CHARACTERIZATON OF VINLYESTER RESIN MODIFIED WITH BNNS FILLED PMMA ELECTROSPUN NANOFIBERS

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Abstract

Polymethylmethacrylate/Boron nitride nanosheets (PMMA/BNNSs) nanofibers were produced by conducting electrospinning. Various different processing parameters, including applied voltage, flow rate, molecular weight and concentration of PMMA, solvent type, and the distance between collector and syringe were taken into account when aiming at gaining an insight into the resulting surface morphology of electro-spun fiber networks. By the way, to promote the wettability of the fibers with the matrix resin, the surface of the fibers were subjected to silane chemical modification (Vinyltrimethoxysilane (VTS)). Of all the produced nano-fibers, the most promising was selected in terms of thermal properties with respect to the surface morphology findings obtained by SEM examination. The best processing parameters were then accordingly executed to produce the nanofibers to be added to vinyl ester resin. The use of BNNSs in the vinyl ester resin together with PMMA is expected to improve its thermal properties at no expense of mechanical integrity. Final thermal properties of the vinyl ester resin were further investigated using DSC. The results obtained were then discussed in a conscience manner.

1. Introduction

Electrospinning is a straightforward and cost-effective method to produce novel fibers with diameters in the range of from less than 3 nm to over 1 mm, which overlaps contemporary textile fiber technology [1]. Electrospinning is a technique that utilizes electric force alone to drive the spinning process and to produce polymer fibres from solutions or melts [2-3]. In the electrospinning process, a polymer solution held by its surface tension at the end of a capillary tube is subjected to an electric field. Charge is meanwhile induced on the liquid surface by an electric field. Mutual charge repulsion causes a force directly opposite to the surface tension. As the intensity of the electric field is increased, the hemispherical surface of the solution at the tip of the capillary tube elongates to form a conical shape, which is known as the Taylor cone [4]. When the electric field reaches a critical value at which the repulsiv electric force overcomes the surface tension force, a charged jet of the solution is ejected from the tip of the Taylor cone. Since this jet is charged, its trajectory can be controlled by an electric field. As the jet travels in air, the solvent evaporates, leaving behind a charged polymer fiber which lays itself randomly on a collecting metal tool. Thus, continuous fibers are laid to form a non-woven fabric. [5] The number of publicatons on electrospinning has increased dramatically during the past decade, focusing on the morphologies of nanofibers. The morphology of electrospun nanofibers is affected by many factors, such as; applied voltage, flow rate, molecular weight and concentration of polymer, distance between collector and syringe, additives.

Vinyl ester resins combine the best properties of epoxies and unsaturated polyesters. They can be easily handled at room temperature and have mechanical properties similar to epoxy resins. They have better chemical resistance than cheaper polyester resins, especially hydrolytic stability, and at the same time offer greater control over cure rate and reaction conditions than epoxy resins. The unsaturated

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bonds on the termini of the vinyl ester oligomers copolymerize with the comonomer to form a crosslinked network similar to the curing reactions of unsaturated polyesters. Vinyl ester resins are similar to unsaturated polyester resins in that both systems contain styrene monomer as a reactive diluent and that both unsaturated polyester and vinyl esters provide crosslink sites. However, the physical properties of the vinyl ester networks are, in general, superior to the unsaturated polyesters[6] Vinyl ester networks have excellent tensile and flexural properties, as well as high elongation[7] Vinyl esters have very good thermal performance, excellent mechanical properties, and toughness which is why they are "preferred" materials for structural composites.[8].

In this paper, we reported the preparation and characterization of BNNS (silanized and pristine) modified PMMA (poly-methyl-methacrylate) nanofibers by electrospinning. Our studies have concentrated on the surface morphology and glass transition temperature (Tg) of the resulting composites as a function of solution concentration, solution molecular weight, solvent, spinning voltage, flow rate, PMMA, distance between collector and syringe , and the amount of BNNSs with and without silane treatment. In other words, the major aim of our study is to ensure homogeneous dispersion particles of BNNS within vinyl ester, after added, at different proportions by weight, to polymethylmethacrylate (PMMA) through electrospinning. The reason why BNNS is preferred as filler constituent lies in the fact that boron nitride (BN) is a chemical compound consisting of equal numbers of boron and nitrogen atoms, and that its hexagonal form is known as the most thermally stable and the softest one. Hexagonal boron nitride (hBN) is composed of layered structure similar to that of graphite and can be used in rigorous environments, either as a solid lubricant, an ultraviolet-light emitter or as thermal conductive filler in composites. The use of BNNS in the vinyl ester resin matrix is expected to improve its thermal stability with improved or at least retained mechanical integrity. The effects of nanofibers of the morphology on thermal properties of nanofiber was highlighted using DSC.

