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Research Paper / Araştırma Makalesi

Effect of Adding Nanofibers into Sunflower (*Helianthus annuus*) Oil on Oil Viscosity

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ABSTRACT

The significant effect of the addition of very small proportions of nanofibres and nano-particulates on the physical and mechanical properties of solid materials has been long observed and described. The effect of addition of electrospun fibres on the physical properties of liquid has not been so widely examined. In this paper, the effect of the addition of polyvinyl alcohol (PVOH), and zein nanofibers in sunflower (*Helianthus annuus*) oil on its viscosity was observed and quantified. For a given amount of material, a trend of increasing effectiveness was found as fibre diameter reduced. The addition of 0.01% (by mass) of fibre increased the kinematic viscosity of oil samples by 15%. The presence of fibre in oil was confirmed by light microscopy whilst the size of the fibres was measured by the analysis of scanning electron microscope images (SEM). This phenomenon of a low concentration of nanofibers significantly increasing viscosity may find practical applications as a foodstuff thickener.

Keywords: Electrospinning, Nanofiber, Viscosity, Sunflower oil, Zein

Nanoliflerin Ayçiçeği (*Helianthus annuus*) Yağına Eklenmesinin Yağın Viskozitesi Üzerine Etkisi

ÖZ

Çok küçük oranlarda nanoliflerin ve nano-partiküllerin eklenmesinin katı malzemelerin fiziksel ve mekanik özellikleri üzerindeki önemli etkisi uzun süredir gözlenmekte ve açıklanmaktadır. Elektrospun nanoliflerin eklenmesinin, sıvının fiziksel özellikleri üzerindeki etkisi çok fazla incelenmemiştir. Bu çalışmada, ayçiçeği (Helianthus annuus) yağına polivinil alkol (PVOH) ve zein nanoliflerin eklenmesinin viskozite üzerindeki etkisi gözlemlenmiş ve ölçülmüştür. Belirli bir malzeme miktarı için, nanolif çapı azaldıkça etkinliği artırma eğilimi bulunmuştur. Kütlece %0.01 nanolif eklenmesi kinematik viskoziteyi %15 artırmıştır. Yağ içindeki nanoliflerin varlığı ışık mikroskopisi ile doğrulanmış, nanoliflerin morfolojisi ve çapları taramalı elektron mikroskobu ile ölçülmüştür. Bu pratik uygulama sayesinde düşük nanolif konsantrasyonu viskoziteyi arttırdığı için gıdalarda kıvam verici olarak kullanılabilirliği belirlenmiştir.

Anahtar Kelimeler: Elektroeğirme, Nanolif, Viskozite, Ayçiçek yağı, Zein

INTRODUCTION

Nanofibres are commonly defined as having an average diameter of less than 100 nm, although effects associated with nanoscale material addition can be observed at significantly larger scales [1]. The bulk of research on the application of nanofibres has traditionally been focussed on filtration, but the technology is now being expanded into other areas requiring materials with high specific strength, or a high surface to volume ratio. Although there are several methods used in the production of nanofibres, the simplest and most efficient nanofibre production method is electrospinning [2].

Electrospinning a conceptually simple and effective route to produce polymer fibres with diameters of sub-micron or nanometre scale of using electrostatic forces to draw a pendant droplet of polymer solution into a fine fibre followed by deposition onto a grounded collector [3]. Nanofibres have very large surface area to volume, aspect ratio and high permeability [4].

Bio-material based nanofibres have been investigated extensively to exploit their biodegradability, biocompatibility, thermal stability and good physical properties [2, 4–7]. Electrospun biopolymer nanofibres have also been highlighted as packaging materials and as additives to adjust texture and quality of solid foods. Electrospun fibre mats generally exhibit excellent film forming properties, emulsifying properties, bioadhesion associated with intrinsic long term electrostatic charge and outstanding resistance to oil [6]. It is therefore reasonable to assume that nanoscale biomaterial fibres can be used as practical physical property adjusters in food stuffs.

