



Fabrication and Characterization of PMMA/Carbon Electro Spun Nanofibers in Two Different Solvents

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Abstract

Polymethyl methacrylate (PMMA) nanofibers have recently found numerous attractive applications due primarily to their high surface area to volume ratio. In literature, the carbon black has not been used before in the preparation of electro spun PMMA nanofibers. In this present work, the production on PMMA/carbon black (PMMA/CB) nanofibers produced by electrospinning technique is the field of interest. The effect of solvent type on the produced PMMA and PMMA/CB nanofibers were investigated. The solvents used for preparing the PMMA solutions for the electrospinning process were dichloromethane (DCM) and chloroform. The criteria used for the evaluation of the solvents and the carbon black effects were the nanofiber morphology and the thermal properties. Scanning electron microscopy (SEM) revealed the effect of the solvents and carbon black on the surface morphology of the fibers. The differences in the structure affect the thermal properties of the nanofibers as indicated by DSC and TGA.

Keywords: Electrospinning; poly-methyl-methacrylate; nanofibers; carbon black; nanocomposites.

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1. Introduction

Since 1980s and especially in the recent years, the electrospinning process has regained more attention probably due to the surging interest in nanotechnology, as ultrafine fibers or fibrous structures of various polymers [1]. Using the electrospinning process, polymer nanofibers (with submicron scale diameters) can be formed when a droplet of viscoelastic polymer solution is subjected to high voltage electrostatic field. As this droplet travels in air, the solvent evaporates leaving behind a charged fiber that can be electrically deflected on a substrate [2]. When the diameters of polymer fiber materials are shrunk from micrometers to sub-microns or nanometers, several amazing characteristics appear such as very large surface area to volume ratio (this ratio for a nanofiber can be as large as 10³ times of that of a microfiber), flexibility in surface functionalities, and superior mechanical performance (e.g. stiffness and tensile strength) compared with any other known form of the material. These outstanding properties make the polymer nanofibers to be the optimum candidate to many important applications [3]. The main applications are tissue scaffolding and other biomedical application [4], reinforcement in transparent composites [5] and nanoelectronics [6].

As long as a polymer can be electrospun into nanofibers, the ideal targets would be: (1) the diameters of the fibers are consistent and controllable, (2) the fiber surface is defect-free or defect-controllable, and (3) continuous single nanofibers are collectable. However, researches so far have shown that the three targets are by no means easily achievable [3]. Many parameters can influence the transformation of polymer solutions into nanofibers through electrospinning. These parameters include (a) the solution properties such as viscosity, elasticity, conductivity, and surface tension, (b) governing variables such as hydrostatic pressure in the capillary tube, electric potential at the capillary tip, and the gap (distance between the tip and the collecting screen); and (c) ambient parameters such as solution temperature, humidity, and air velocity in the electrospinning chamber [7]. Qian et al. [8] presented a study in which PMMA was chosen as the solute and processed into nanofibers by means of electrospinning. Seven solvents were separately used to dissolve PMMA at the concentration of 0.06 g/mL. Ring-like, bead-like, ultrafine, and nano-porous nanofibres were generated from PMMA solutions by electrospinning. The different morphologies were not due to solvents ability to dissolve PMMA, but rather due to other properties such as boiling points, molecular weight, and molecular structure. Piperno et al. [2] prepared a series of nanofibers with various wt.% of PMMA to acetone. They characterized the PMMA nanofibers regarding their morphology and chemical composition. Their results revealed that increasing the PMMA concentration leads to an increase in the nanofibers homogeneity and disappearance of beads. Moreover, increasing the polymer concentration results in an increase in the nanofibers diameter. Moreover, the nanofibers present the same chemical composition of the PMMA compound.

