study, are cellulose acetate (CA) nanofibers. CA is a derivative of cellulose that has chains of glucose molecule units with some of the hydroxyl units of cellulose substituted by acetate. The solubility of CA depends on the average degree of substitution and distribution of substituents along its molecular chain. CA with degree of substitution 0.5-1 is water soluble, but on increasing the degree of substitution, CA becomes water insoluble with good solubility in various organic solvents[5,6]. CA nanofibers has been electrospun in solvents such as acetone, acetic acid, pyridine, dimethylacetamide (DMAc), dioxane and their mixtures[7], N, N-dimethylacetamide/acetone[8], acetone/water[9], acetic acid/water[10], formic acid, dichloromethane, acetic acid, trifluoroacetic acid (TFA)[11], and acetone/Dimethylformamide/trifluoroethylene mixture[12]. The increase in research on CA nanofibers is due to its unique properties that make it suitable for use in various applications ranging from filtration to affinity membranes in biomedical applications[9,13,14]. The factors that affect electrospinning of CA nanofibers include the process parameters (applied voltage, nozzle to collector distance, polymer flow rate, and the spinning environment) and solution parameters (concentration, conductivity and volatility of the solvent)[3]. Various studies have been done and are continually being done to fully understand the effects of the aforementioned factors on the morphology of electrospun nanofibers. This is because the application of nanofibers is dependent upon many factors which include efficient production and physical properties of the nanofibers.

In our previous study, during optimization of CA electrospinning conditions in trifluoroacetic acid[15], CA solution was left for about 2 weeks without performing any experiment. This was due to the breakdown of our electrospinning equipment. On electrospinning the CA solution, it was found that its electrospinnability had reduced. This study was done to investigate the effect of aging CA solution on the morphology of the electrospun nanofibers. Study on spinning solution aging can be helpful in determining how long a solution of a certain polymer can be kept before it loses its property of producing fibers of good morphology. Apart from equipment failure, long national holidays, illness or even long queues before equipment use can force researchers to store spinning solutions for unprecedented periods of time. Given that there is little literature available in the public domain on the aging of CA spinning solution, there is an urgent need to try and bridge this gap in the body of knowledge.

A similar scenario has been reported by Chuangchote et al, where they accidentally left spinning solutions of PS/MEH-PPV in sealed glass containers for a period of one month without performing any experiment. They later discovered that their solution changed colour on aging, which led to their study of effect of aging period on morphology and size of as-spun fibers[16]. Knowledge on spinning solution aging of a polymer can also be useful in biomedical applications during nanoparticle loading. Aging spinning solution during nanoparticle loading increased the amount of silver ions converted to silver nanoparticles. Aging period ranged from 3 hours to 10 days. This was observed when loading gelatin solution with silver nanoparticles prior to electrospinning mats to be used as antibacterial wound dressers[17]. Therefore, prior knowledge on aging effects of a polymer solution on its spinnability and properties of the nanofiber can prove useful.

EXPERIMENTAL

CA pellets of acetyl content 39.8%, degree of acetyl substitution of 2.5 and molecular weight 30,000 and Trifluoroacetic acid (TFA) solvent were purchased from the Shanghai representatives of Deng Wei Zhangmutou Plastics and Bepharm Ltd respectively.

15wt. % CA solution was prepared under room conditions by dissolving CA pellets in TFA in a glass container. The solution was then stirred using an electromagnetic stirrer for 24 hours ensuring a homogeneous mixture. A portion of the solution was then drawn and electrospun. The remaining solution was then aged by keeping it in the sealed glass container at room conditions for interval periods of time. A portion of the solution was drawn for electrospinning each time the aging period was reached. The periods for aging used were 0 day, 5 days, 10 days, 15 days, 20 days and 30 days. 0 days represented the solution that was electrospun without aging.

Prior to electrospinning, each solution of CA was loaded into a syringe of internal diameter 0.7mm and the syringe was mounted on a syringe pump (Multi-

Syringe Pump TS2-60, BaoDing Longer Precision Pump Co. Ltd, China) to regulate the feed rate which was kept constant at 0.3ml/h. The needle of the syringe was connected to an electrode connected to a power source. The collector screen, which was an aluminum plate covered with aluminum foil for collecting CA nanofibers connected to another grounded electrode. Electrospinning was done under room conditions with voltage and tip to collector distance being kept constant at 25KV and 10cm respectively.

The morphology of CA nanofibers was observed using Scanning Electron Microscope (Quanta 250). SEM images of magnification X10,000 were analyzed using Adobe Acrobat X Pro 10.1.2.45. A study of the chemical groups in the nanofibers spun from 0 days aging (no aging) and 30 days aging solutions was done using Fourier Transform-Infrared (FT-IR) Spectroscopy (Nicolet Nexus670 (Thermo Nicolet Co., USA)). FT-IR data was processed using Origin Pro v8. Photographic images of CA solution before and after the aging periods were taken using a digital camera at approximately 30cm from the sample bottle.