A preliminary electrospinning trial was carried out to produce electrospin fibre mats from PVOH and zein. The production of zein nanofibres by electrospinning has been widely reported elsewhere [2, 8], and glacial acetic acid was confirmed to give better spinning continuity than aqueous ethanol [10]. This choice of polymer and solvent system gave a range of fibre sizes, so that the effect of change in surface to volume ratio could be examined.

As previously noted it has been reported that small quantities of nanoscale material can have a significant effect on the macroscale properties of solids. The addition of sub one percent levels of nanoparticles can significant affect the strength of polymers [11], for example, the addition of nanoscale exfoliated montmorillonite clay significantly alters the permeability of polymers by raising the mean tortuous path of the diffusing species through a film. It has also been reported that substantial increases in composite tensile strength and stiffness are gained by the addition of a fraction of a percent of electrospun fibres. The reason for the high level if property variation associated with low levels of nano-scale material has been attributed to the formation of an interphase zone surrounding the fibre surface [12]. It is suggested that contact with a solid phase affects the local molecular organisation of the liquid phase [13]. In the case of a solidifying polymer resin, this may influence the development of the structural morphology of the composite matrix.

It seems reasonable to extend this thinking to assume that a similar effect on the short-term order of a liquid might be observable as a change in liquid phase properties. To test these hypotheses insoluble fibres were added to a liquid, and the apparent viscosity of the suspension was measured and related to the degree of fibre addition.

The rheological properties of whisker suspensions have been extensively studied both from theoretical and experimental points [14]. However, the effects on rheological characteristics of varying proportions and amounts of long nanofibres dispersed in vegetable oil (as an example foodstuff) have not thus far been widely discussed or systematically investigated.

This paper seeks to extend the use of nanofibres into the modification of liquid properties by using nanofibres made from a combination of the water soluble and semi crystalline synthetic polymer, Polyvinyl alcohol (PVOH), and from the ethanol extracted corn protein zein, and the use of this spun material to alter the viscosity of sunflower (*Helianthus annuus*) oil.

The main objective of this work was to examine the effect of blending PVOH and zein nanofibres in sunflower oil at different concentrations. It was determined rheological behaviour added to very low concentration of these suspensions to interact with sunflower oil. Dynamic and kinematic viscosity values were performed in rotational viscometer and standard ASTM methods.

MATERIALS and METHODS

The polyvinyl alcohol (PVOH) had an average molecular weight of 118,000 g mol^{-1} and degree of hydrolysis (DH) in the range of 85-90%. A stock polymer solution was prepared by dissolving PVOH in distilled water for approximately 2 hours at 60°C with constant stirring using a hot plate with a magnetic stirrer. The stock polymer concentration was determined by drying a small sample in a convection oven at 80°C to determine the weight of solids. This stock solution was then diluted to a final concentration of 10%.

Pure sunflower oil (KTC (Edibles) Ltd, West Midlands, UK) was used as supplied. Zein (Flo Chemical Corporation, MA, USA) solution was prepared as 25% by dissolving zein in glacial acetic acid (Sigma-Aldrich, St. Louis, MO) with a magnetic stirrer for 30 min at room temperature (22±2°C). The proportions of all the solutions were prepared by weight.

Electrospinning Application

The electrospinning process was carried out using with a Model ES4 "Adam" electrospinning machine (Electrospinz Ltd., New Zealand) at ambient conditions (temperature 22°C and relative humidity 64%). This electrospinning machine was fed by a constant pressure header tank. The feed pressure was varied by adjusting the feed head (Figure 1).

The zein solution were introduced in feed head tank and the needle tip to collector distance was adjusted to 10 cm and the applied voltage was set to 12 kV. The distance and voltage of PVOH solutions in feed head tank were set to 12 cm and 16 kV, respectively for electrospinning process. These values were found as optimum according to preliminary trials.