The electrospinning process easily incorporates particles of materials such as pigments, metal oxides, and many other particles into the nanofibers that are produced. It was found that the addition of some filler material into a polymer solution can also result in fibers free of beads [9]. Carbon black is a common polymer additive that is used for reinforcement and for its ability to enhance the polymeric compounds' properties, in addition to its availability and low cost [10, 11]. PMMA is an important commercial plastic, which has extensive application in many sectors such as in aircraft glazing, signs, lighting, architecture, transportation and merchandising [12, 13].

Up to our knowledge, it has not been reported that carbon black was previously used as filler for PMMA nanofibers fabricated by electrospinning.

The aim of this paper is to study the effect of two different solvents, which are dichloromethane (DCM) and chloroform, on the morphology of PMMA electro-spun nanofibers. In addition, super abrasion furnace carbon black (SAF- N115) was added to the two different PMMA solutions to get the benefit of carbon black properties as filler of low cost. The characterization of the produced PMMA nanofibers was carried out by SEM, DSC, and TGA techniques.

2. Materials and Methods

2.1. Materials

Poly methyl methacrylate (PMMA) with $M_w = 350\,000$ g/mol. The two solvents used were dichloromethane (DCM) and chloroform. The polymer and the solvents were obtained from Sigma Aldrich (Germany) and were used without any further purification. Super Abrasion Furnace Carbon black (SAF- N115) having particle size 20–25 nm was purchased from Transportation & Engineering Company (TRENCO) – Alexandria, Egypt.

Polymer solutions for the electrospinning of PMMA were prepared by dissolving 10 wt% PMMA in the solvents separately. Carbon black was added with 30 wt% relative to the PMMA powder. The formulations of the prepared samples are given in Table 1.

Table 1. Formulations of the PMMA /Carbon electro-spun nanocomposites.

Sample no.	PMMA	Methylene chloride	Chloroform	SAF-N115
S1	√	√	--	--
S2	√	√	--	√
S3	√	--	√	--
S4	√	--	√	√

2.2. Electrospinning process

In the electrospinning process, PMMA solutions were heated and stirred for four hours on a CB 162 hot plate magnetic stirrer. All solutions were stored in conical flask with stoppers for at least one day before electrospinning. An "infusion only" programmable syringe pump (NE-300) from New Era Pump Systems, Inc; and a high voltage power supply from Leybold Didactic GMBH were used in a horizontal arrangement as shown in Fig. 1. The syringe pump can accommodate syringes up to 60 cc. 5 ml plastic syringes and their needles (18Gx1.25) were used to spin the fibers at a flow rate of 10 ml/hr. Electrospinning was done at a voltage of 25 kV. The separation between the tip of the needle and the collector was kept between 15 cm and 20 cm. Metallic plates with dimensions of 5 cm x 5 cm were used as collectors.

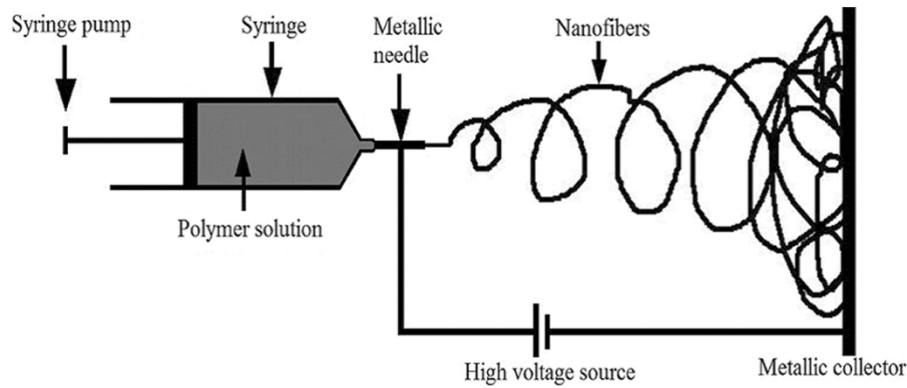


Figure 1: Schematic of electrospinning setup

2.3. Characterization

The morphology of the resulting PMMA nanofibers was characterized by Scanning Electron Microscope (SEM). The SEM photographs were carried out Using SEM Model Philips XL 30 attached with EDX Unit, at an accelerating voltage of 30 K.V. Before the observation, the samples were covered with a very thin layer of gold to avoid electrostatic charging during examination.

