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Research article

Hexagonal boron nitride filled polymer nanofibers producing and characterization via electrospinning technique

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Abstract

Nanofillers contained polymer fibers have improved mechanical, morphological and thermal properties. In this study, hexagonal boron nitride filled polymer nanofibers were produced from different weight percentages of hexagonal boron nitride mixed TPU-DMF colloid polymer solutions via electrospinning method under fixed electrospinning parameters. Micro structure investigation of hexagonal boron nitride/TPU nanofibers were carried out with Scanning Electron Microscopy (FE-SEM) under the morphological characterization, and determined the nanofibers diameter changes. Thermal characterization of nanofibers was carried out with Differential Scanning Calorimetry (DSC). The morphological characterization of nanofibers shows, diameter values of nanofibers were increased with addition of nanofillers and contrary formation of beads were decreased. Thermal investigation of nanofibers showed, even if melting points of nanofibers were not changed, the enthalpy values were changed depending on filler concentration.

Keywords: *Electrospinning, hexagonal boron nitride, thermoplastic polyuretan, nanofiber*

1. Introduction

Under the micron sized fibers are basicly accepted as nanofibers. Wtih their large surface areas, porous structures and characteristic properties, nanofibers are widely used materials in nanotechnology and biotechnology [1].

With low reactivity and other good properties, boron nitride is an inorganic material which has a great number of application areas. It's superior electrical, mechanical and physical properties gives different application oppurtinities for the boron nitride in the industry.

Boron nitride can be two different crystal structure as hexagonal and cubic crystal structure. Hexagonal boron nitride is produced with nitriding of boron oxide at high temperature values. The crsytal structure of the hexagonal boron nitride and the crystal structure of graphite show a great resemblance; therefore hexagonal boron nitride can be called as a "white graphite" material. Hexagonal boron nitride is widely used in engineering and refractory industries. Its high chemical resistance, high thermal

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resistance, high electrical resistance, lubricity, lightness, processability, and high thermal conductivity are the superior properties of the hexagonal boron nitride and the reason of broad application areas [2-3].

During produced fibers from the polymer solutions via electrospinning process with a high potential tension, polymer solution is charged, and orientated to the collector which is grounded, from thin nozzles. During this orientation of the polymer solution, polymer jet spreads as an extremely small fiber and with that can be achieved nano sized fibers on the collector [1]. Producing fibers via conventional methods has some difficulties of producing under micron sized fibers and with this fact electrospinning technique has a great advantage. In addition, nanofibers which are produced via electrospinning technique have more porous structure and its an important difference and advantage of electrospinning method to be prefered than the other conventional methods.

With elastomeric properties, resistance to the microorganisms, resistance to abrasion, resistance to flammability and hydrolytic stability properties of thermoplastic polyuretan (TPU) is widely used industrial electrospinning polymer [4]. In this study, hexagonal boron nitride and TPU have both good thermal properties, abrasion resistance, and flammability resistance.

2. Material and Method

TPU was dissolved in N, N-Dimethylformamide (HCON $(CH_3)_2$) which has a 99.8% purity with a concentration of 13 wt.% for electrospinning process. Four different polymer solutions were prepared with different percentages of hexagonal boron nitride which are 1%, 3% and 5 wt.%. For a better observation for the effect of the hexagonal boron nitride, one polymer solution was prepared without h-BN. Thermoplastic polyuretan has a 229000 molecular wight value. Hexagonal boron nitride powders which have 200-300 nm particule size is provided from BORTEK Ltd. (Eskisehir, Turkey) and used as a filler material.

3. Experimental

The homogeneity of the mixture between polymer solution and hexagonal boron nitride has an great importance for the final product such as fibers diameter or thermal and morphological properties of the nanofibers. As a reason of that, TPU/DMF polymer solution and hexagonal boron nitride were mixed with magnetic stirrer for 3 hours at 50°C with 500 rpm. Hexagonal boron nitride filled polymer solutions total volume was decided as a 20 ml. For conventional electrospinning processes, filler materials should be dissolved in the polymer solution, but with hexagonal boron nitride, as a noval approach in this study, we obtained a colloidal solution and its suitable for the electrospinning process.