The PVOH or zein fibres were spun into pure sunflower oil, which was poured into a circular catchment vessel containing 200 mL of oil, with timed depositions of 30, 60, 90 and 120 min. The polypropylene pipette tip used as a spinneret was an Axygen T-200-Y 200 µL pipette tip with an orifice diameter of 0.5 mm. Measurements of the processing parameters was done to an accuracy of ±1 mm for the working distance, ±250 V for the potential difference and ±0.5 mm for the head distance that gives the hydrostatic pressure.

The mass deposition rate was estimated by depositing fibre onto an aluminium foil target of similar surface area using the same processing conditions. For each set of voltage and distances samples were produced by depositing over periods of 1, 5, 10, 20, 30, 45 and 60 min. The as-spun electrospun fibres were dried for 24 hr at room temperature. To determine the mass deposited, each aluminium foil target was weighed (Mettler Toledo AG204) before and after deposition.

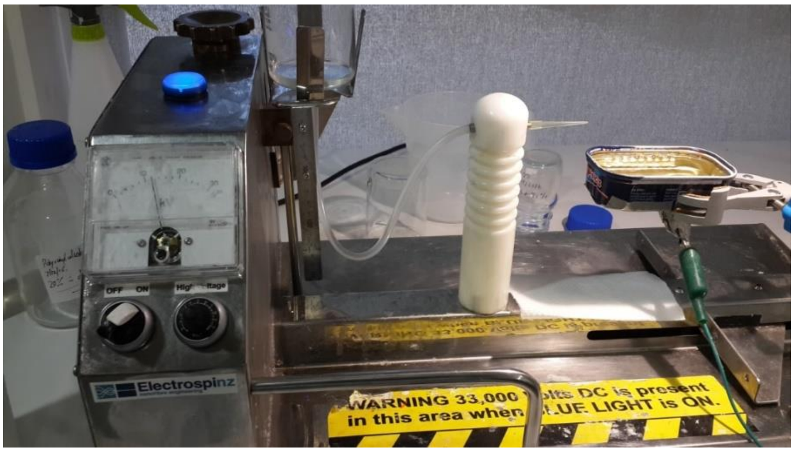

Figure 1. Electrospinning apparatus

Scanning Electron Microscopy

PVOH fibres were collected on a scanning electron microscopy (SEM) sample stub until the stub was fully covered. The morphology of the fibres was examined using a Jeol NeoScope JCM-5000 Benchtop Scanning Electron Microscope after sputter coating the samples with gold under vacuum for 120 second at 20 mA using Quorum Q150R-S sputter coater (Quorum Technologies Ltd., Ashford, Kent, UK) to reduce electron charging effects. The fibre diameter was measured as the average diameter of about 1000 fibres using SEM analyser Software (Electrospinz Ltd, NZ).

Measuring Viscosity

Viscosity measurements were performed for a range (0, 0.0075, 0.0150 and 0.0300%) of PVOH and zein fibre suspensions in sunflower oil at a temperature of 22°C using a digital rotational Brookfield Viscometer (Model E2-RV8, Brookfield Engineering Laboratories, Stoughton, MA), using a No. 2 Spindle rotating at 50 rev/min. A 200 mL sunflower oil sample was used for all measurements, being sufficient to just cover the immersion groove on the spindle shaft. The measurements were repeated three times and the average values were used to estimate the dynamic viscosity.

To measure apparent viscosity, we measured the flow of the oil samples through a standard orifice using a Ford cup-type viscometer (Ford-4). The measurement is based on recording the time required for the sunflower oil samples to flow through a 4.12 mm diameter orifice in the bottom of the cup [15].

The kinematic viscosity in centistokes (cSt) was calculated from the flow time with Eq. 1.

$$v=K*(t-c) \qquad (1)$$

where v=kinematic viscosity (cSt), t=time of flow (s), K=3.85 for a Ford-4 cup, and c=4.49 for a Ford-4 cup.

