CHEMICAL CROSSLINKING OF POLY (VINYL ALCOHOL)/ POLY ETHYLENE GLYCOL WITH GLUTARALDEHYDE NANOFIBERS

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How to Cite This Article

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ABSTRACT

Poly (vinyl alcohol) (PVA)/ poly ethylene glycol (PEG) with different concentration were prepared by electrospinning and chemically crosslinked using glutaraldehyde (GA) to improve the water resistance of nanofibers. The effects of the different concentration of PEG on the solution properties of PVA/PEG/GA blends and on the morphology of the resultant nanofibers were studied. The surface morphology and the average diameter of the blend nanofibers are dependent on initially added PEG concentrations. The effects of the glutaraldehyde on the morphology, average diameter, contact angle, mechanical properties and swelling properties of the PVA/PEG nanofibers were examined. The PVA/PEG/GA nanofiber mats were characterized by scanning electron microscope (SEM), fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) . The swelling and water uptake ability resulted in no morphological changes in the fibers with GA crosslinking.

Keywords: Electrospinning; Poly (vinyl alcohol); Poly ethylene glycol; Glutaraldehyde.

INTRODUCTION

Since the mid 1990s, there has been a growing interest in the production of nanofibres by electrospinning. Electrospinning is a process carried out at room temperature that allows the production of polymer fibres with diameters in the sub-micron size range, through the application of an external electric field, keeping intact the bulk properties of the polymers. Electrospun membranes possess some unique structural features, such as a high surface to volume ratio and very good mechanical performance, properties that are determinant to their use in several applications such as air and liquid filtration, tissue engineering, optical and chemical sensors [1].Although electrospun nanofibres have been used in industrial, consumer and defense filtration applications for more than twenty years, most of the research conducted to date has focused on synthetic polymers. Examples of electrospinning of natural polymers are limited to silk collagen, DNA, alginate, chitosan and more recently fibrinogen, gelatine

and hyaluronic acid [2]. Moreover, complex polysaccharides and proteins from bacteria and plant sources have not been sufficiently explored for their ability tobe electrospun into nanofibres. Because of the very different chain conformations, hydrodynamic responses and repulsive forces in solution among the polyanions of natural polymers, the efficiency and reproducibility of the electrospinning process and the fibre uniformity remains a challenge, thus limiting their practical application [3].A method to overcome this drawback is blending the bio-polyelectrolytes with a non-toxic, water soluble, biocompatible, synthetic polymer such as Poly(vinyl alcohol) (PVA) since it can reduce repulsive forces within the charged biopolymer solutions and allow fibres spinning [5].

Electrospinning is a powerful and effective method of producing continuous polymeric nanofibers with nano-scaled diameters [6], but electrospinning of polymer nanofibers are not easily obtained. Parameters such as flow rate of polymeric solution, voltage applied and, distance between needle and

drum, solvent for the polymer preparation, all required for obtaining electrospun nanofibers. Polyvinyl alcohol (PVA) is a hydrophilic, nontoxic, with good chemical, thermal, and mechanical stability [7], Polyethylene Glycol (PEG) is a thermoplastic polymer with perfect crystalline and good water-soluble. At ambient temperature, it can acquire large enthalpy through the transition from amorphous state to crystalline state. It can absorb, store and deliver energy in form of latent heat[8].When the PVA,PEG electrospun, the obtained nanofibers are insoluble in water[9]which limits its applications in wet state. So we cross linked the nanofiber with glutaraldehyde. Glutaraldehyde (GA) is a more effective cross-linking agent than other aldehydes [10]. In recent years, GA has gained increasing attention as a PVA crosslinking agent because of the absence of thermal treatment needed to drive the reaction. Additionally, it is also well known that GA can bind nonspecifically to biomolecules, such as proteins. The polymerization of hemoglobin for the production of artificial blood is an example of GA's ability to join the polypeptide backbone [11]. Because the crosslinker has two active sites, it can be successfully used to bind proteins and PVA together. This feature enables the development of tailored structures to be used in biosensors once the constraints imposed by the biomolecules are considered. In this paper, phase change composite nanofibers were prepared by electrospinning using PVA, PEG blend solution crosslinked by GA. Electrospun blended nanofibers containing various ratios of GA concentrations were obtained. The structure of the blended nanofibers containing GA was characterized. In this study, fabrication of crosslinked PVA/PEG nanofibers was using electrospinning technique and using GA as crosslinking agent and evaluation of the effect of GA cross-linking on the morphology and physico chemical of the cross-linked mats. The SEM, FT-IR,

le were used to analyze the changes of the morphology, functional groups of nanofibers.