RESULTS AND DISCUSSION

The morphology of the CA nanofibers

The surfaces of CA nanofibers electrospun from solutions of different aging times were observed using SEM and the microphotographs obtained. The SEM images were as shown in Figure 1. From the images, it can be seen that when the 15wt. % concentration of CA solution was electrospun immediately (0 days), the CA nanofibers obtained appeared to be relatively uniform and bead free. On aging the 15wt. % CA solution for 5 days, the CA nanofibers also appeared to be relatively uniform and bead free. From the images which are at the same magnification, CA nanofibers electrospun after 5 days of aging seem to be finer than the CA nanofibers electrospun immediately. On aging the CA spinning solution for 10 days, the uniformity of the nanofibers deteriorated and beads begun to form. A similar trend was followed by CA nanofibers electrospun after 15 days, with the bead size appearing to increase in size. At 20 days and 30 days of aging, the morphology of electrospun CA nanofibers was completely non-uniform and fiber breakage was widely evident. Therefore according to the results obtained in this research work the CA solution electrospun after 0 and 5 days of aging appeared to form a continuous fiber in form of a non-woven web, with no fiber breakage which is as expected for electrospun nanofibers[18].

Fiber diameter distribution of the CA nanofibers

Analysis of the SEM images was undertaken with an aim of studying the distribution of the fiber diameter of the CA nanofibers. The results of the aforementioned study are given in Figure 2. CA nanofibers electrospun immediately after dissolving in TFA solvent (0 days) was found to have a unifrom fiber distribution with the fibers centrally distributed around the mean (normal distribution). The average diameters of the fibers were in the range of 160 to 180nm. On aging the CA solution for 5 days, as seen earlier, the electrospun CA nanofibers became finer with average fiber diameters ranging from 100 to 110nm.

The fiber distribution was somewhat uniform with a slight deviation from a normal distribution. Further aging the electrospinning solution for 10 days, the resultant CA nanofibers did not have a normal distribution, indicating the non-uniform distribution of the fibers. The fiber range also increased drastically. Similarly for CA nanofibers electrospun after aging CA solution for 15, 20 and 30 days, the fiber distribution deviated from the normal distribution. Their fiber ranges also increased. These could be indications of non-uniformity in electrospun fibers. From the SEM analysis, it is obvious that CA nanofibers morphology is dependent on the period of aging of the electrospinning solution. For 0 days and 5 days, the fibers produced were uniform, normally distributed, continuous and bead free. After 5 days of aging the CA solution, the nanofibers began to form beads and deviate from a normal distribution indicating non-uniformity with extreme cases of fiber breakage being observed for periods greater than 20 days. It can therefore be deduced that the electrospinnability of CA solution kept for longer than 5 days reduces drastically.

FTIR analysis of CA nanofibers before and after spinning solution aging

In order to determine the cumulative changes that occur during the aging of CA spinning solution from 0-30 days, FTIR spectroscopy was done for CA nanofibers at 0 days and at 30 days.

The FTIR spectra from CA nanofibers electrospun at 0 days of aging and 30 days of aging are presented in Figure 3.

For both CA nanofibers electrospun immediately after dissolving CA pellets and CA nanofibers electrospun after aging the solution for 30 days, there was an absorption peak associated with stretching of OH groups at 3486cm^{-1} and 3485cm^{-1} respectively. The intenstity of transmittance slighlty reduced with aging of the CA solution for 30 days. This indicates that the absorbance for this particular group had slightly increased. A change in absorption intensity between the original spectra (0 days aging) and the spectra of CA nanofibers after aging for 30 days depicts a change in the state of the molecule. The change in absorption intensities has been used to determine the removal of side groups from a chemical structure after aging[16]. Absorption peaks observed at 2942cm^{-1} (0 days) and 2987cm^{-1} (30 days) could be due to CH stretching of CH_2 and CH_3 groups. The intensity of transmittance