The dynamic viscosity (cP, µ) was calculated from the kinematic viscosity by Eq. 2 multiplying the kinematic viscosity by the fluid density (g cm^{-3}, ρ):

$$v = \mu / \rho \qquad (2)$$

Light Microscopy

Micrographs of sunflower oil samples were obtained using a light microscope (Olympus System Microscope model BX51TF, Olympus America Inc., Center Valley, PA, USA) equipped with a digital camera (Olympus EX300, Olympus America Inc., Center Valley, PA, USA). One drop of the sunflower oil sample was placed in the cavity (15 mm diameter) of a glass microscope slide, covered with glass cover-slip, and examined using a magnification of 20x. Images were acquired with a video camera mentioned above.

Statistical Analysis

All experiments were performed twice with at least three replications of each fibre concentration. SPSS statistic program (Statistical Package IBM SPSS statistics 22 software, USA) was performed for all calculations, and the significance was determined by one-way ANOVA, while statistical significance was measured at a confidence level of 95%. Post hoc analysis using Tukey's Test was also employed for all samples ($p<0.05$).

RESULTS and DISCUSSION

For a given voltage and distance the mass deposited on the collector electrode increases linearly with time. Figure 2 shows variations of dynamic viscosity with different concentration of zein and PVOH nanofibers in sunflower oil. The gradient of the linear trend is the mass deposition rate. The intercept is not at zero because there is a constant and consistent offset effect associated with the effect of the intrinsic charge of the fibre on the mechanism of the balance.

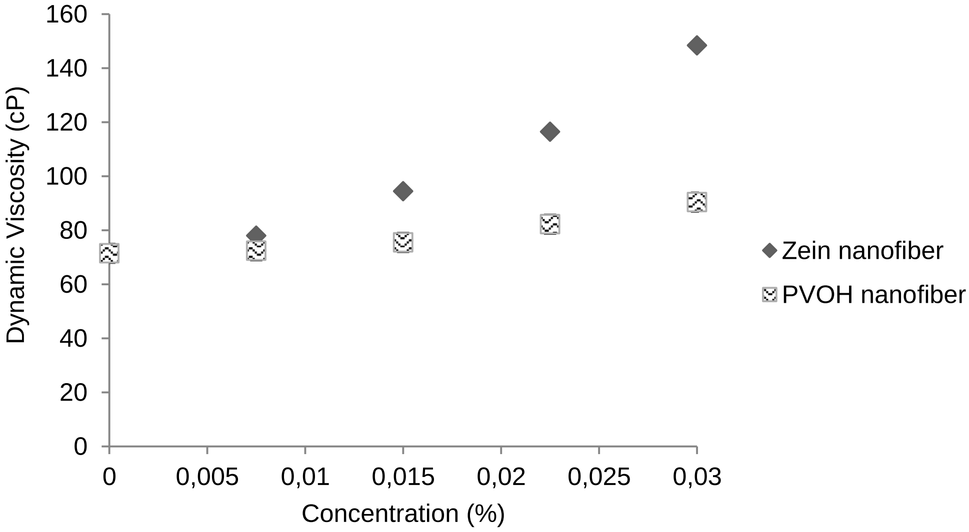

Figure 2. Variations of dynamic viscosity with different concentration of Zein and PVOH nanofibers in sunflower oil

