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Production and thermal characterization of MWCNT reinforced polimethyl methacrylate (PMMA) nanofibers by electrospinning

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Abstract

In this study, the production of weight ratio of 1% multi-walled carbon nanotubes (MWCNT) reinforced / unreinforced Polymethyl Methacrylate (PMMA) nanofiber mats was carried out by electrospinning. PMMA concentration of 10, 12.5 and 15% weight in Dimethylformamide (DMF) solvent used in order to reach optimized electrospinning conditions. PMMA solutions with higher concentration ratio leading to higher viscosity and conductivity properties eliminates defects and imperfections and results improved quality of the products. In addition, different feed rates of 0.25, 0.50 and 0.75 ml/hour with 10 kV applied voltage power were compared for given MWCNT reinforced PMMA solutions electrospinning at specified concentration rate of solution were analyzed. Higher feed rates result thicker nanofiber diameters. Furthermore, Scanning Electron Microscope (SEM) images were investigated to determine the morphological properties of PMMA with MWCNT nanofibers and the average diameter of nanofibers. Optimum production parameters for 15 % wt. ratio and 0.5 ml/hr feed rate for electrospinning of PMMA-MWCNT solution were determined after comparison of results of alternative production options. We produced high quality bead-free nanofibers during electrospinning of PMMA fibers with MWCNT by manipulating dispersion methods, composition rates and electrospinning conditions. Thermal analysis of nanofibers was done by using Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA) in order to obtain Glass Transition Temperature (Tg), Melting Temperature (Tm) and Decomposition Temperatures (Td) with respect to mass loss.

Keywords: Electrospun, Multi Wall Carbon Nanotubes, Polymethyl Methacrylate, Nanofibers

1. Introduction

Nano composite materials with a polymer matrix and different nano fillers are studied widely with variety of different production parameters. Electrospinning technique enabling continuous nanofiber production is known as the best method in fiber production with many advantages such as manipulation of variety of different properties of the fibers (diameter, porosity, orientation, density and weight per area etc.) [1,2].

While there are several different compositions practiced, common high level expectations such as mechanical, electrical, chemical and thermal properties are based on some typical challenges during production [3,4].

First of all, dispersion quality of the fillers inside a matrix has a big role for improved performances. Uniform dispersion of filler material also has a vital role to provide similar properties for whole product since uniformity is required to sustain expected high quality under same production conditions [5-7]. Secondly, composition ratios for a solution can directly affect both process quality and the final properties of a product [8,9].

Another basic criteria to acquire target quality for all specimens is obtaining an optimized electrospinning conditions such as feed rate, applied voltage and tip-to-collector distance at different concentrations [6]. Minimizing product imperfections to an acceptable level can be possible by changing the electrospinning conditions to different predetermined levels and by comparing the results of different specimens produced by each conditions in order to understand how their affects would be on the final product [10].

We have tried to reach the best quality nanofibers during electrospinning of PMMA fibers with MWCNT by manipulating dispersion methods, composition rates and electrospinning conditions in order to understand their effects on dispersion quality, product property and material defects respectively [11,12].

Poly (methyl methacrylate) (PMMA) has known as one of the strongest engineering polymers with respect to perform chemical and biological assays due to its excellent chemical, physical, biological, mechanical, thermal and optical properties [13-16]. PMMA, a transparent thermoplastic polymer, has been widely used in many commercial applications such as drug delivery, actuators, sensors, batteries, his high impact-resistance, ease of fabrication, low density, and cost-effective technologies [17-20].

It is well known that nano-sized materials such as carbon nanotubes (CNT) have a disadvantage with respect to their high aspect ratios (L/D) and surface area which creates difficulties for their dispersion characteristics [21,22]. In many studies, Dimethylformamide (DMF) was used as a solvent to successfully dissolve PMMA and increase CNT dispersion within the matrix [23].

Aggregation of CNTs by the effect of van der Waals forces within carbon nanotube stacks and interaction between each CNT particles and solution is phenomena that needs to be well understand. Extensive research has been done in order to explain this behavior and its effect on mechanical strength of the material [24,25].

Related to mixing of CNTs with PMMA homogenously, ultrasonic mixing is a leading method of increasing dispersion applied in many similar studies successfully. By using ultrasound, interaction and effective stress transfer between CNTs and PMMA can be established by means of generating covalent bonding [26,27].

In this work, a series of laboratory studies were performed to select optimum production parameters for electrospinning of 10, 12.5 and 15% wt. PMMA, %1 wt. MWCNT and DMF solutions in order to improve quality of the products by eliminating possible defects and imperfections resulting bead-free uniform electrospun nanofibers. In addition, electrospinning conditions feed rates were altered during electrospinning at given concentration rate of solution aiming to reach optimized production variables.