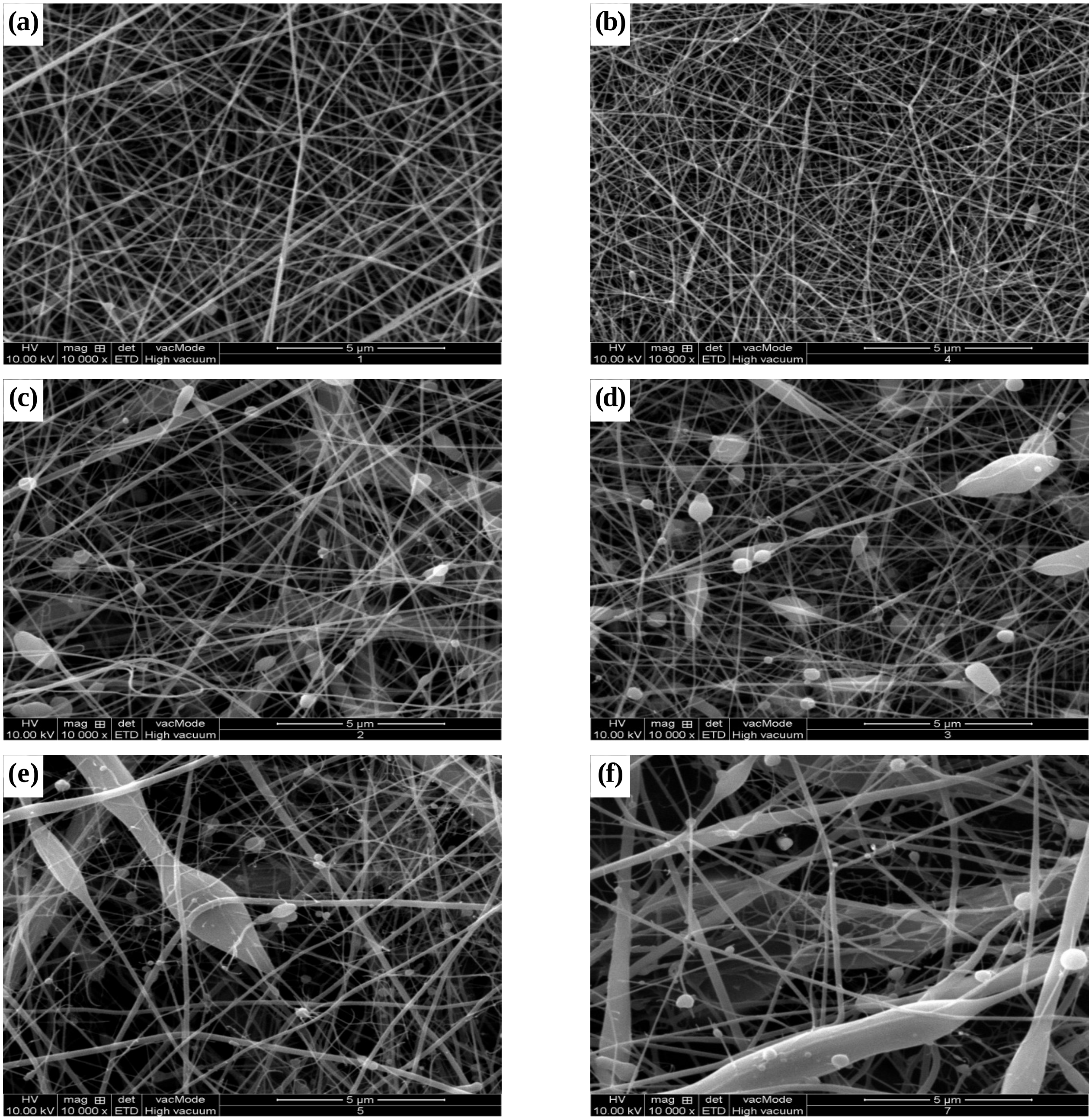