Experimental

Materials.

PVA, 98% hydrolysis (Mt. 72.000), and PEG, (Mt, 1200) were obtained from Merck Schuchardt OHG, Germany. GA, 25% aqueous solution was purchased from Alfa Aesar GmbH & CoKG, Germany. All other chemicals were of analytical grade and were purchased from Sigma.

Preparation of crosslinked PVA/PEG/GA blend
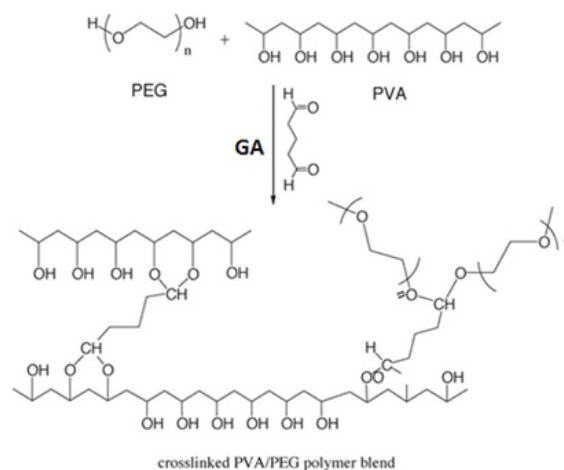
Figure 1: Schematic diagram of crosslinking PVA/ PEG with GA.

At first PVA powder was dissolved in distilled water by heating the solution to 85 °C with vigorous stirring for 2hr. The concentration of PVA solutions tested was 8wt %. After the solution was cooled to room temperature and no particles remained, PEG with different concentration (0.25, 0.5, 1, 1.5 wt. %) was added to the polymer solutions by the desired ratio to the PVA final content maintained at 8 wt %. Then each solution was heated to 70°C for 1 hr. The solution was mechanically stirred until completely homogenous. After that, the GA crosslinked with different concentration (0.5, 1, 1.5, 2, 3, 4 wt %) was gradually dropped into the above solutions. The mixture was stirred for different reaction time (15, 30, 60, 90, 120min) with vigorous stirring (Fig. 1).

Electrospinning of PVA/PEG/GA nanofiber
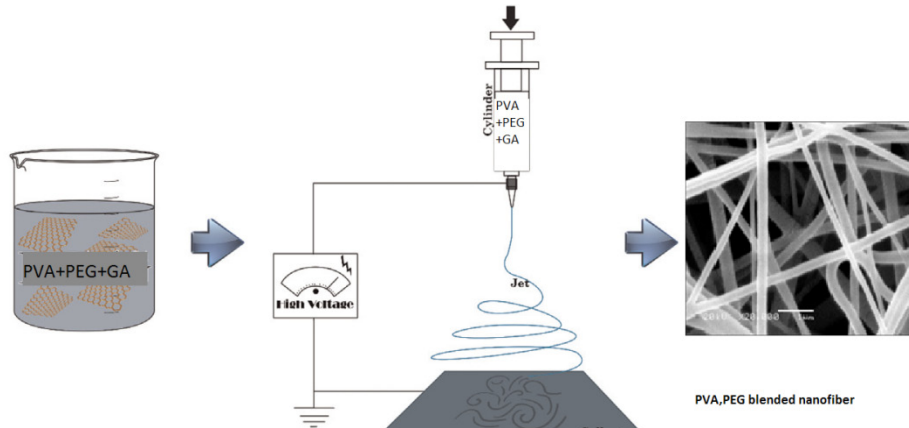
Figure 2: Schematic diagram of the electrospinning of nanofiber

In this process the above mentioned PVA/PEG/GA solutions were placed into a 10 mL plastic syringe connected to a stainless steel needle. A high voltage (20-25) KV is applied gradually. When the applied voltage overcomes the surface tension of the polymer solution a Taylor cone appears and it spins down as a fiber to reach the collector (Fig 2). The collector was covered with aluminum foil and the nanofibers were collected on it at room temperature. Before reaching the collector, the solvent evaporates and the polymer solidifies and gets collected as fibers. The distance between the needle tip and collector was fixed at 10cm. The feed rate was chosen to be 0.1 mL/hr. Then nanofibers were dried for 24 hr at room temperature.