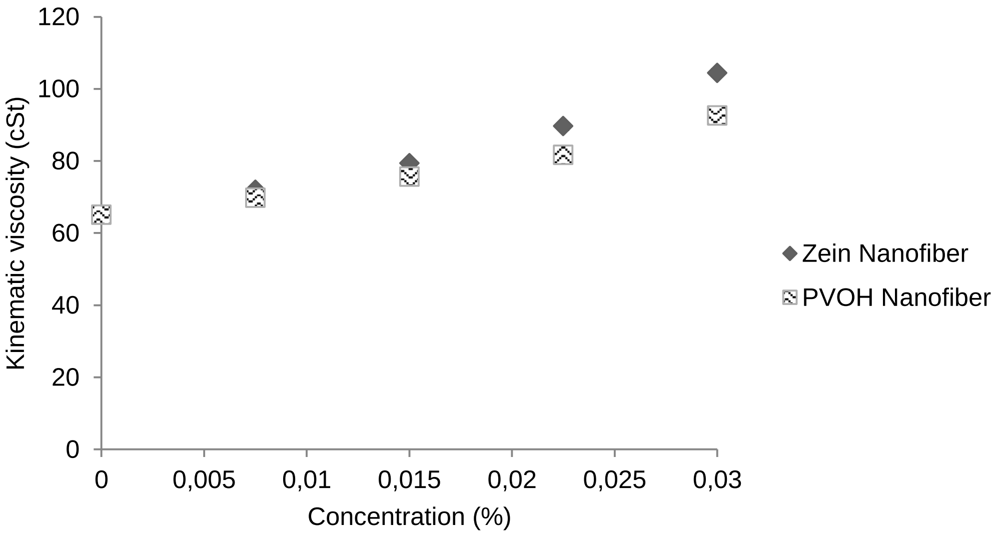

Figure 3. Variations of kinematic viscosity with different concentration of Zein and PVOH nanofibers in sunflower oil

The viscometer used is of rotating bob type. Hence, the shear rate is produced by a spindle rotating at a certain rotational speed, N (rpm). Figure 3 indicates that the variation of kinematic viscosity respectively with different concentration for each of the samples in the sunflower oil. The viscosity also increases significantly with the increases in concentration (%) of nanoparticles in sunflower oil ($p<0.05$). This represents that the nanofiber concentration is an effective viscosity control parameter.

The results found that dynamic and kinematic viscosity for zein nanofiber increases significantly as the nanofibre concentration in sunflower oil is increased from 0.0225 to 0.0300% – the viscosity increases very sharply ($p<0.05$). It is clear that the addition of electrospun nanofibres leads to a significant increase in the viscosity of the sunflower oil. The results show that zein nanofibres have greater effect on viscosity than the PVOH nanofibres. The dynamic viscosity of neat sunflower oil is 71.5 cP. The dynamic viscosity results show that in comparison to sunflower oil at 0.03% for zein nanofibres is increased by 107.7% and PVOH nanofibres by 26.6%. Kinematic viscosity results show that in comparison to sunflower oil at 0.03% for zein nanofibers the enhancement in viscosity is 60.5% and PVOH nanofibers is 42.3%.

Shear thickening behaviour was as an increase in viscosity with increase in shear rate. This shear thickening effect can be explained by possible agglomeration of tangled nanofibers and, resulting in more viscous drag. By increasing the concentration of nano particulates, particle to particle interactions increase which results in a rise in viscosity. At constant temperature, the viscosity of sunflower oil containing nanofibres increases with degree of nanofibre loading. When the concentration of nanoparticulates is increased, particle to particle bonding increases which in turn increases viscosity. The results indicate that viscosity increases with the nanofibre concentration, while going from 0.015 to 0.300% concentration and this viscosity increase is sharp as shown in results. These nanofibres exhibited increasing viscosity with concentration because of an increase network structural interactions.

Optical microscope pictures showing the morphology of PVOH electrospun fibres in sunflower oil are represented in Figure 4.