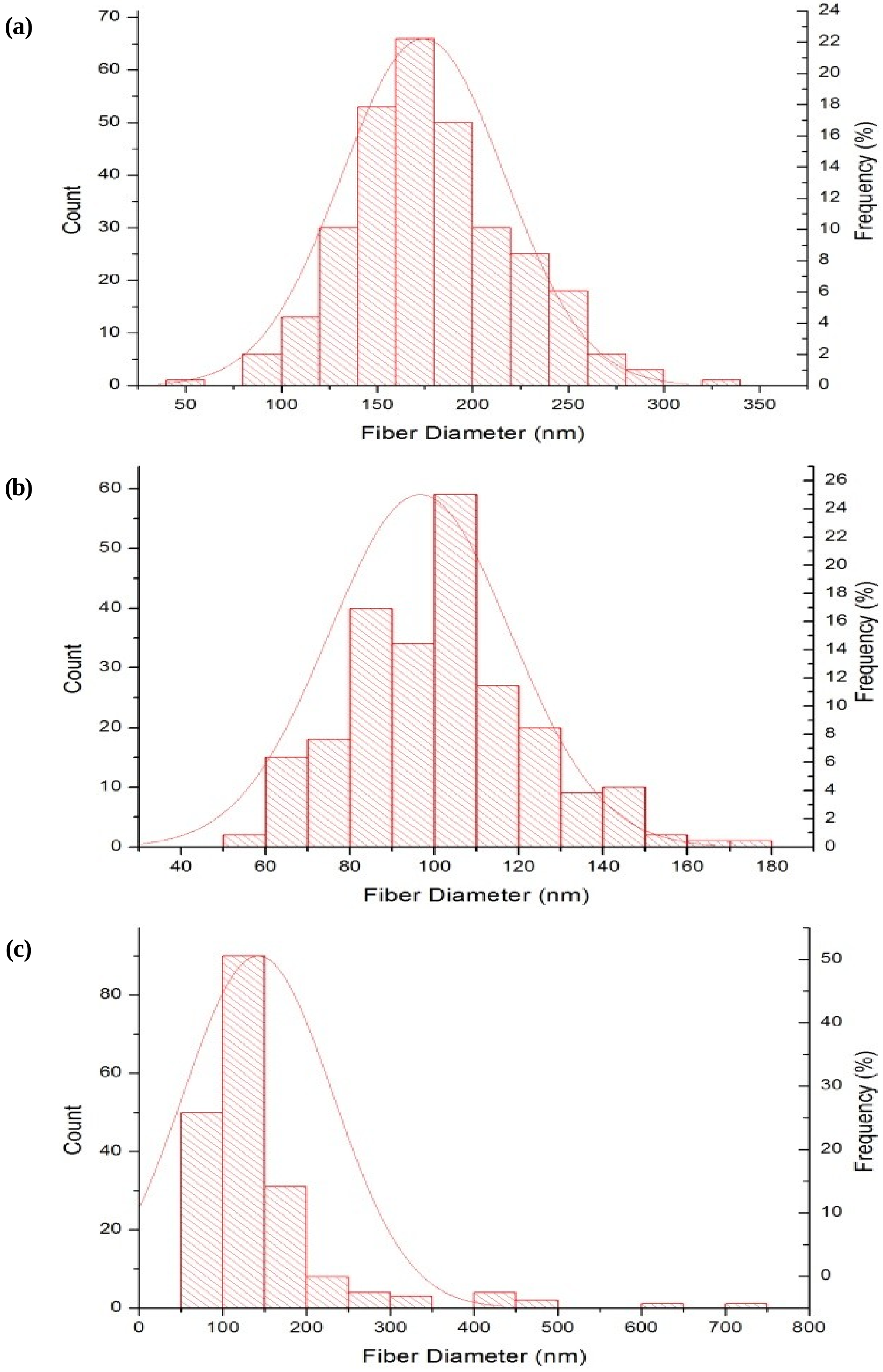