2.4. Electrospun nanofibers characterization

2.4.1. Scanning electron microscope (SEM).

The fiber surface morphologies of the electrospun PVA/PEG blend nanofibers and PVA/PEG/GA nanofibers were assessed via a scanning electron microscope (SEM, JEOL GSM-6610LV. Japan) operating at acceleration voltage of 20 kV. Specimen surfaces were coated with a thin layer of gold before observed. The fiber diameter of the electrospun fibers was measured using Image J software from the SEM pictures in original magnification. At least 100 isolated nanofibers were randomly selected, and their diameters and diameter distributions were measured and averaged.

2.4.2. Fourier-transform infra-red spectra (FT-IR).

FT-IR of blend nanofibers was recorded by a Fourier transform infrared spectrometer (FTIR, Shimadzu FTIR-8400 S, Japan) FTIR spectra. The experiments were carried out in the range of 4000 to 400 cm^{-1}. The infrared spectra were recorded in the transmission mode using thick mats of electrospun nanofibers.

2.4.3. Thermo-gravimetric analysis (TGA).

Thermal stability of electrospinning nanofibers was characterized using Thermo-Gravimetric Analyzer (Shimadzu Thermal Gravimetric Analysis (TGA)—50, Japan). All measurements were performed under a nitrogen atmosphere with a flow rate of 10 mL/min by heating the material from 25C^0 to 600C^0 at a heating rate of 10 C^0 min^{-1}.

2.4.4. Swelling properties.

The water content of the nanofibers after swelling value (S) was calculated using equation(1):

$$S=\frac{Wa-Wd}{Wd}X100 \quad (1) \qquad [12]$$

Where (Wa) was the water up-take per gram of the nanofibers, and (Wd) and (Wa) were the weight of the nanofibers after swelling and subsequent drying, respectively. The time duration for Swelling was (15, 30, 60, 120. 240, 360, 1440 min). The excess water on the swollen fibers was wiped out with a filter paper. Each sample for swelling should be checked in 3 times.

RESULT AND DISCUSSION.

3.1. Morphological characterization of nanofibers.

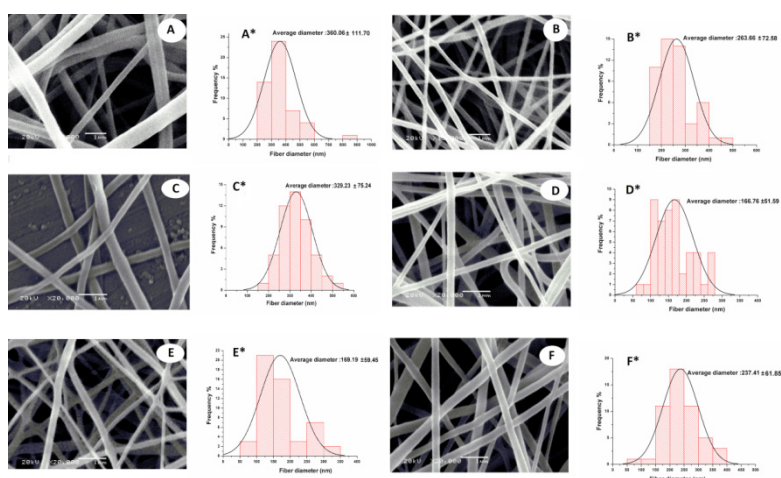*3.1.1. Effect of PEG content on the morphology of the resultant nanofibers.*
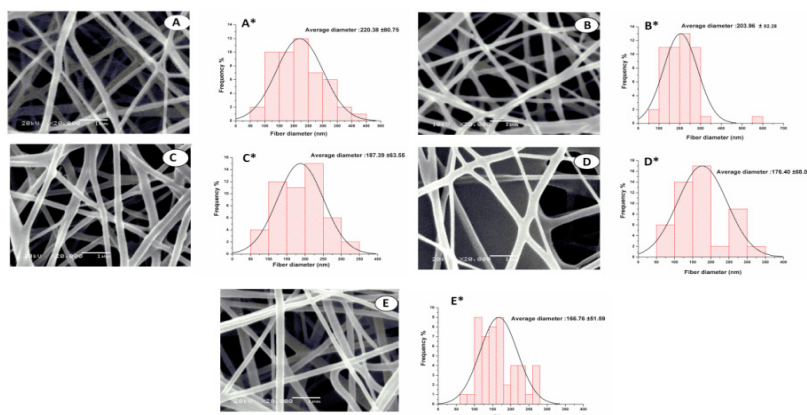
Figure 3: SEM photographs and distribution of the average diameter of nanofibers with various blend ratios (PVA: PEG), A) 7.9: 0.1%, (B) 7.75: 0.25%, (C) 7.5:0.5%, (D) 7: 1%, and (E) 6.5: 1.5%.