2. Experimental

2.1. Materials

MWCNT with the outer diameter of 10-20 nm and the length of 30 μm were purchased from Sunnano, N,N-Dimethylformamide (DMF) and Polymethyl methacrylate (M_w ~ 350,000) were obtained from Sigma-Aldrich.

2.2. Solution preparation

PMMA with different concentrations (10, 12.5 and 15% wt.) were solved completely in DMF solvent by a magnetic stirrer at 60 °C for 60 min. At lower temperatures PMMA was not successfully solved within the DMF solvent. The first attempt done at room temperature (~25 °C) for 3 hours did not enable PMMA to solve and leaded PMMA particles stacked. Other trials at higher temperatures such as 40 °C and 50 °C shows better results at which PMMA tends to solve in DMF at some degree with increasing temperature. However, this procedure took extended period of times as long as 4 and 2.5 hours respectively. As a result, solution preparation works were decided to be continued with optimum speed of 60 min. mixing by magnetic stirrer at optimum temperature of 60 °C.

In addition, DMF solvent was chosen by comparing with various solvents such as dodecyl sulfate salt (SDS) and water in order to analyze solubility of both PMMA and also dispersion states of MWCNT contents in solvents since studies reveal that different solvents shows incompatible results [28]. For example, dodecyl sulfate salt (SDS) solvent caused deterioration of PMMA very fast and leaded solution to solidify uncontrollably.

2.3. Dispersion of multi-walled carbon nanotubes

1% MWCNT with respect to PMMA contents were added into the prepared saturated PMMA-DMF solutions and mixed by an ultrasonic homogenizer in order to acquire homogenous solutions. Uniform distribution of MWCNTs within solutions were achieved after mixing for 15 min. (3 x 5 min.) with 3min. intervals between each mixing to keep the temperature stabilized below 50 °C.

Ultrasonic homogenizer was set to give pulses at specified cycles. Water bath was used when the temperature of solution raise above 50 °C during intervals to prevent undesirable effects of high temperature such as boiling and faster vaporization or deterioration of the solution.

Figure 1 shows dispersing of MWCNTs within PMMA solution by an ultrasonic homogenizer in our study. It is clearly seen that MWCNT particles are separated from each other and even dispersion is achieved successfully.

Figure 1. Dispersion of MWCNT within PMMA solution by an ultrasonic homogenizer

2.4. Electrospinning

5 ml syringe with a metallic needle of 0.7 mm inner dia. was filled with the homogenous PMMA/MWCNT solutions and fixed vertically. A syringe pump was set to drive the polymer solution at different fixed feed rates of 0.25, 0.5 and 0.75 ml/hr while 10 kV voltage power was applied for 10, 12.5 and 15% wt. PMMA, %1 wt. MWCNT and DMF solutions. An electrospinning machine (Innovenso - NE300) having electrically insulated closed cabinet was used to produce uniform nanofiber sheets on 100 mm diameter. of plate collector at different pre-determined production parameters. Tip to plate

collector distance was set to 150 mm in order to produce equal diameters of products. Temperature was kept constant during the production process which takes 2-3 hours depending on the feed rates in order to have similar thickness of samples.

Figure 2 shows the steps of electrospinning process of PMMA/MWCNT solution inside electrospinning machine. The process was designed by using different production parameters with different PMMA concentrations and %1 MWCNT contents at specified feed rates. Alternatively, three different sets of production parameters were chosen as specified below.

Figure 2. Electrospinning process of PMMA/MWCNT solution a) preparation of injectors, b) system set-up, c) electrospinning of solution and d) 12.5 % wt. PMMA+1% wt. MWCNT nanofibers

Finally, a series of nanofiber production was done with 10, 12.5 and 15 % PMMA+1% wt. MWCNT contents at different specified feed rates of 0.25, 0.5 and 0.75 ml/hr by applying the power of fixed 10 kV voltage. Thus, the total of nine different nanofibers were acquired.

2.5. Characterization

SEM images were compared after scanning various electrospun samples by applying 20 kV voltage with ZEISS Evo LS 10 scanning electron microscopy at Selcuk University Advanced Technology Research & Application Center. We decided to focus on specific successful production parameters which are identified as a result of many trial and error processes.

TGA/DTA analysis were carried out to determine energy changes of %1 weight MWCNT reinforced PMMA nanofibers. TGA/DTA measurements were performed with Setaram-Labsys Evo Instruments at Necmettin Erbakan University Technology Research & Application Center (BITAM). The test samples (10-20 mg) were heated at 25 °C to 500 °C with a heating rate of 10°C/min under a nitrogen atmosphere.