Figure 1 : SEM images of CA nanofibers electrospun at varying solution aging period; (a) 0 days, (b) 5 days, (c) 10 days, (d) 15 days, (e) 20 days, and (f) 30 days


(a)
Count
0
10
20
30
40
50
60
70
Frequency (%)
0
2
4
6
8
10
12
14
16
18
20
22
24
50
100
150
200
250
300
350
Fiber Diameter (nm)
(b)
Count
0
10
20
30
40
50
60
Frequency (%)
0
2
4
6
8
10
12
14
16
18
20
22
24
26
40
60
80
100
120
140
160
180
Fiber Diameter (nm)
(c)
Count
0
20
40
60
80
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Fiber Diameter (nm)

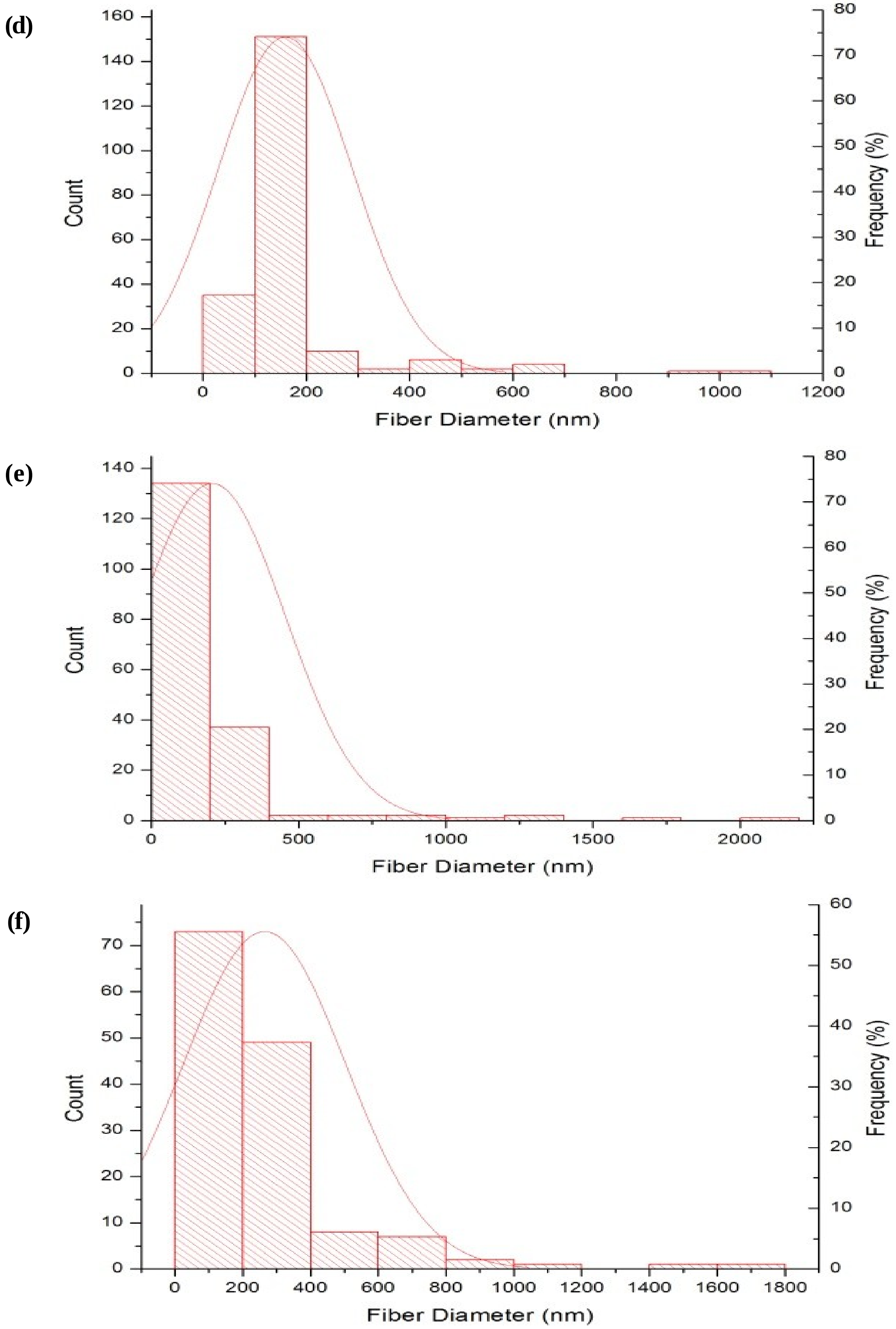

Figure 2 : Fibre distribution graphs of CA nanofibers electrospun at varying solution aging period; (a) 0 days, (b) 5 days, (c) 10 days, (d) 15 days, (e) 20 days, and (f) 30 days

seemed to have slighlty reduced for CA aged for 30 days. There is also a shift of absorption peak from 2942cm^{-1} to 2987cm^{-1}. Absorption peak at 1790cm^{-1} (0 days) and 1793cm^{-1} (30 days) assigned to stretching of carbonyl group (C=O) on a carboxylic acid was seen to have a huge variation in intensity of transmittance. The intensity of transmittance reduced with a big margin for CA (30 days), indicating a substantial change in the state of this group when the CA solution was aged for 30 days. At absorption peaks 1748cm^{-1} for both CA (0 days) and CA (30 days) assigned to vibration of the carbonyl (C=O) in the acetate group, the intensity of transmittance slightly increased on aging CA solution.