2. Experimental Section

2.1. Materials

To prepare electrospun fibers of Polymethylmethacrylate / Boron Nitride Nanosheets (PMMA/BNNS) with and without silane treatment at different weight contents (0.5, 1 ,1.5 wt. %), different solution concentrations (2, 4, 6 wt. %) , different molecular weights (PMMA: 81 000, 350.000 g/mol) together with different solvents (Acetone, chloroform, toluene, DMF/THF (2:1)) were systematically utilized. The corresponding solutions were prepared at room temperature using a magnetic stirrer. A bisphenol epoxy based vinyl ester thermosetting resin (Polives 701) was obtained from POLİYA. Cobalt naphanate (CoNAP) (0.2 % wt.) and Methyl ethyl ketone peroxide (MEKP) (2% wt.) were, respectively, used to solidfy the resin suspensions.

2.2. Electrospinning Procedures

A polymer solution was placed in a 5 mL syringe attached to a syringe pump in a horizontal mount. The electric potential was applied to the hypodermic needle on the end of the syringe, using a high voltage power supply. The electrospun nanofibres were collected on a piece of thick aluminium foil placed at a distance of the tip and the syringe needle. The mass flow rate, applied voltage, working distance (the needle to substrate distance) and solution concentration were optimized for each set of experiments. The electrospinning was conducted at room temperature. On the basis of the preliminary results obtained, it was determined that the best solvent be acetone. Using acetone, BNNSs (with and without silane treatment at different weight percentages (0.5, 1, and 1.5% wt)) containing solution concentrations with different amounts (2,4, and 6% wt.) of two different molecular weights of PMMA beads (81.000 g/mol, 350.000 g/mol) were produced to see concentration and molecular weight effect on nanofiber properties. On the other hand, in order to see the effect of flow rate on the properties of nanofiber, different feeding rates (4,6 9 ml/h) were chosen. Taking advantage of the electrical potential difference between the collector and the injector end, different electric voltages (22, 25, 28 kV) were

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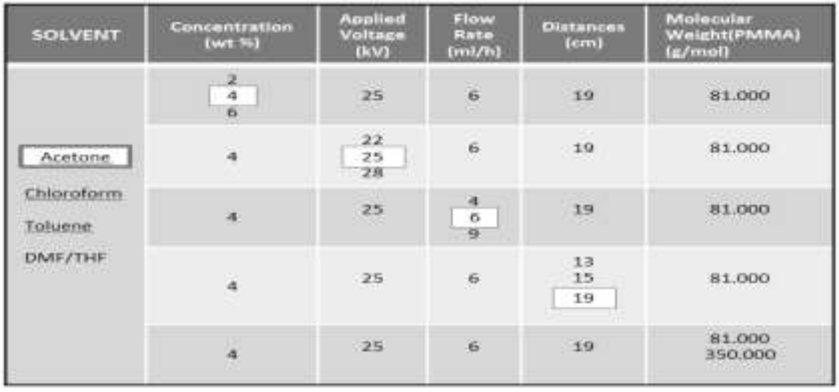
then provided to the system to evaluate its effect. To observe the effect of the working distance between the collector and the injector, different working distances were taken into account (13,15,19 cm). The fibers were collected on the cylinder collector wraped by a thick aluminum foil. Process were carried out under ambient conditions (at about 23°C with 60% humidity). 20 ml syringes were used for the solution. Optimized experimental conditions were determined with a focus on the best fiber formation. **Table 1** summarizes experimental steps to get the final optimized combination of parameters.