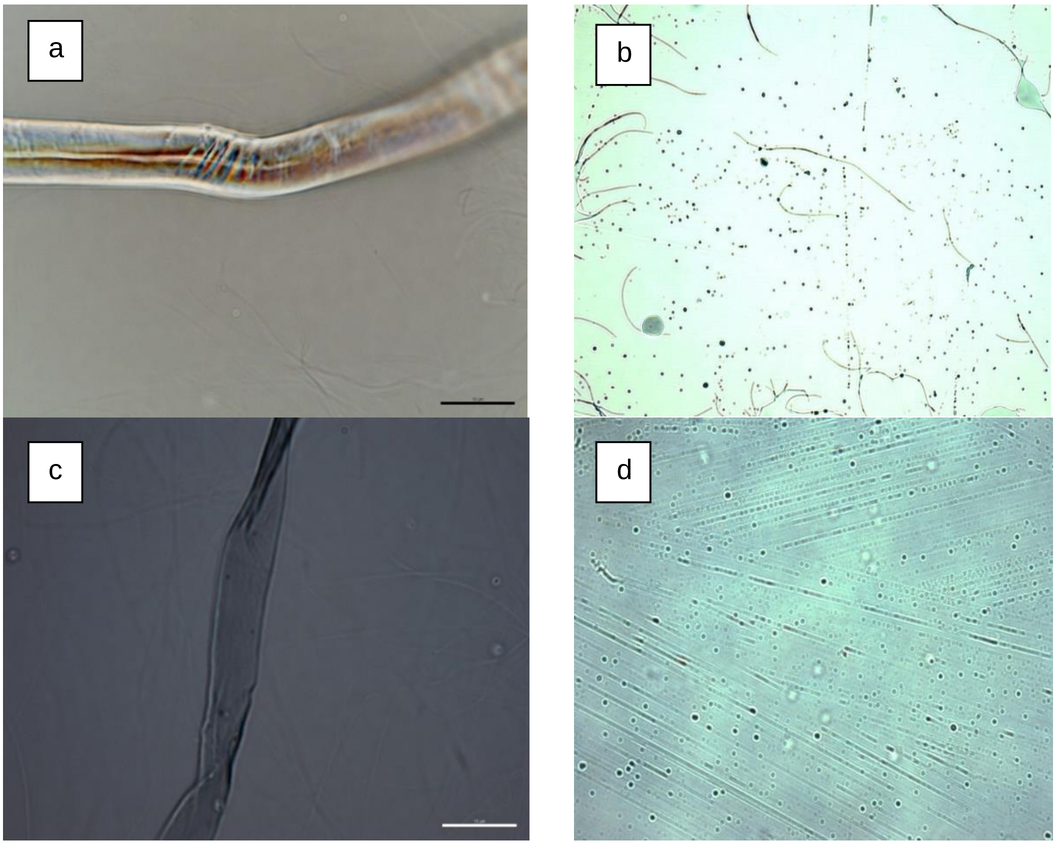

Figure 4. Optical microscopy image a few layers of nanofiber suspensions in sunflower oil deposited on a glass slide a) PVOH nanofiber at 100x magnification, b) PVOH nanofiber at 20x magnification, c) Zein nanofiber at 100x magnification, d) Zein nanofiber at 20x magnification

The images show PVOH fibres from electrospinning processing created in sunflower oil. The images in Figure 5(a) and 5(b) are SEM images of the PVOH and zein nanofibres, respectively. The SEM images taken during the study ranged in magnification with 5000x images used for fibre diameter measurements. The SEM images of PVOH and zein nanofibres were of fibres obtained using the following electrospinning parameters: Voltage: 12 kV and 16 kV, Distance: 10 and 12 cm, respectively. It can be seen that the diameter of the PVOH nanofibres is less that the zein fibres. It is clear from the characterisation results that the addition of electrospun nanofibres led to an increase in the dynamic and kinematic viscosities of the sunflower oil: as the percentage of the nanofibre increased, the viscosity increased. The increase in the viscosity was highest with the addition of 0.0300% concentration of zein nanofibres and the lowest for neat sunflower oil. The zein nanofibre diameters are smaller than the PVOH fibres. This supports the theory that the viscosity increases in a dispersed sample is due to increased attractive surface interactions as a result of a greater surface-to volume ratio [1].

PVOH is synthetic biopolymer and is difficult to disperse in the liquids. This is probably because PVOH is water-soluble and oil is a hydrophobic, resulting in a challenging mixing process. The size measurements from the SEM micrographs determined that the average diameter of fibers. The average diameters of zein and PVOH nanofibers were calculated 219 and 286 nm, respectively. Goksen et al. [16, 17] found similar diameter of neat zein and PVOH nanofibers. The smooth and homogeneous bead-free ultrathin fibers were fabricated (Figure 5). These selected two food grade and biodegradable polymers have spinable capability [18, 19].