The SEM photographs and distribution of the average diameter as shown in Fig 3, PVA/PEG/GA solutions were maintained at a total concentration of 8% PVA were electrospun resulting various fiber morphology. The fiber morphology and average diameter were most influenced by the existence of PEG, including bond, irregular block, and small rough, uneven diameter distribution in Fig 3. When PVA/PEG blend fiber diameter and diameter distribution were seen to decrease as the concentration of PEG increased from 0.1 % to 1.5% the morphology of fiber improved, as show in Fig 3, the fiber diameter decrease from 220.38 ±80.75nm to 166.76 ±51.59nm. These results could be related to the well compatibility of the polymer solution at this ratio 1.5 wt % of PEG. Similar observations have been made by Lin et al [13] and Ignatova et al [14] who investigated a series of blend nanofibers membranes at different weight ratios and found a decrease in the average diameter of the nanofibers with increasing the blended content. Also formation of fibers with uniform morphology after electrospinning of PVA/PEG due to the high viscosity increases the interaction of two polymers, mainly through hydrogen bonding, and decreases the effects of surface tension [15].

3.1.2. Effect of GA on the morphology of the resultant nanofibers.

Figure 4: SEM photographs and distribution of the average diameter of PVA/PEG/GA nanofibers with various concentration of GA, (A) 0.5%, (B) 1%, (C) 1.5%, (D) 2%, (E)3%, and (F) 4%

The effects of the different concentration of GA on the solution properties of PVA/PEG/GA blends and on the morphology of the resultant nanofibers were studied using a scanning electron microscope (SEM). The surface morphology of electrospun nanofibers are presented in Fig. 4A–F.According to the SEM images, the surface morphology and the average diameter of the nanofibers are dependent on initially added GA concentrations. GA is a more effective cross-linking agent than other aldehydes [13]. When the concentration of GA increased the nanofibers morphology changed and the fiber become continuous and enhanced fiber-structures. As show in Fig 4 as the concentration of GA increase from 0.5 to 2 wt% the fiber diameter decrease from (360.06 ±111.70 to 166.76±51.59) then fiber diameter increase as the concentration of GA reached to 4% (237.41± 61.85) that is due to the cross-linked of fibers show a wider distribution, indicated by the increased standard deviation, due to the constantly changing viscosity of the electrospinning sample [16] .
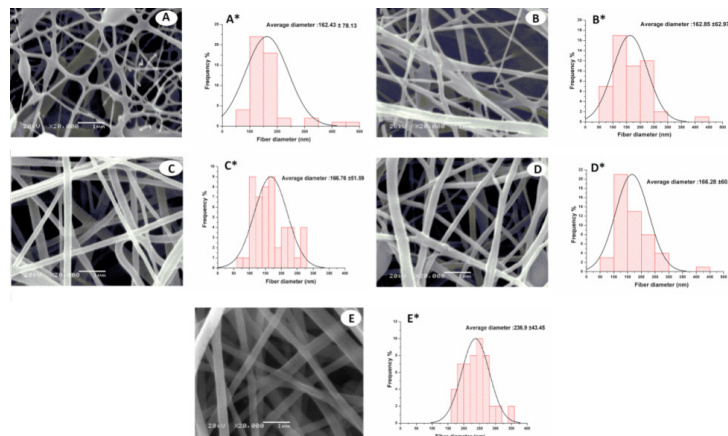