Table 1. Effect of electrospinning parameters with different solvents



SOLVENT	Concentration (wt %)	Applied Voltage (kV)	Flow Rate (ml/h)	Distances (cm)	Molecular Weight(PMMA) (g/mol)
Acetone Chloroform Toluene DMF/THF	2 4 6	25	6	19	81.000
	4	22 25 28	6	19	81.000
	4	25	4 6 9	19	81.000
	4	25	6	13 15 19	81.000
	4	25	6	19	81.000 350.000

2.3. Modified vinylester suspension preparation

5 g of silanized BNNS (1 wt.%) modified PMMA nanofibers obtained under the best optimized experimental conditions were blended with 95 g of vinyl-ester resin using a jiffy mixer at a very slow stirring speed for 24 h to let the nanofibers to dissolve in the surrounding vinyl ester matrix. The catalyzed resin suspensions were allowed to cure at room temperature followed by post curing at 120^{o}C for 2h. Note that two different molecular weights of PMMA (81.000 and 350.000 g/mol) were taken into account. The resulting composites were machined into the required specimen dimensions for thermal and mechanical property characterization.

2.4. Fiber Morphology

Morphology of the nanofibres was observed using a scanning electron microscope (SEM) PHENOM at an accelerated voltage of 15 kV. Prior to scanning by electron microscope, the fibers were collected on an aluminum SEM disk then coated for 40 s with gold.

2.5. Thermal property characterization

Glass transition temperature of the samples were investigated by DSC Q-2000, TA Instrument device. Samples were for this purpose first heated from room temperature to 140°C with heating rate of 5°C/min, followed by cooling at the same rate to room temperature and then once again heated to 250°C with same heating rate. Glass transition temperatures (T_g) were determined from the inflection point in the heat flow vs. temperature curves.

3. Results And Discussion

3.1.1. Effect of solvent

Various different samples were accordingly prepared, keeping some specific parameters intact *(1wt.% BNNS, applied voltage: 25 kV, flow rate: 6 ml/h, and the distance between the collector and the tip: 19cm)* while playing with others, including the concentration of PMMA to acetone *as follows; 2 wt.% (81.000 Mw) (A), 4 wt.% (81.000 Mw) (B) and 6 wt.% (81.000 Mw) (C), 2* toluene (A), chloroform (B),acetone (C), DMF/THF (2:1) (D) [concentration of PMMA/BNNS: 4% applied voltage: 25 kV flow rate: 6ml/h distance between the collector and the tip:19 cm]. **Figure 1** shows

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SEM images of the four samples. Within the electrospinning process, solvent is the most important factor. However, the effect of the solvent on the diameter of electrospun fibers is a little controversial. Some researh have demonstrated that acetone is the best solvent, others suggested that chloroform is the best solvent, while the rest has demonstrated that DMF/THF is the best solvent . Toluene is also sometimes reported to be the best for PMMA as well. In the images A and B, fiber formation was not observed, but only film formation was observed instead. In the images of C and D, fiber formation was observed with beads. Beads might be the result of different combinations of experimental parameters in a manner in which each has its own weight on their degree.

3.1.2. Solution Concentration

Various different samples were accordingly prepared, keeping some specific parameters intact *(1wt.% BNNS, solvent: acetone, applied voltage: 25 kV, flow rate: 6 ml/h, and the distance between the collector and the tip: 19cm)* while playing with others, including the concentration of PMMA to acetone *as follows; 2 wt.% (81.000 Mw) (A), 4 wt.% (81.000 Mw) (B) and 6 wt.% (81.000 Mw) (C), 2 wt.% (350.000 Mw) (D), 4 wt.% (350.000 Mw) (E) and 6 wt.% (350.000 Mw) (F).* **Figure 2** depict SEM images of the prepared samples. Please note that each alphabet (A,B,C,D, E, and F) designated to each SEM image corresponds to the same alphabet as in the preparation order stated above. Regardless of types of any samples or adjusted parameters involved, all the images confirms the occurrence of nanofibers. The images showed that the polymer concentration influences the formation of nanofibers. As the concentration is very low, polymeric fibers in rarely microlevel, but in majority at nanolevel were found coexisted. Overall speaking, increasing the PMMA concentration resulted in an increase in the number of the fibers produced. In addition to this, the beads, characteristic of the lowest concentration solution, disappeared and homogenity was found at the desired level when 2 wt.% of PMMA/acetone concentration was used. These results found are proportional to those reported in earlier studies [11-12]. As the concentration became little higher (4 wt.%), a mixture of beads and fibers were obtained. When the concentration reached very high (6 wt.%), nano-scaled fibers switched to micro-scaled fibers, with their diameters increased. To sum up, according to SEM images in Figure 1, nano-scaled fibers accompanied by beads occurred in A and D, while relatively low or no bead involving nanofibers occurred in B and E. Micro scaled fibers rather than nano-scaled ones occurred in C and F, as stated above in detail. This is consistent with the conclusion of the earlier studies. [13-14].