Differential Scanning Calorimetry (DSC) and thermo gravimetric Analysis (TGA) experiments were carried out using a differential thermal analysis of type Shimadzu 50 with thermo gravimetric module. For DSC analysis, about 5 mg of sample was hermetically sealed in an aluminum pan for the measurements. The samples were heated from 25 to 250°C at a heating rate of 10°C/min. The value of the glass transition (T_g) was determined by using the microprocessor of the thermal analyzer.

3. Results and discussion

3.1. Morphology of the electro spun PMMA fibers

The SEM images of the electro-spun PMMA nanofibers are shown in Fig. 2. It is clear that all samples are in the form of continuous singel nanofibers that are randomly oriented. Figures 2 a and 2c showed the electro-spun fibers produced by dissolving PMMA in DCM and chloroform respectively. Both samples showed porous surface, yet the pores' size in fibers produced in chloroform as a solvent are bigger. Pore formation can be explained as a result of the fast evaporation of the used solvent, which pressurizes vapor inside fiber structure and subsequently spouts through the electro-spun fiber surfaces leading to a porous appearance [14]. These findings are supported by the low boiling temperature of DCM (39.8 °C) and chloroform (61.2 °C). The difference in pores size is probably due to the higher molecular weight of chloroform (119.38 gm/mol) compared to that of DCM (84.93 gm/mol). Pore formation could be helpful when nanofibers are used as filters since the pores increase the roughness of the fibers' surfaces. Regarding the fibers' shape, fibers produced in chloroform as a solvent are fairly uniform cylindrically shaped with different diameters. While fibers produced in DCM as a solvent showed some flattened rods besides these of the cylindrical shape, as well.

Figs. 2 (b & d) showed the SEM images of PMMA/CB nanofibers produced using DMC and chloroform as solvents respectively. It is obvious that the addition of CB to both series alters the fibers geometry to be smoother and porous free. This could be explained by due to the physical interlock between the CB particles and the polymer matrix within the nanofiber [15]. The shape of fibers in the series produced using chloroform as a solvent changed from cylindrical shape (Fig. 2 c) to flattened shape (Fig. 2 d) by the addition of CB. This might be due to the increase in the viscosity of the polymer solution in presence of CB. However, with carbon interlocked in the fibers, those fibers are expected to have higher conductivity than other polymer nanofibers. This feature increases the opportunity for their usage in microelectronic applications. This will be extensively investigated in future work.