3.1. Electrospinning Process

Such as working distance, applied voltage value, enjection pump rate, electrospinning parameters have directly effect on the obtained nanofibers diameters, porous structure, and fiber characteristics. All the electrospinning process parameters were determined and fixed same for all the polymer solutions to obtain a better observation for the thermal and mechanical properties of hexagonal boron nitride. Working distance was 9 cm, applied voltage value was 25 kV, and the pump rate was 0.085. Electrospinning process was carried out under the normal weather conditions such as 23°C temperature and 67.2% humidity. 20 ml syringes were used. Obtained nanofibers were kept under 50°C for 24 hours to remove the solvent, DMF. 50×30 cm aluminum foil was used as a colletor above the cylindirical collector. The Fig. 1 shows the electrospinning experiment setup.

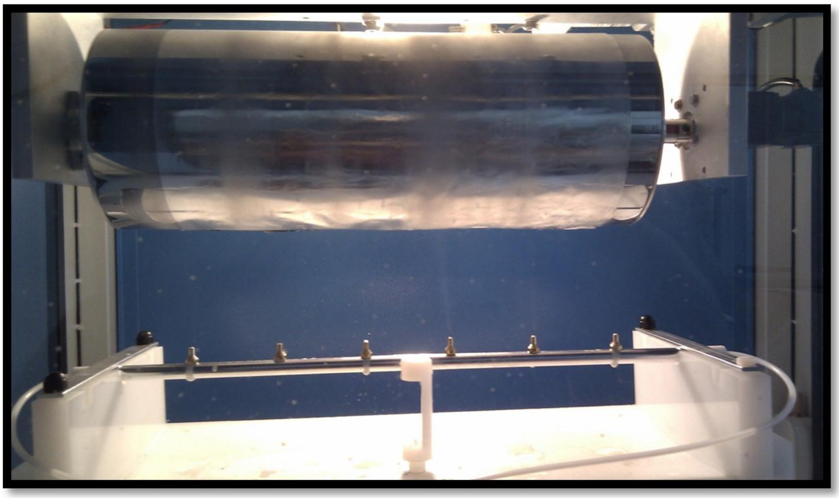

Fig. 1 Electrospinning experiment setup

3.2. Characterization

Field Emission Gun-Scanning Electron Microscope (FE-SEM), Zeiss Supra 50 VP, is used to investigation of TPU/h-BN nanofibers morphological characterization, nanofibers diameters and, formation of beads. Differential Scanning Calorimetry (DSC), DSC Q2000, is used for the investigation of thermal behaviors of nanofibers such as enthalpy changing and melting temperatures with 5°C/min heating rate from 40°C to 250°C under the N_2 atmosphere. Investigation of functional groups of the nanofibers is carried out with FT-IR spectrometer, Bruker Tensor 27, between 400-4000 cm^{-1} wavelength, 64 scanning.

4. Conclusion

The morphology of the electrospun fiber mats was studied by high resolution scanning electron microscopy (Zeiss Supra 50 VP Scanning Electron Microscope) operating at an accelerating voltage of 10 kV. All specimens were coated with gold-palladium prior to SEM. SEM reveals that, in fact, the electro spun material is fibrous and highly porous, held together by bonding sites among many fibers. Fig. 2 indicates the electro spun TPU/DMF solvent nanofibers morphologic characterization.

As shown in the Fig. 2, there are so many fibers which are under the 100 nm and in addition that, we can see a lot of beads in the fibers. On the other hand, with morphologic characterization of fibers, it can be proved that, with adding fillers to the polymer solution, the beads were decreased and with boron nitride nanosheets additive, the beads completely removed from the system. It has been found that the polymer concentration also affects the formation of the beads. Fong [5] recognized that higher polymer concentration resulted in fewer beads. Furthermore, adding some filler material into a polymer solution can also result in fibers free of beads. Zong et al. realized this while electrospinning biodegradable PLDA polymers [6]. They found that with 1 wt.% salt addition, the resulting nanofibers were bead-free. In Fig. 3, 4 and 5 shows us, with addition of hexagonal boron nitride, with increasing the viscosity of the polymer solution, nanofibers diameters were increased contrary of decreasing the beads.