3.1.3. Spinning Voltage

Three different voltages applied. (A) 22 kV (81.000 Mw PMMA) (B) 25 kV (81.000 Mw PMMA) (C) 28 kV (81.000 Mw PMMA), (D) 22 kV (350.000 Mw PMMA) (E) 25 kV (350.000 Mw PMMA) (F) 28 kV (350.000 Mw PMMA) were used keeping fixed the other parameters including concentration 4 % wt., flow rate: 6ml/h, distance between the collector and the tip:19 cm. Based on the appereance of the nanofibers given in the images in **Figure 3**, nanofibers were confirmed to take place. During the electrospinning process, applied voltage is the crucial factor. Only the applied voltage is higher than the threshold voltage, charged jets ejected from Taylor Cone can occur. However, the effect of the applied voltages on the diameter of electrospun fibers is a little controversial. Some researhs have demonstrated that there is not much effect of electric field on the diameter of fiber. Others suggested that higher voltages facilitated the formation of large diameter fiber. That is why we doublechecked this issue at different voltages as well. Irrespective of any voltage applied higher or lower than 25 kV, no significant effect was found in the occurence of nanofibers, which backs up our approach that 25 kV was the optimum value.

3.1.4. Solution Flow Rate

To see the flow rate effect, different flow rates were chosen, ranging from 4 ml/h to 9 ml/h, with the same parameters fixed as in other cases reported above. **Figure 4** depict SEM images of the samples accordingly produced The flow rate of the polymer from the syringe is an important process parameter as it influences the jet velocity and the material transfer rate[17]. It was found that lower flow rates yielded fibers with smaller diameters, when the feedrate is increased, there occurred the corresponding increase in the fiber diameter combined with the changed beads size[13]. More bead

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formation is observed when the flow rate was adjusted to either 4 (A and D) or to 9 mL/h (C and F). Almost no beads involving fiber formation was determined to occur when the flow rate was adjusted to 6 mL/h.

3.1.5. Working Distance Between the Collector and the Tip

The gap between the highly charged needle and the grounded target was narrowed from 19 to 15 and 13 cm. at the optimum level of the other parameters fixed as outlined above. **Figure 5** depict SEM images of the samples accordingly produced. The structure and morphology of electrospun fibers were found to be easily affected by the tip to collector distance because of their dependency on the deposition time, evaporation rate, and whipping or instability interval. It has been found that a minimum distance is required to allow the fibers to have sufficient time to dry before reaching the collector [16]. At distances that are either too close or too far, beading would most probably be observed. In the sample A and D, because of low distances fiber formation was observed to be very low, beads seemed denser. The best working distance was found to be 19 cm.

3.1.6. Molecular Weight

Of all, the best concentration ratio (PMMA/acetone) was found to be 4 wt.%. On the basis of this result, Mw effect of PMMA was separttely investigated using two different MWs, (A) 81.000 MW of PMMA to acetone, (B) 350.000 MW of PMMA to acetone at the applied voltage of 25 kV with a flow rate of 6ml/h, and the distance between the collector and the tip:19 cm. **Figure 6** depict SEM images of the two samples. All the images show the presence of nanofibers. The images show that the polymer molecular weight influences the characteristics formation of nanofibers. Molecular weight of the polymer also has an important effect on morphologies of electrospun fiber. In principle, molecular weight reflects the entanglement of polymer chains in solutions, namely the solution viscosity. Keep the concentration fixed, lowering the molecular weight of the polymer tends to form beads rather than smooth fiber [15]. The higher molecular weight is, the smoother fiber is obtained. In the sample A the beads are dense, while in the sample B, they disappeared partially. The higher molecular weight is, the higher fiber diameters were obtained.

3.2. Effect amount of BNNS

To see the amount of BNNS effect on fibers morphology, three samples have been prepared. Different amount of BNNS were chosen; 0.5 % BNNS, 1 % BNNS, 1.5% BNNS at the optimum level of the other parameters fixed as outlined above. SEM images of the three samples are reported in **Figure 7**. In the image of A, beads seemed very dense. After increasing the amount of BNNS, more fiber formation was obtained and the number of beads was diminished. Image C showed beads whose size is bigger than those observed in the image A. Among all, in image B is the lowest number of beads, indicating that the optimum amount of BNNS is around 1 wt.%.