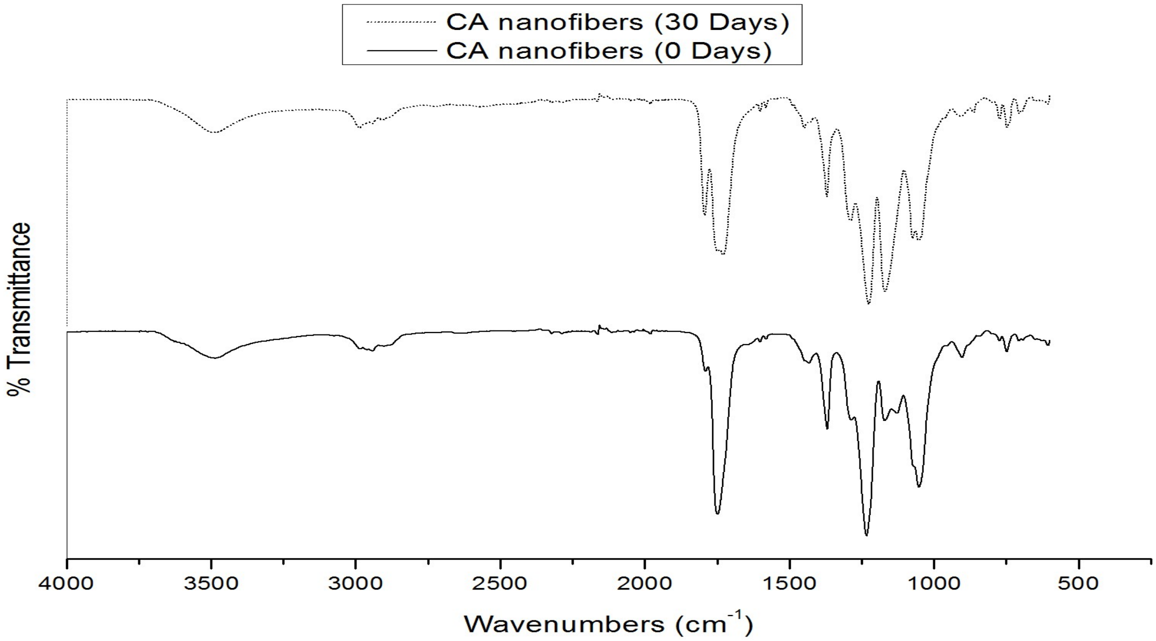

Figure 3 : FTIR spectra for CA nanofibers before and after 30 days of solution aging

There was an appearance of an absorption peak at 1728cm^{-1} for CA (30 days) which was initially absent for CA (0 days). The appearance of this absorption peak is an indicator of presence of an aldehyde group, initially absent in the CA nanofibers electrospun immediately. Absorption peaks at 1601cm^{-1} and 1581cm^{-1} for both CA (0 days) and CA (30 days), associated with C=C stretching, showed slight change in intensity of transmittance. CH_2 or OH bending was observed at 1433cm^{-1} (0 days) and 1448cm^{-1} (30 days) and there was slight decrease in transmittance intensity. A peak shift was also observed at this frequency. At 1369cm^{-1} (0 days) and 1370cm^{-1} (30 days), there was approximately no change in transmittance intensity. The peaks correspond to stretching of methyl group in acetate. There was a significant change in transmittance intensity at 1284 cm^{-1} (0 days) and 1288cm^{-1} (30 days). The peaks indicated stretching vibration of CO. The major absorption peak on both spectra at 1233cm^{-1} (0 days) and 1225cm^{-1} (30 days), corresponding to C-O stretching range of an acetyl group, showed no change with aging of CA solution. A big change in transmittance intensity was observed at peaks 1171 cm^{-1} (0 days) and 1170cm^{-1} (30 days). The intensity of transmittance reduced on aging, showing that some molecules associated with this peaks (C-O-C antisymmetric bridge stretching) had undergone some changes. An absorption peak previously not present for CA (0 days), showed at 1074cm^{-1} for CA (30 days). At around 1050cm^{-1}, a peak associated with the symmetrical stretching of C-O of a primary alcohol, was observed for both CA (0 days) and CA (30 days) with the transmittance intensity reducing slighlty on aging. The small absorption peaks at 903cm^{-1}, 748cm^{-1} and 705cm^{-1} for CA (0 days) showed slight decrease in transmittance intensities on aging at 905cm^{-1}, 747cm^{-1} and 706cm^{-1}.

Quantitative analysis of the FT-IR results

To further understanding the extent of change in the molecular vibrations in the CA structure during aging in TFA solvent, TABLE 1 was prepared.

TABLE 1 : Analysis of FTIR spectra for CA nanofibers

CA electrospun after 0 days aging		CA electrospun after 30 days aging		T_0-T_{30}	Assignment
Peak (cm^{-1})	%Transmittance (T_0)	Peak (cm^{-1})	%Transmittance (T_{30})		
3486	86	3485	83	Slight	OH stretching
2942	89	2987	85	Slight	CH stretching of CH2 & CH3
1790	81	1793	49	32	C=O stretching on carboxylic acid
1748	19	1748	33	-14	C=O vibration on acetate group
-		1728	32	+ peak	Presence of aldehyde
1601	94	1601	93	Slight	C=C stretching
1581	94	1581	95	Slight	C=C stretching
1433	84	1448	87	Slight	CH2 bending/OH bending
1369	57	1370	55	Slight	CH3 stretching in acetate
1284	59	1288	45	14	Vibration of CO
1233	12	1225	10	Slight	C-O stretching in acetyl group
1171	59	1170	16	43	C-O-C asymmetric bridge stretching
-		1074	37	+ peak	C-O stretching in esters
1051	32	1052	37	Slight	C-O stretching of primary alcohol

The difference in intensity at each absorption peak was calculated by subtracting the transmittance for CA electrospun after 30 days of spinning solution aging (T_{30}) from transmittance of CA electrospun immediately after spinning solution preparation (T_0). Positive values of these difference (T_0-T_{30}) indicated decreased transmittance with aging, which translates to an increase in absorbance. Negative values of the difference indicated increased transmittance, translating to decreased absorbance. Differences below 5%, were categorised as 'slight' to indicate slight difference between the two spectras of CA (0 days) and CA (30 days). '+ peak' was used to indicate the appearance of a peak (after aging for 30 days), initially absent.