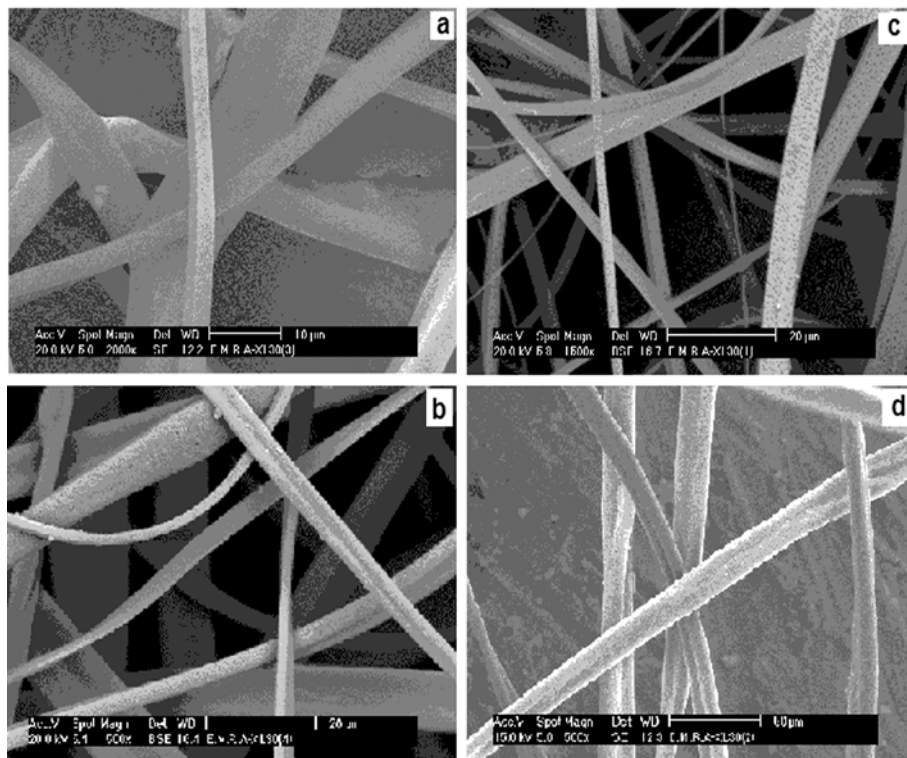


Figure 2: Sem images of (a) PMMA/ methylene glycol; (b) PMMA/ methylene glycol/SAF; (c) PMMA/chloroform; (d) PMMA/chloroform/SAF.

3.2. Thermal Properties of the PMMA electro-spun fibers

- **Differential scanning calorimetry (DSC)**

DSC was done on the electro-spun PMMA nanofibers in order to determine the thermal behavior of the nanofibers. The glass transition temperature (T_g) of the different samples are presented in Fig. 3. It can be seen from the figure the presence of multiple T_g peaks. This might be due to non homogeneity of the considered polymer. However the introduction of CB to the polymer increases the thermal stability of the produced fibers

as indicated by the shift of the T_g to higher values upon addition of CB. For the polymer dissolved in chloroform, Fig. 3 (b 3 & 4), T_g values shifted from 97.58 °C to 99.65 °C while for the polymer dissolved in DCM, Fig. 3 (a 1 & 2), T_g values increased from 102.45 °C to 107.215 °C.

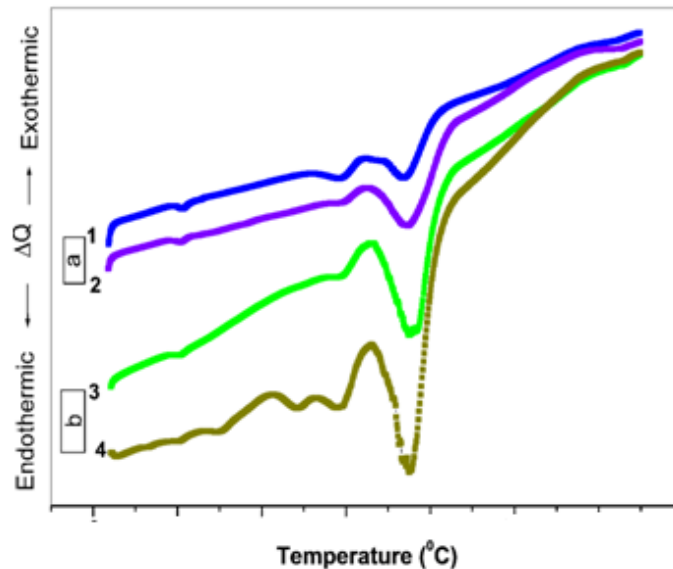


Figure 3: DCS analysis of PMMA nanofibers electrospun: (a) PMMA/DCM without and with CB (1&2) respectively; (b) PMMA/chloroform without and with CB (3&4) respectively.