3.3. Silane treatment induced effects on nanofiber morphology

Evaulation of silane treatment effect on fiber morphology, four samples were prepared. Silane treated and untreated BNNS modified PMMA fibers of different molecular weights (81.000 g/mole and 350.000 g/mole) were produced under the same experimental conditions as in those reported above upto now. Note that 1 wt.% of silane was added to the solution for chemical functionalization.

Figure 8 depict SEM images. In the images of B and D, although the size of beads remained the same, the diamaeter of the fibers were found decreased, which might be asserted to the affirmative effect of silane treatment.

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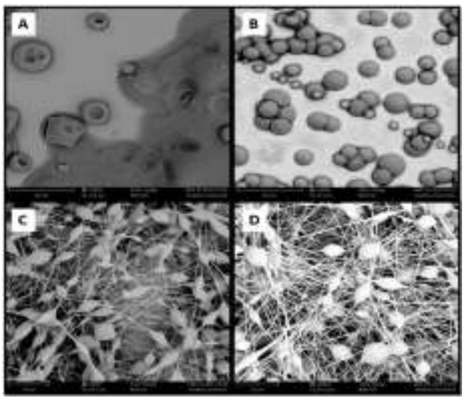

Figure 1. SEM images of the samples at different solvents: Toluen (A), Chloroform (B), Acetone (C), DMF/THF (D)

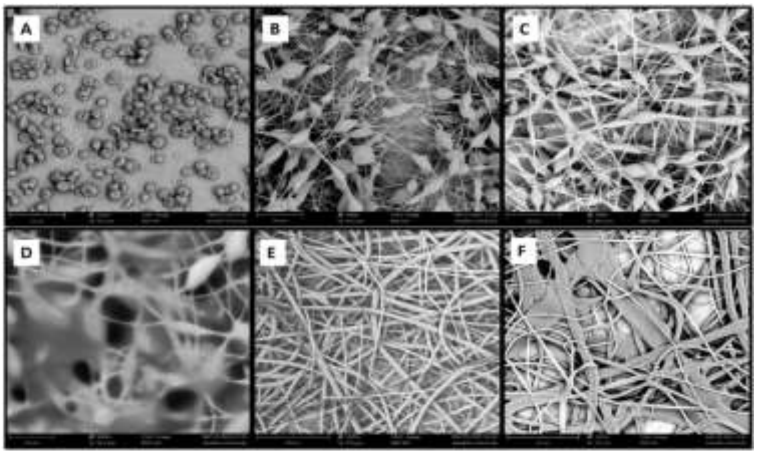

Figure 2. SEM images of the samples at different PMMA concentrations: 2 wt.% (81.000 Mw) (A), 4 wt.% (81.000 Mw) (B) and 6 wt.% (81.000 Mw) (C), 2 wt.% (350.000 Mw) (D), 4 wt.% (350.000 Mw) (E) and 6 wt.% (350.000 Mw) (F).

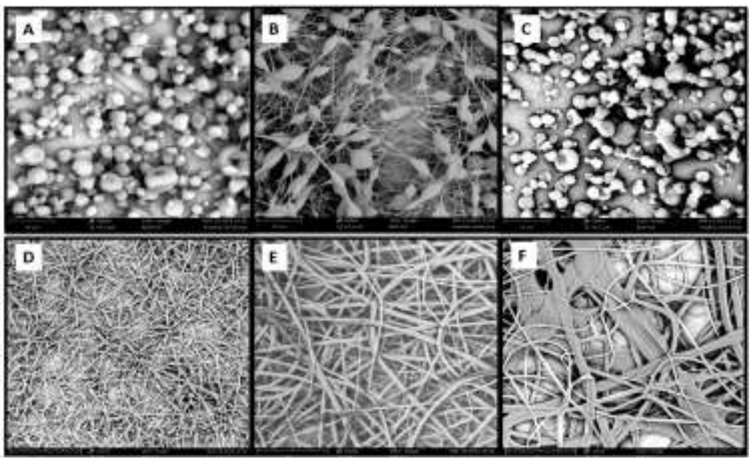

Figure 3. SEM images of the samples at different spinning voltage: (A) 22 kV (81.000 Mw PMMA) (B) 25 kV (81.000 Mw PMMA) (C) 28 kV (81.000 Mw PMMA), (D) 22 kV (350.000 Mw PMMA) (E) 25 kV (350.000 Mw PMMA) (F) 28 kV (350.000 Mw PMMA).