From the analysis, it is obvious that there was great decrease in intensity transmittance for C=O stretching on carboxylic group. The percentage decrease in transmittance of carbonyl groups was calculated using equation 1.

$$\textbf{\% Change in transmittance} = \frac{T_0 - T_{30}}{T_0} \textbf{X100} \qquad \textbf{(1)}$$

The percentage reduction in transmittance of C=O molecules in a carboxyl group in the CA nanofibers due to aging spinning solution for 30 days was 39.5%. Similarly, for C-O molecules reduction in transmittance due to aging was 23.7% and for C-O-C molecules was found to be 72.9%. C=O vibrations on acetate group showed an increase of 73.7% in transmittance intensity.

It is known that the energy required to cause vibration, which is a characteristic of functional groups, depends on the type of bond in a molecule. The vibrations of bonds are caused by interaction of electric field with resonant vibrational frequency of the bond. Therefore if there is no change in dipole upon vibration, electric field will not cause a vibration. The intensity of absorption of radiation by a molecule is related to the dipole of the bond and the relationship is that the greater the dipole, the greater the absorption intensity. On the other hand, the position of absorbance relates the force constant of the bond[19,20]. It could be deduced that the reduction and increment in transmittance intensity in certain molecules of CA experienced in CA nanofibers electrospun after aging for 30 days may have been caused by a change in molecular dipole of the bonds. A change in molecular dipole is caused by an imbalance of charge in a molecule. In this case, the imbalance might have been caused by a free radical. Since the samples were aged under room conditions, without shielding the CA solutions from sunlight and other artificial lights, it is obvious that the solution might have absorbed light energy. Studies by Hon[21] into photo degradation of cellulose acetate has revealed that at ambient temperature, CA loses bound acetic acid with formation of gaseous products during these degradation. He also found that photo degradation of CA is a free radical reaction that leads to main chain and side group scission and formation of small molecules. Free radical formation is as a result of main chain and side chain cleavage and also as a result of loss of hydrogen atoms due to light. He also revealed that the main chromophore in CA is the carbonyl of acetyl group in the polymer.

Therefore it can be deduced that on aging CA photo degradation occurs. This caused a change in molecule dipoles that in turn caused a change in intensity of transmittance when CA was aged for 30 days. C-O-C asymmetrical bridge stretching with 72.9% reduction in transmittance therefore shows that there was a great deal of disturbance of these molecules in CA nanofibers electrospun after aging. In cellulose structure, C-O-C bond, otherwise known as glucosidic bond, joins one molecule to another. The great disturbance in this molecule could be an evidence of main chain cleavage. 73.7% change in transmittance intensity of vibration of C=O in acetate group, which is also a great change from the original intensity of CA before solution aging, can also be an indicator of dipole disturbance during acetate side group loss. The appearance of two peaks initially absent from the CA nanofibers before aging is an indicator of formation of molecules previously absent, which is in line with production of small molecules. A peak at 1728 cm^{-1} indicating presence of an aldehyde and at 1074 cm^{-1} assigned to stretching C-O in esters, could be as a result of formation of degradation by-products with CA solution aging. Moeen et al, assigned an absorption band around 1074 cm^{-1} to indicate formation of esters[22]. Photo-oxidation could also have occurred during sample aging since the glass bottles were not sealed under a vacuum and therefore oxygen was present in the CA solution.

Use of FT-IR results to explain electrospinning of CA nanofibers

With the results of FTIR spectra of CA before and after aging, the production and properties of the electrospun nanofiber morphology can be further explained.

It was observed that nanofibers produced from solution of 5 days of aging produced finer fibers than those electrospun from CA solution without aging. Since it has been ascertained that main chain and side chains break with aging, at constant electrospinning conditions, the CA solution with shorter chains will be stretched more. Voltage causes charge build up in electrospinning solution, that allows electrostatic force in the solution to overcome solutions intra-molecular and intermolecular forces[1]. Shorter chains have lower intra-molecular and intermolecular forces, and therefore more aged CA solution will have less resistance to stretching. This is why CA nanofibers after aging for 5 days are finer. At 10 days, 15days, 20 days and 30 days of aging, non-uniform beaded fibers are formed.