The nanofibre size was another influence parameter on viscosity. Similar concentrations of zein nanofibres in sunflower oil with had higher viscosity than PVOH nanofibres. As previously noted, PVOH nanofibres were more difficult to blend than zein nanofibres in the sunflower oil. Although with PVOH nanofibres it seems that fibre diameter influences viscosity, the effect of the other issues also should be taken into account such as mechanical and morphological properties of fibres.

The PVOH nanofibres readily agglomerated and made clusters, and so were more difficult to disperse in sunflower oil than the zein electrospun fibres. This result is in accordance with the study by Jarahnejad *et al* [20] that a vigorous dispersion method avoids clustering and agglomeration. A second theory is that for homogeneously dispersed zein nanofibres, the growth in exposed nanoparticlate surface with an increase in the number of nanoparticulates was much greater than in a clustered sample, and hence greater viscosity was observed. The higher viscosity observed for the more concentrated nanofibres can be attributed to the stronger internal shear force among nanoparticulates. With increasing number of nanoparticulates, larger agglomerates form and consequently a larger force is required to disperse them. In addition, the greater effect of zein nanofibres on sunflower oil viscosity than that noted with PVOH nanofibres can be explained by possible agglomeration of bundled nanofibres, resulting in more viscous drag [20].

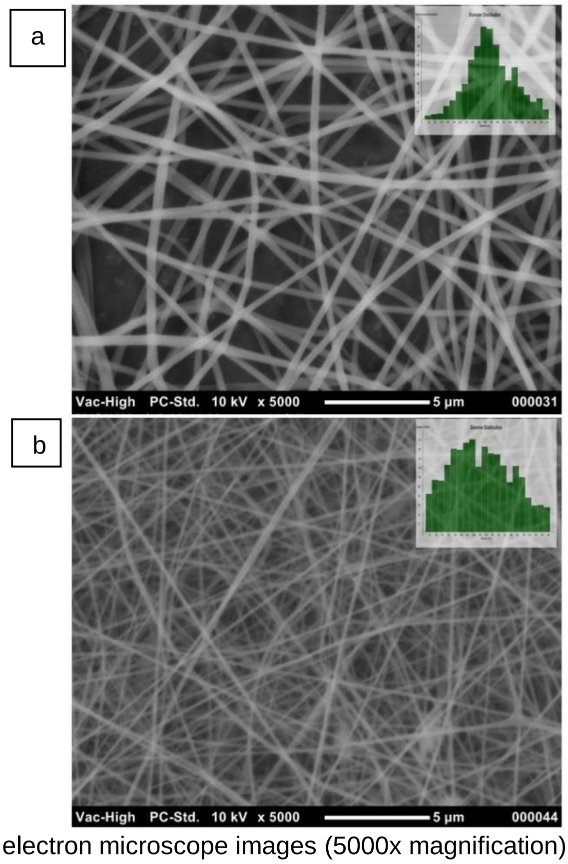

Figure 5. Scanning electron microscope images (5000x magnification) and diameter distribution histograms (a) PVOH nanofibers (b) zein nanofibers. The scale bar size is 5 µm.

CONCLUSION

The viscosity data with- and without- nanofibres shows that nanofibres have potential to be used instead of hydrocolloids for viscosity control in liquid or semi liquid foods. Our results also show that sunflower oil with modified by the addition of small quantities of electrospun biopolymers nanofibre exhibit non-Newtonian behaviour. Increasing the nanofibre concentration increases viscosity from that of the control neat sunflower oil. The effect of zein electrospun nanofibre on viscosity was greater than PVOH electrospun nanofibre. The viscosity increased with the concentration of all nanofibres showing that addition of these nanofibres, even in small amount, increase the viscosity of the sunflower oil. In brief, the addition of nanofibre increased dynamic and kinematic viscosities as compared to sunflower without any nanofibre even when added in very small amounts. In this study, it could be revealed that the use of nanofibers in low quantity can increase the viscosity of foods due to their tiny diameter, fibrous and porous structure.

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