Figure 5: SEM photographs and distribution of the average diameter of   PVA/PEG/GA nanofibers with various reaction times with GA, (A) 15, (B) 30, (C) 60, (D) 90, and (E)120 min

Figure 5 shows SEM morphology and diameter distribution of PVA/PEG/GA blend nanofibers with various reaction times with GA. The increase in the time of crosslinking affect on the morphology and average diameter and distribution of the nanofibers. When the reaction times with GA increased the nanofibers morphology changed and the fiber become continuous and enhanced fiber-structures. Also, the amount of nanofibers cross linked increased and the nanofibers morphology changed [17], and the fiber diameter increase from (162.43 ±78.13 to 236.9 ±43.45). Moreover, the distribution of the PVA/PEG/GA blend nanofiber became broader. This behavior mainly attributed to the charge density increases in the PVA/PEG/GA blend solutions during electrospinning, resulting in strong electrostatic repulsion among the sprays. This repulsive force easily overcomes the surface tension of the jet to reduce diameters of the nanofibers [18].
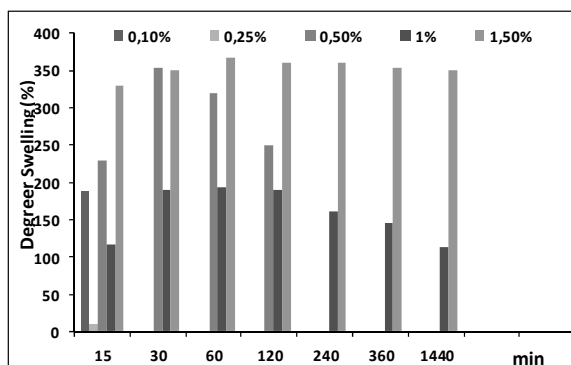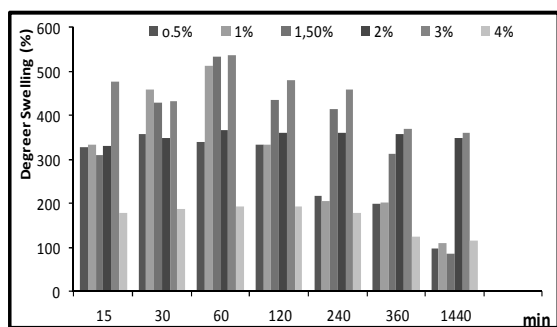
3.2. Swelling properties.

Figure 6: Swelling properties of PVA/PEG/GA nanofiber with various blend ratios.

Figure 6 revealed the relationship between the swelling ratio of the PVA/ PEG blend and the PEG content in the blend at 20 C⁰. It could be seen that as PVA/PEG mass ration increased the PVA/ PEG blend become more insoluble in water due to the addition of PEG to PVA each other will increase the surface of the fiber and increase the free (-OH) that formed hydrogen bond with water[19] .So, PEG content was increasing from (0.25 to 1.5wt%) lots of pore fiber formed to do dissolution of some portion of fiber allowing incorporation of amount of water, which resulted in an increase in degree of swelling. So, the charge density of PVA and PEG will play a major role in the swelling and stability of the formed blend. Finally, the swelling ratio of a blend is related to physic-chemical factors, such as the crosslinking density, blend composition, network structure, etc.

Figure 7: Swelling properties of PVA/PEG/GA nanofiber with various GA crosslinking.

The swelling property of PVA/PEG/GA nanofiber was studied in water with different GA concentrations (0.5–4%) for different time periods (from 15 to 1440 min). Differences in swelling tendency are shown in Figure 7. It was observed that the effect of cross-linking is still more important, swelling ratio for PVA/PEG with 1, 1.5, and 3% GA more than 500% after 1 hour. After that the nanofibers showed a slight decrease in the swelling ratio as the length of exposure was increased. The presence of a large number of hydroxyl groups in nanofiber results in strong hydrogen bonding (may be of both intermolecular and intermolecular types), which in turn affects the solubility of nano fiber in water [20] .When PVA/PEG nanofiber crosslinked with GA formation of acetyl bridges between