It is known that for fibers to be produced during electrospinning process there is a critical polymer concentration that must be exceeded and below this con-

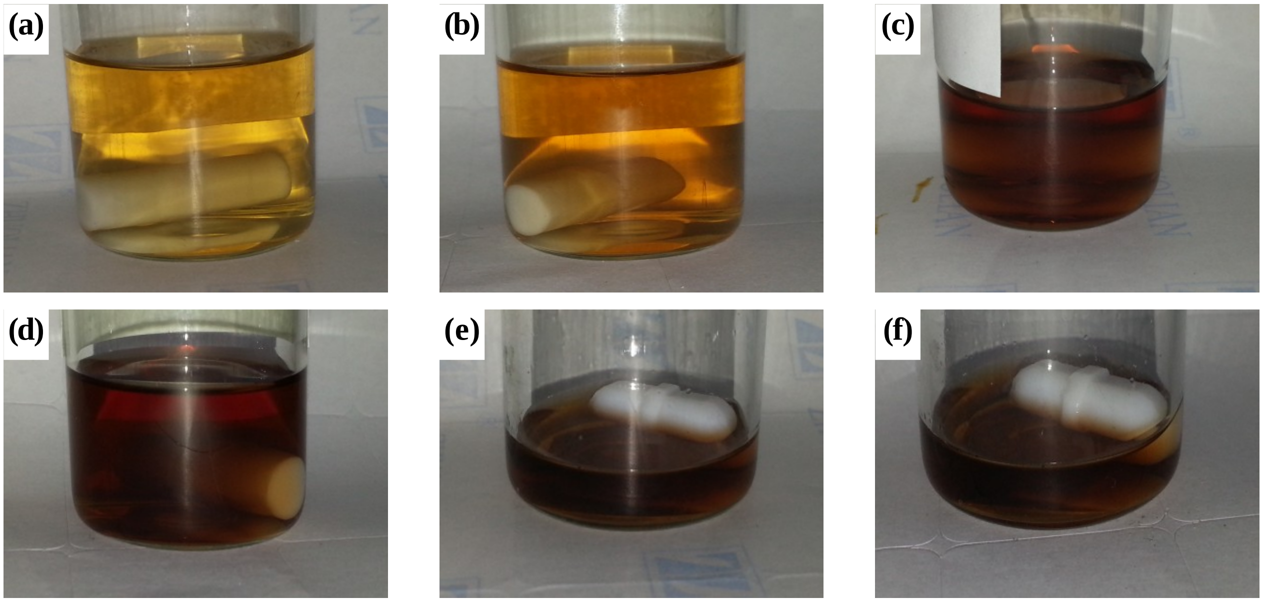

Figure 4 : Digital photographs of CA solution at (a) 0 days, (b) 5 days, (c) 10 days, (d) 15 days, (e) 20 days and (f) 30 days of aging

centration, chain entanglement in the spinning solution is not sufficient to stabilize the electrospinning jet, thus contraction of jet diameter driven by surface tension causing bead formation[23]. Degradation of CA polymer chains led to reduction in the concentration of CA in the solution below the limit required to stabilize the jet hence leading to non-uniform and beaded fibers beyond 10 days of aging. Fiber breakage witnessed for CA solution aged beyond 20 days could be as a result of main chain cleavage. Long polymer chains have more intermolecular and intra-molecular forces, and therefore can resist the stretching force of applied voltage. After 20 days of aging, the CA solution main chain and side chains are reduced to a point where the applied voltage force is greater than the molecular forces thus causing fiber breakage as seen in SEM images for CA electrospun after 20 and 30 days of aging.

There was also solution color change that occurred with aging CA solution. The images are shown in Figure 4. As the number of days of aging increased, the color became darker, with the 30 days aging solution giving the darkest color observed.

CONCLUSION

A study of the effects of solution degradation due to aging on Electrospun Cellulose Acetate (CA) nanofibers was undertaken with the aging time varied from 0 (no aging) to 30 days. The change in the electrospinnabilty of the fibers, the fiber morphology and chemical groups were analyzed.

According to the results obtained in this research Cellulose Acetate (CA) solution aged for a period not exceeding 5 days produced finer nanofibers but of relatively lower fiber distribution compared to nanofibers produced from cellulose acetate solution electrospun without aging. Aging a spinning solution for over 10 days reduced electrospinnability and therefore the production of good nanofibers was not possible. Keeping CA solution for over 20 days, leads to complete deterioration, with nanofiber breakage occurring. Results of FTIR analysis for the no aging (0 days) and 30 days aging of the CA spinning solution indicated that there were significant chemical changes in CA solution during aging. This could explain the changes observed in the fiber morphology and the distribution of fiber diameter as aging progressed. Therefore CA solutions should not be kept or stored for over 5 days after dissolving.

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