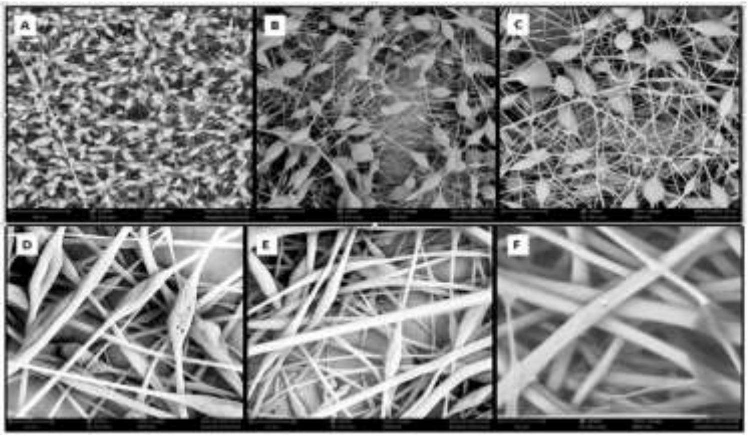

Figure 4. SEM images of the samples at different Solution Flow Rate: 4 ml/h (81.000 Mw PMMA) (A) , 6 ml/h (81.000 Mw PMMA) (B), 9 ml/h (81.000 Mw PMMA) (C), 4 ml/h (350.000 Mw PMMA) (D) , 6 ml/h (350.000 Mw PMMA) (E), 9 ml/h (350.000 Mw PMMA) (F).

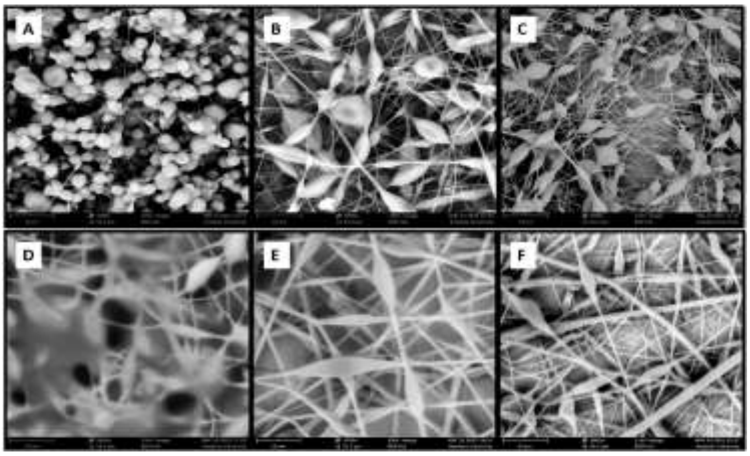

Figure 5. SEM images of the samples at different working distance between the collector and the Tip: 13 cm (81.000 Mw PMMA) (A) , 15 cm (81.000 Mw PMMA) (B), 19 cm (81.000 Mw PMMA) (C), 13 cm (350.000 Mw PMMA) (D) , 15 cm (350.000 Mw PMMA) (E), 19 cm (350.000 Mw PMMA) (F).

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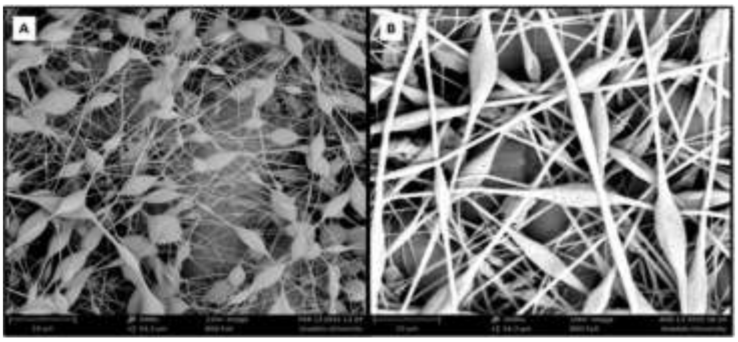

Figure 6. SEM images of the samples at different PMMA molecular weight: 81.000 MW (A),350.000 MW (B) .