the aldehyde ends of the GA and the hydroxyl groups of nanofibers both in intermolecular and/or intermolecular fashion occurred within and at the point of contact between nanofibers. We also observed that with the increase in GA concentration and the crosslinking reaction time the nanofibers crosslinked increased. Also, when the GA concentration increased from 0.5% to 4wt % the SEM micrograph showed swollen fiber network and the morphology of nanofibers changed with increased cross-linking time, the nanofibers became more swell [21] .
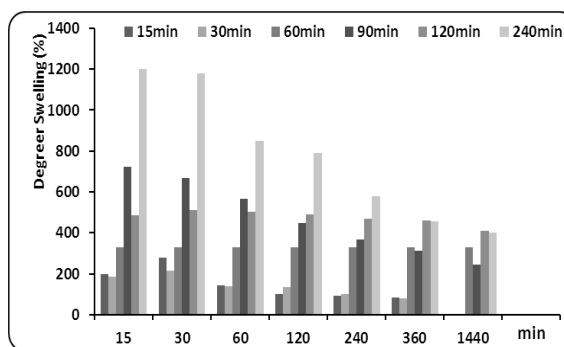
Figure 8: Swelling properties of PVA/PEG/GA nanofiber with various GA crosslinking reaction times.

Figure 8 indicates the swelling results of PVA/PEG/GA nanofiber in water with different GA reaction times (15 and 240 min). As shown in Fig. 8 a higher swelling and water uptake ability were observed for the PVA/PEG/GA nanofiber after 15 min reaction time with GA. PVA/PEG/GA nanofiber exhibited a completely swollen morphology that may be due to the hydrophilic properties of PVA/PEG/GA crosslinked nanofiber. However, the PVA/PEG/GA crosslinked nanofiber with reaction time 240 min showed a lower swelling ratio compared to reaction time 15 min. increasing the crosslinking time from 15 min to 1440 min decreased their swelling capabilities noticeably from 1200% to 400%. The reduced fiber swelling in the PVA/PEG/GA crosslinked nanofiber may be a result of increased PVA/PEG/GA nanofiber hydrophobicity reducing the interaction of the aqueous medium with the fibers.

### 3.3. FTIR spectrum of PVA/PEG/GA nanofiber.
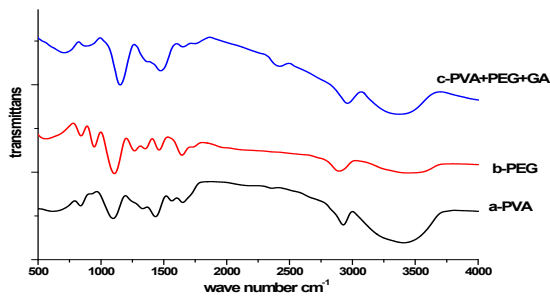
Figure 9: FTIR spectra of (a) PVA, (b) PEG, and (c) PVA/PEG/GA nanofibers.

FTIR spectrum of pure PVA reference shown in Fig 9a the major peaks associated with PVA for instance, it can be observed (C–H) broad alkyl stretching band (2850–3000 cm⁻¹) and typical strong hydroxyl bands for free alcohol no bonded (–OH) stretching band at (3600–3650 cm⁻¹), and hydrogen bonded band (3200–3570 cm⁻¹) [22] Intra molecular and intermolecular hydrogen bonding are expected to occur among PVA chains due to high hydrophilic forces. An import absorption peak was verified absorption band(C-O) at 1142 cm⁻¹ has been used as an assessment tool of poly (vinyl alcohol) structure because it is a semi crystalline synthetic polymer able to form some domains depending on several process parameters [23]. In Fig 9b, the IR spectra of PEG have exhibited important absorption bands from FTIR spectroscopy measurements as shown in the figure. It was verified contributions associated with stretching of ether groups [24] .from (1050 to 1150 cm⁻¹) with maximum peak at 1150 cm⁻¹. Characteristic alkyl (R–CH□) stretching modes from (2850–3000 cm⁻¹) were observed [25]. Also, (OH) hydroxyl group contribution was observed with absorption ranging from (3200–3600 cm⁻¹). It should be noted that the presence of hydrophilic and hydrophobic moieties in poly ethylene glycol chains verified by FTIR spectroscopy generally gives them a unique ability of to be soluble in both aqueous and organic solvents. As a consequence, PEG is widely used separated, conjugated or blended with other polymers such as PVA [23]. Fig 9c shows FTIR spectroscopy for the blend fiber with GA. The large broad band observed at(3200−3650 cm⁻¹) are associated with the stretching vibration of hydroxyl (−OH) group from intermolecular and intra molecular hydrogen bonds and their intensity were observed relatively decreasing when compared to electro spun PVA Nano fibrous mat as the cross-linking increases indicating that more of the −OH groups are involved in the formation of acetyl bridge .The two vibrational bands observed between (2730 and 2860 cm⁻¹) refer to the stretching vibration of C−H from alkyl and O=C−H from the aldehyde and the bands between(1700 and 1750 cm⁻¹) are due to the C=O stretching of the unreacted end of the aldehyde in the cross-linked PVA,PEG nanofiber. The band observed at (1000−1140 cm⁻¹) with gradual broadening of the peak width as the cross-linking reaction time increase is attributed to O−C−O vibration of the acetyl group [26].