- **Thermo gravimetric analyses (TGA)**

TGA of samples were carried out. The TGA plot of the PMMA nanofibers produced using DCM and chloroform as solvents are respectively shown in Figs. 4 a and 4b, in absence and presence of SAF carbon black. It is clear that PMMA fibers obtained by using chloroform as a solvent are thermally more stable than those obtained by DCM (samples 1 & 3). This may be referred to that chloroform has higher boiling point and molecular weight (61.2 °C and 119.38 gm/mol) relative to those of methylene chloride (39.8 °C and 84.93 gm/mol). The incorporation of CB in the PMMA fibers enhances their thermal stability. The presence of CB in the PMMA electro-spun leads to a delay of the onset temperature of the polymer degradation. The PMMA/DCM and the PMMA/DCM/CB samples completely decomposed at 400 °C, as shown in Fig. 4a. The PMMA/chloroform/CB fibers completely decomposed at a higher temperature than that of PMMA/chloroform, Fig. 4b. The improved thermal stability of the nanofibers resulted from the enhanced distribution of the CB particles which in turn raised the surface area in the polymer matrix [16].

4. Conclusion

Electrospinning technique was used to prepare PMMA/CB nanofibers. The PMMA solutions were prepared by using chloroform and DCM. The results revealed that the solvent type affects the morphology of the electrospun nanofibers. Incorporation of super abrasion furnace carbon black (SAF- N115) having particle size 20–25 nm affects to a great extent the shape dimensions and surface geometry of the PMMA regardless of the solvent

type. Moreover, the thermal properties of the PMMA nanofibers were enhanced by the incorporation of CB. Improvement of the PMMA/CB nanofibers thermal properties is more pronounced in samples prepared with the chloroform as a solvent. As a conclusion, the morphology and thermal properties of PMMA nanofibers were enhanced by the incorporation of CB. These features increase the opportunity of the electro-spun PMMA/CB nanofibers usage as reinforcing fibers for many polymeric matrices. This will be extensively investigated in our future research.

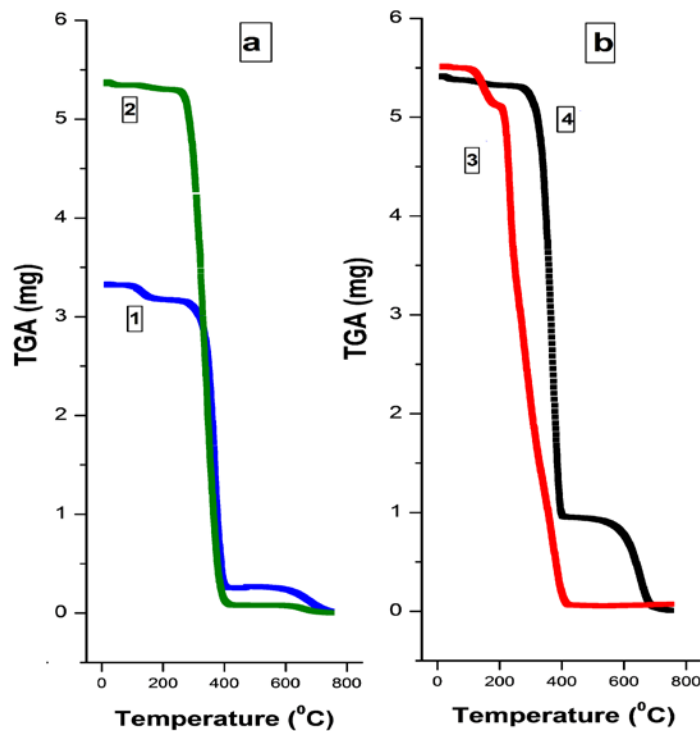


Figure 4: TGA analysis of PMMA nanofibers electrospun of: (a) methylene chloride, without and with CB (1&2) respectively; (b) chloroform, without and with CB (3&4) respectively.