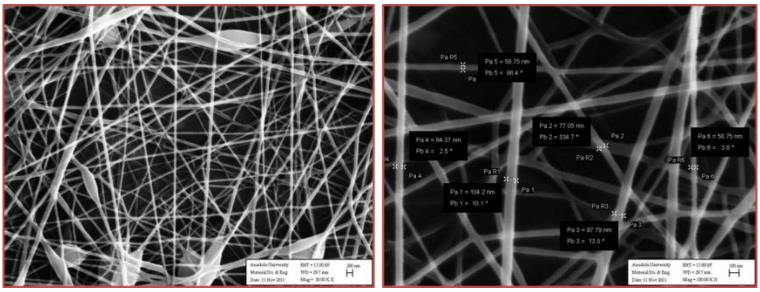

Fig. 2 TPU/DMF polymer solution electro spun nanofibers

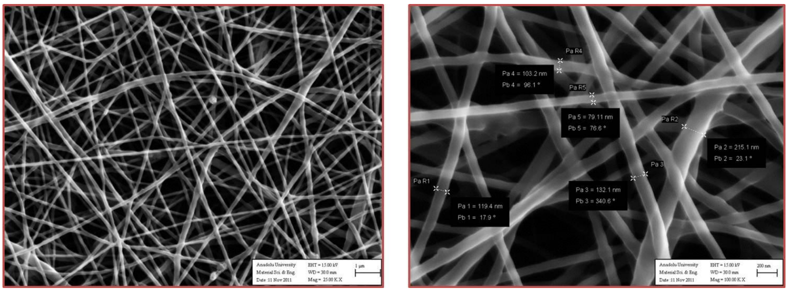

Fig. 3 TPU/DMF + 1 wt.% h-BN electro spun fibers

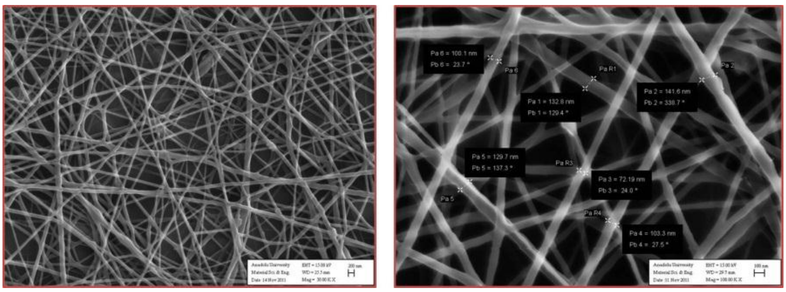

Fig. 4 TPU/DMF + 3 wt.% h-BN electro spun fibers

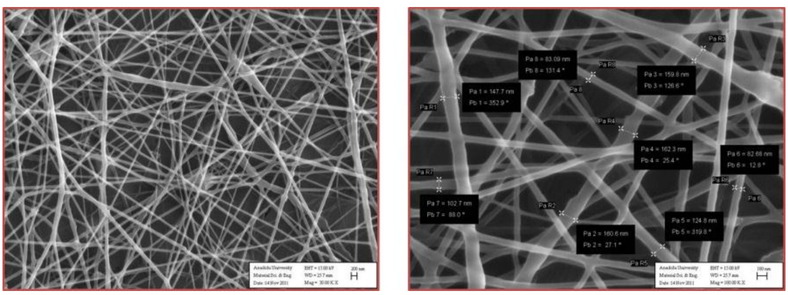

Fig. 5 TPU/DMF + 5 wt.% h-BN electro spun fibers

FT-IR spectrometer is used for the investigation of the functional groups of nanofibers. Fig. 6 shows characteristic peaks of TPU nanofibers without h-BN filler with FT-IR and Fig. 7 shows the characteristic peaks of hexagonal boron nitride powders, and finally Fig. 8 shows characteristic peaks of TPU/h-BN nanofibers. TPU/h-BN nanofibers FT-IR analysis shows both TPU polymer and hexagonal boron nitride peaks, and its showed that h-BN is succesfully integrated into the polymer nanofibers with the electrospinning technique. With higher concentration of hexagonal boron nitride, characteristic peaks of h-BN can be obtained more clearly with FT-IR.