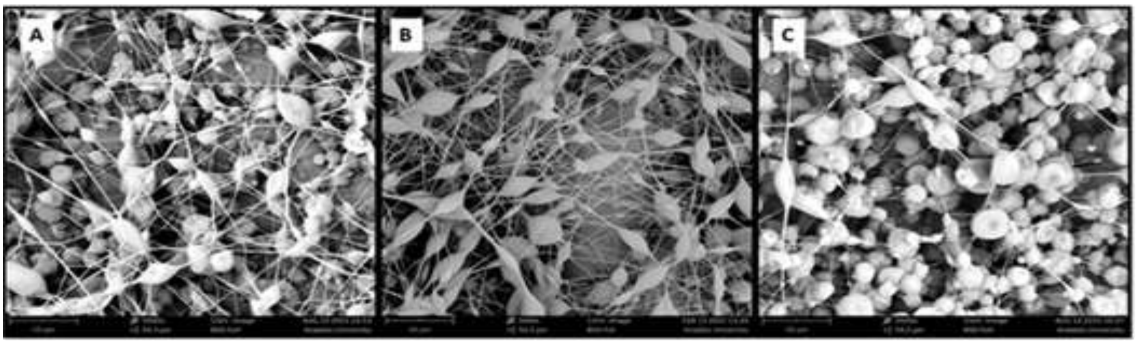

Figure 7. SEM images of the samples at different amount of BNNS (A) %0.5 BNNS (B) %1 BNNS (C) %1.5 BNNS

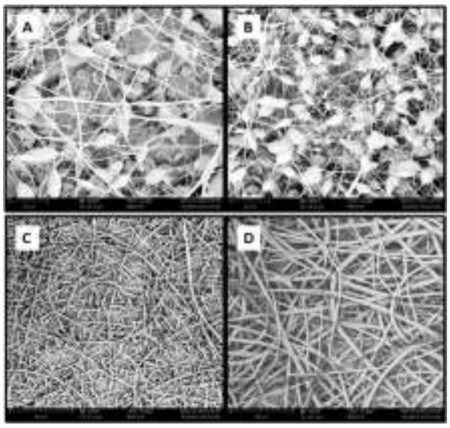

Figure 8. SEM images of the samples uner the effect of Silane additives (A) pure PMMA/BNNS nanofiber (81.000 g/mole PMMA) (B) with silane additives PMMA/BNNS nanofiber (81.000 g/mole PMMA) (C) pure PMMA/BNNS nanofiber (350.000 g/mole PMMA) (D) with silane additives (350.000 g/mole PMMA)

3.4. Thermal behaviour of the resulting nanofibers.

According to heat flow values found in DSC thermograms, the effects of molecular weight of PMMA, amount of BNNS, silane treatment, and concentration of PMMA on glass transition temperature (Tg) of the resulting fibers were investigated. Tg was found to be decreasing, as the molecular weight (MW) of PMMA decreased. Silane treated BNNS modified PMMA fibers exhibited high Tg values relative to fibers modified with untreated BNNS. As the BNNS concentration increases, Tg of the resulting fibers were also increased. As the solution concentration increased, T_g of the resultant fibers were also increased.

3.5. BNNS /PMMA Nanofibers-Vinylester Composite Characterization

Characterizaton of vinlyester resin containing BNNS modified PMMA electrospun nanofibers was performed based on the glass transition temperature of the resulting composites. For this purpose, optimum combination of the experimental parameters (4 wt.% concentration, 25 kV voltage, 6 ml/h flow rate, 19 cm working distance, silanized BNNS 1 wt.%) were first used to produce PMMA nanofibers. The produced fibers were then blended with vinylester resin at a ratio of 5:95 w/w, using a

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jiffy mixer. The final suspensions were first allowed to cure at room temperature followed by post curing 120 °C for 2h to promote the crosslinking. As a result, DSC measurements performed on the samples showed that Tg of the BNNS modified vinyl ester composites was increased by 3 % compared to neat vinyl ester /PMMA blend.

4. Conclusions

Electropsinning was used to produced BNNS modified PMMA nanofibers. Of all the trials, the experimental set comprised of PMMA concentration of 4%, silanized BNNS concentration of 1%, electric voltage 25kV, flow rate (6 ml/h) working distance of 19 cm, and acetone emerged as the best. The produced nanofibers were added to the vinyl-ester resin and the resulting composite structure was investigated. It was found that T_g of the samples increased with addition of BNNS modified PMMA nanofibers.

5.Acknowledgments

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