3. Results and Discussion

3.1. SEM images of nanofibers

In this study, we further investigated SEM images of electrospun nanofibers produced with three pre-determined specified parameters of 10, 12.5 and 15% wt. PMMA with the %1 wt. MWCNT contents with respect to PMMA.

High resolution Scanning Electron Microscopy (SEM) technique was used to investigate produced electrospun nanofiber samples and measure basically nanofiber diameter, orientation, pore sizes and fiber distributions to identify the quality of the product in conjunction with defects and imperfections of the material. SEM images are successfully used in many researches about material science at nanoscales thus allow us to examine and characterize morphological features at nanofiber scale. This essential scanning method also helps us to evaluate nanofiber orientation and visual inspection of the sample microstructure in order to predict and interpret its mechanical properties.

After the investigation of SEM images for the first series of production with 10% PMMA-MWCNT solutions, it is clearly seen that bead formations were formed inside nanofibers as shown in Figure 3.a. It is well known that the number of beads are inversely correlated to the mechanical properties of nanofibers so that we can assume the quality of the materials can be increased by means of decreased number of beads or obtaining uniform bead-free PMMA nanofibers by totally eliminating imperfections.

As given in Fig.3.b, SEM images for the second series of production with 12,5% PMMA-MWCNT solutions shows that while the number of beads were decreased at some level, it was not considered satisfactorily and still far from having bead-free nanofibers.

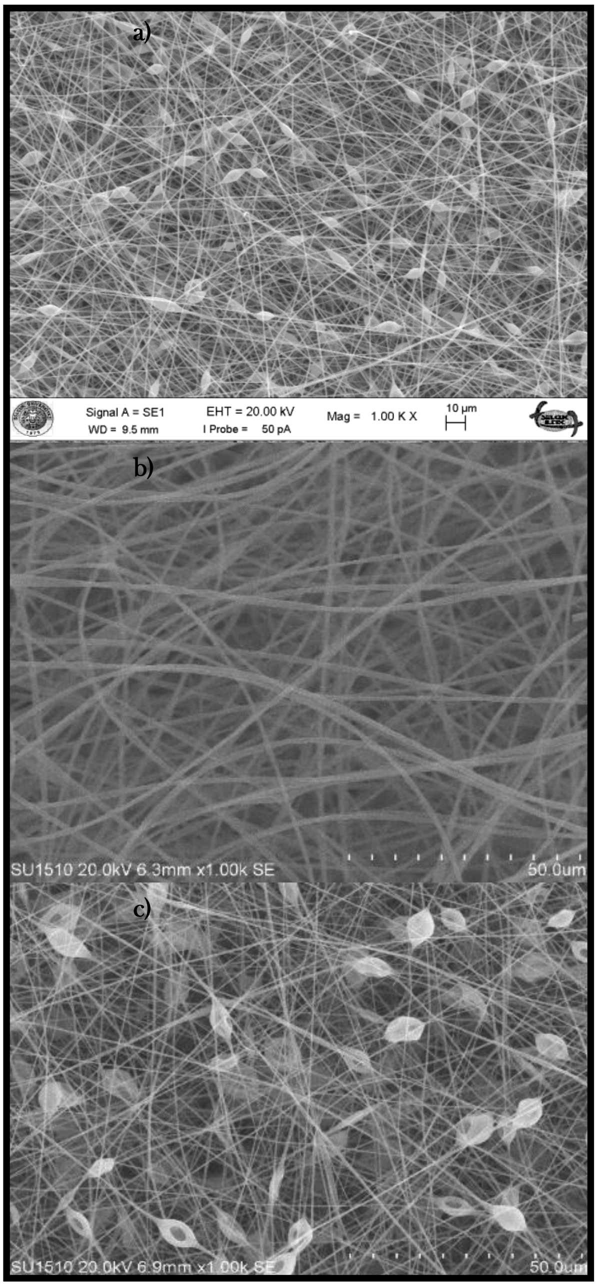

Figure 3. 1.0 KX SEM images of the PMMA-MWCNT nanofibers a) 10% (w/v), b) 12.5 % (w/v) and c) 15 % (w/v)

Increasing the PMMA concentration in DMF from 10% (w/v) to 12,5 15% (w/v) and finally to 15% (w/v) caused significant viscosity increase due to higher concentration of PMMA polymer. Since we kept the amount of MWCNT at 1% (w/w) with respect to PMMA concentration, the density of solution was increased not only by means of PMMA but also with the effect of MWCNT additive. It can be concluded that the increase of viscosity of solution as a result of MWCNT addition was considerably effective. Because of the high surface area of MWCNT and its contribution to interaction in PMMA/MWCNT solution causing strong bonding between MWCNT molecules and PMMA polymer chains, viscosity of the solution was increased further than that the PMMA could cause.