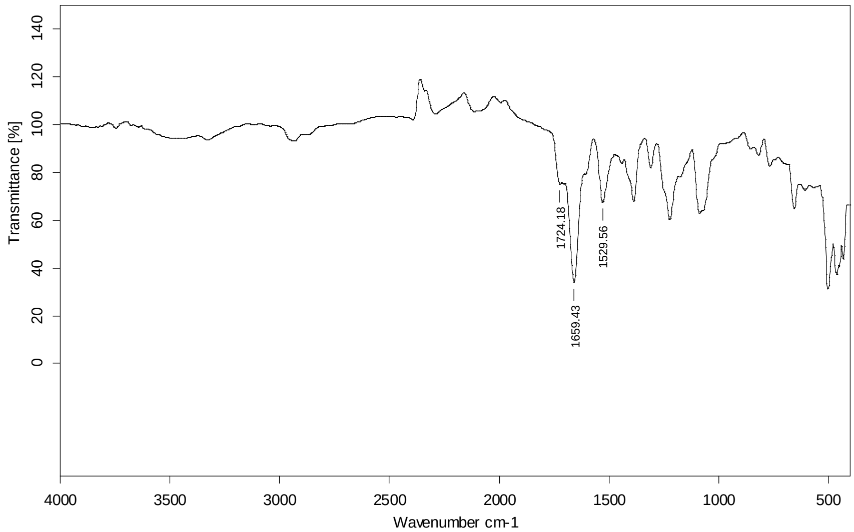

Fig. 6 TPU nanofibers FT-IR peaks

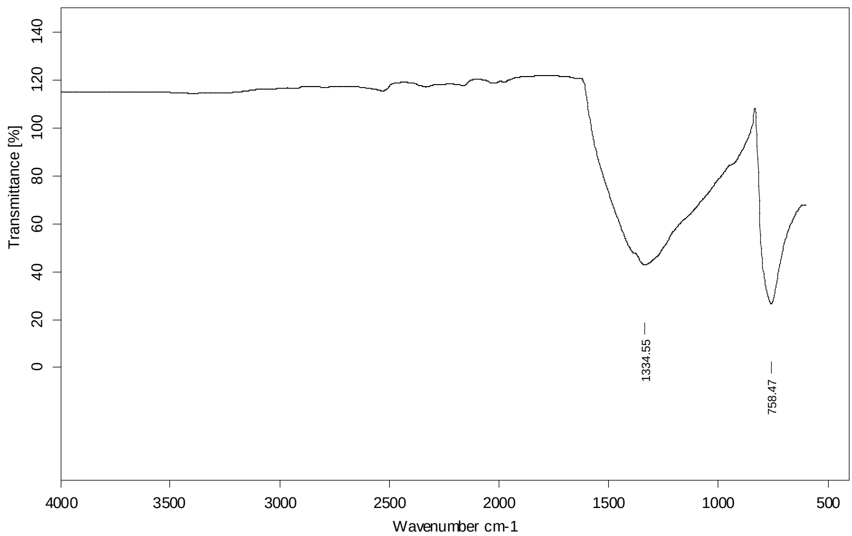

Fig. 7 Hexagonal boron nitride FT-IR peaks

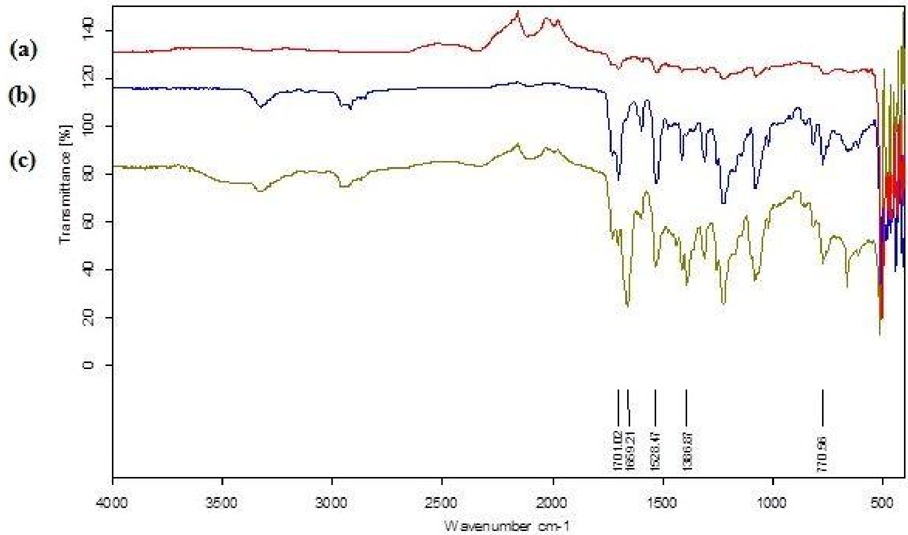

Fig. 8 h-BN filled TPU nanofibers, (a) 1 wt.%, (b) 3 wt.%, (c) 5 wt.%

Differential scanning calorimetry can be used to measure a number of characteristic parameters of a sample. Electro spun materials were tested by using M-DSC. Differential scanning calorimeter Q2000 used in experiments. The experiments were run with modulated DSC technique and started with 40°C and ended at the 250°C with heating only 5°/min in the nitrogen, N_2, atmosphere. The analysis results are given in the Fig. 9.