3.4. TGA of PVA/PEG/GA nanofiber.
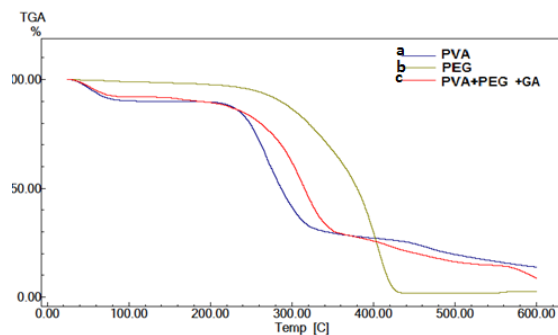
Figure 10: TGA thermograms of (a) PVA, (b) PEG, and (c) PVA/PEG/GA nanofibers.

Figure 10 shows the TGA of PVA, PEG, and PVA/PEG/GA nanofibers. TGA is a powerful technique, usually employed for the analysis of the decomposition and thermal stability of materials. TGA measures the weight change as a function of temperature. As the temperature increases, the weight of the sample decreases, indicating the continuous composition of the sample In the TGA thermogram. The PVA nanofiber lost about 8% mass at temperatures up to 77 °C due to the evaporation of absorbed moisture Fig 10a, the decomposition of PVA began around 218 °C and lost half of its mass at 324 °C, leaving merely 5% residue at 600 °C. The TGA thermogram of PEG nanofiber Fig 10b showed slightly lowered

moisture absorption as well as onset temperature of decomposition It lose about 3% at 229 °C leaving 6% residue at 431°C. The extents of lowered moisture absorption and onset decomposition temperature of decomposition were generally increased with longer PEG chain lengths and higher PEG contents. Also, fig10c illustrates the TGA of the crosslinked PVA/PEG/GA nanofiber, the first region at a temperature of 80 °C the sample loss of 7% it was due to the evaporation of free and bound water. The transition region at around 206-356 C° loss about 59% was due to the degradation of the GA, leaving merely 5% residue at 600 °C. The slight shifting represents the increase in the thermal stability which probably ascribed to the formation of crystalline polymer matrix as a result of cross-linking between the two polymers and formation of interpenetrating polymer network structure.

CONCLUSIONS

Electrospun PVA/PEG/GA nanofibers have been prepared using PVA, PEG and GTA as cross-linkers by an electrospinning technique. The effects of PEG and crosslinking method on the properties of crosslinked nanofibers were examined. PVA/PEG/GA nanofibers with a 1.5% PEG concentration exhibited a nanoscale fiber diameter. Also, the PVA/PEG nanofibers with GA crosslinking exhibited better properties. The physiochemical characterization of PVA/PEG/GA nanofibers confirmed their crosslinking and stability. Thermal studies show that incorporation of GA change the thermal stability of pure PVA/PEG nanofibers to a higher value due to the formation of crosslinked nanofibers. Also, the swelling and water uptake ability in water showed that the crosslinked nanofibers exhibited a slight change in morphology. The crosslinked nanofibers showed resistance to water and had enhanced thermal stability which may have important implications for industrial applications.

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