Figure 3.c shows the result of increasing amount of the PMMA/MWCNT in solution resulting higher viscosity rates which positively affect the quality of electrospuns. In addition, it was clearly observed that we obtained bead-free electrospun nanofibers thanks to higher viscosity of solution.

3.2. Thermal analysis of nanofibers

TGA/DTA result of the PMMA-MWCNT nanofibers is shown in Figure 4. DTA/TGA curves of PMMA-MWCNT nanofibers are similar to other PMMA curves found in the literature [29]. Deterioration of PMMA-MWCNT nanofibers takes place two-steps that starts at 65 C° to scission at the vinyl terminated end and at 280 C° to random scission of the PMMA back bone respectively [30]. Addition of MWCNT powders into PMMA polymer under the nitrogen atmosphere causes significant effects on thermal behaviors of PMMA deterioration. In the literature, the temperature of PMMA deterioration and residual mass quantity are 475 C° and %10 respectively. However, deterioration temperature and residual mass quantity of PMMA-MWCNT nanofibers are 485 C° and %12. Increase of residual mass is originated from the addition of MWCNT with %1 wt. into PMMA polymer. Furthermore, DTA curve shows that the glass transition temperature (Tg) of PMMA-MWCNT nanofibers is 130 C° while the glass transition temperature (Tg) of PMMA is 122 C° [31]. In addition, endothermic reaction takes place for PMMA-MWCNT nanofibers according to DTA curve.

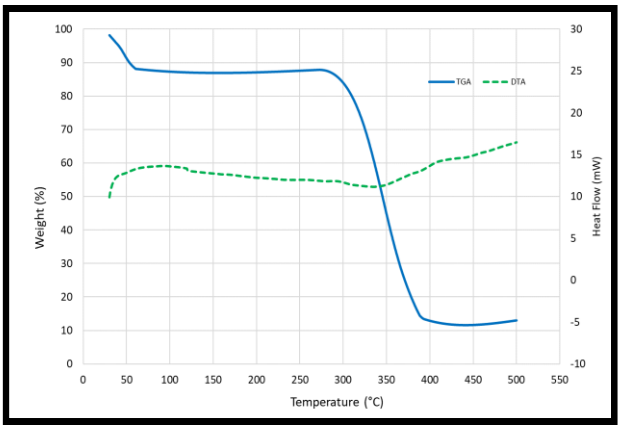

Figure 4. TGA plot of the PMMA-MWCNT nanofibers

Reasons for both thermal stability and the glass transition temperature (Tg) increase of the PMMA polymer from the presence of the MWCNT additive are; i) structural inhibition of the rotation, entanglement and bending motion of the molecular shaped chain, ii) reduction of the chain density of molecular weight, iii) effect on the structure of the molecular chains and iv) bonding of some polymers to the functionalized/non-functionalized oxide surfaces via the carbonyl group due to the adsorption of the oxide nanoparticles [32]. The reason for this fact is associated with resistance to variability of rotational motion, segmental mobility of polymer chains and chain density, which becomes relatively more effective by homogeneous distribution of MWCNTs in PMMA solution.

4. Conclusion

This study reveals that there are basically two main issues need to be considered regarding the quality of nanofibers production. The first one is solution preparation issue which is vital for solving PMMA content within a proper solvent at optimum temperature successfully by trying with DMF solvent by alternating temperature parameters. DMF solvent with optimum speed of 60 min. mixing by magnetic stirrer at optimum temperature of 60 °C was used to solve PMMA.

The second issue need be under control is identifying the optimum electrospinning parameters which have a vital role to keep the nanofiber electrospun quality higher especially for obtaining homogenous material properties for each sample and within each sample. Alternative feed rates of 0.25, 0.5 and 0.75 ml/hr was used to inject the polymer solution at 10 kV voltage power. Different parameters of 10, 12.5 and 15% wt. PMMA with the %1 wt. MWCNT contents with respect to PMMA were applied. After deciding the optimum production parameters of electrospinning process as feed rate of 0.5 ml/hr and concentration of solution with 15% wt. PMMA, we produced high quality PMMA fibers including 1% wt. content of MWCNT.

It can be clearly seen from SEM images that continuous and bead-free nanofibers production were acquired as well as decreasing defects of electrospun resulting increased quality of nanofibers.

Furthermore, higher concentration of PMMA solution in DMF yields higher viscosity rates thus the higher viscosity results higher quality for fiber production by minimizing defects such as bead formation and other technical problems during production. The findings of the study also clearly reveal that increasing density of the solution to the specified optimum level plays an important role for each steps of the process.

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