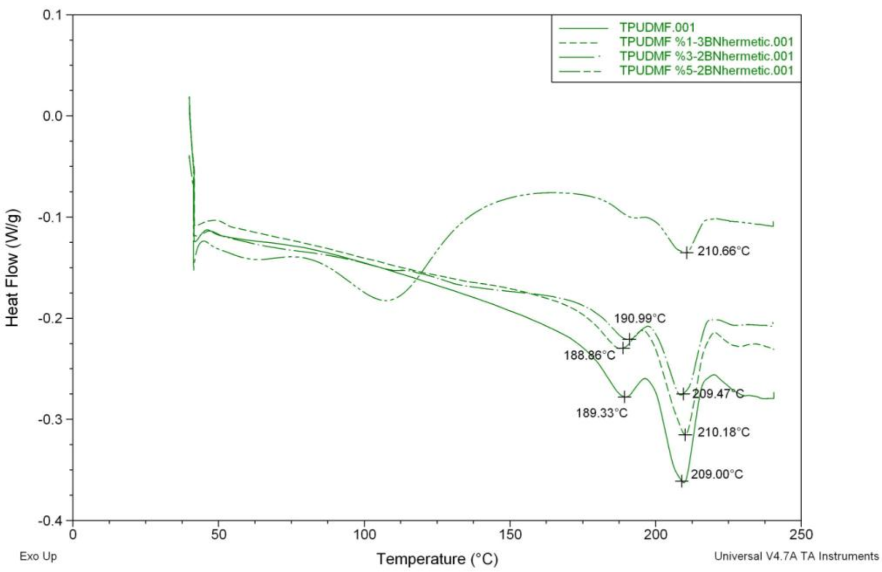

Fig. 9 M-DSC analysis of nanofibers

As shown in the Fig. 9, adding hexagonal boron nitride could not effect significantly the melting point of the fibers. The change is very low value which can be underestimated. However, with additive of fillers to the fibers, the heat flow values are changed significantly and when the boron nitride concentration is increased in the system, boron nitride particules conducted the heat in the system and therefore the enthalpy values were changed because of high thermal conductive nature of boron nitride.

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