References

- [1] P.K. Baumgarten. "Electrostatic spinning of acrylic microfibers." *J. of Colloid and Interface Science*, vol. 36 pp. 71–9, 1971.
- [2] S. Piperno , L. Lozzi, R. Rastelli, M. Passacantando, S. Santucci. "PMMA nanofibers production by electrospinning," *Applied Surface Science*, vol. 252, pp. 5583–5586, 2006.
- [3] Z. M. Huanga, Y. Z. Zhangb, M. Kotakic, S. Ramakrishna. "A review on polymer nanofibers by electrospinning and their applications in nanocomposites," *Composites Science and Technology*, vol. 63, pp. 2223–2253, 2003.
- [4] C.J. Buchko, L.C. Chen, Y. Shen, D.C. Martin. "Processing and microstructural characterization of porous biocompatible protein polymer thin films," *Polymer*, vol. 40, pp. 7397- 7407, 1999.

- [5] M.M. Burgshoef, G.J. Vancso. "Transparent Nanocomposites with Ultrathin, Electrospun Nylon-4,6 Fiber Reinforcement," *Adv. Mate*, Vol. 11, pp. 1362-1365, 1999.
- [6] I.D. Norris, M.M. Shaker, F.K. Ko, A.G. MacDiarmid. "Electrostatic fabrication of ultrafine conducting fibers: polyanilinerpolyethylene oxide blends," *Synth. Met.*, vol. 114, pp. 109- 114, 2000.
- [7] J. Doshi, D.H. Reneker. "Electrospinning process and applications of electrospun fibers," *J Electrostatics*, vol. 35(2-3), pp.151–160,1995.
- [8] Y. F. Qian, Y. Su, X. Q. Li, H. S. Wang, C. L. He. " Electrospinning of Polymethyl Methacrylate Nanofibres in Different Solvents, *Iranian Polymer Journal*, vol. 19 (2), pp.123-129, 2010.
- [9] E. Zussman, A. L. Yarin, D. Weihs. "A micro-aerodynamic decelerator based on permeable surfaces of nanofiber mats," *Experiments in Fluids*, vol. 33, pp. 315–20, 2002
- [10] A. Zhang, L.Wang, Y. Lin, X. Mi. "Carbon black filled powdered natural rubber: Preparation, particle size distribution, mechanical properties and structures," *Journal of Applied Polymer Science*, vol. 101, pp. 1763–1774, 2006.
- [11] S. N. Lawandy, S. F. Halim, N. A. Darwish. "Structure aggregation of carbon black in ethylene-propylene diene polymer, *eXPRESS Polymer Letters*, vol. 3, No.3, pp.152–158, 2009.
- [12] W. Pan, H. Zhang, Y. Chen. "Electrical and Mechanical Properties of PMMA/nano-ATO Composites," *J. Mater. Sci. Technol.*, vol. 25, no.2, pp. 247-250, 2009.
- [13] K. P. Matabola¹, A. R. de Vries, A. S. Luyt, R. Kumar. "Studies on single polymer composites of poly(methyl methacrylate) reinforced with electrospun nanofibers with a focus on their dynamic mechanical properties, *eXPRESS Polymer Letters*, vol.5, no.7, pp. 635–642, 2011
- [14] T. Jarusuwannapoom, W. Hongrojjanawiwat, S. Jitjaicham, L. Wannatong, M. Nithitanakul, C. Pattamaprom. "Effect of solvents on electrospinnability of polystyrene solutions and morphological appearance of resulting electrospun polystyrene fibers," *Eur Polym J*, vol. 41, pp. 409-421, 2005.
- [15] G. Selling, A. Biswas, A. Patel, D. Walls, C. Dunlap, Y. Wei. "Impact of solvent on electrospinning of zein and analysis of resulting fibers," *Macromol. Chem. Phys.*, vol. 208, pp.1002-1010, 2007.
- [16] B. Sundaray, V. Jagadeesh Babu, V. Subramanian, T.S. Natarajan. "Preparation and Characterization of Electrospun Fibers of Poly(methyl methacrylate) - Single Walled Carbon Nanotube Nanocomposites," *Journal of Engineered Fibers and Fabrics*, vol. 3, no.4, pp. 39-45, 2008.