International Journal of Polymer Science & Engineering
Volume 11, Issue 1, 2025, ISSN: 2455-8745

Nanofibers of Ultra-High Molecular Weight Polypropylene (UHMWPP) Composites: Processing, Properties and Applications

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RESEARCH ARTICLE

Received Date: January 06, 2025

Acceptance Date: February 03, 2025

Published Date:

ABSTRACT

The nanofibers of ultra-high molecular weight polypropylene (UHMWPP) composite made with polyethylene terephthalate (PET) by electrospinning process. The high-temperature setup developed by hardware modifications in electrospinning machine to perform such experiments. Bilayer composite mat of UHMWPP and PET nanofiber was fabricated by deposition of monolayer of UHMWPP over PET monolayer by electrospining process. The developed composite mat products were characterized by SEM, DSC and other physico-chemical methods. The composite mat of UHMWPP with PET observed 30% improvement in breaking force compared to mat of neat PET material. The developed UHMWPP/PEt composite mat used as reinforcing fabric in ethylene/1-octene copolymer based elastomeric matrix for mechanical performance studies. We observed significant improvement in mechanical properties for developed UHMWPP and PET composite mat products.

Keywords: UHMWPP; PET; Nanofibres; Electrospinning; Composites mat products.

INTRODUCTION

Electrospinning is well-known process for fabrication of nano to micro-scale fibres from various polymers. It involves the stretching of a polymeric fluid by electrostatic attraction in the presence of an external electric field [1-4]. Because of its practical uses in high-performance filter media, protective clothing, composites, drug delivery systems, scaffolds for tissue engineering, sensors, and electrical devices, electrospun nanofibrous membranes with large surface areas have attracted a lot of interest [4, 5]. Fiber diameter, surface chemistry and topology, and interior structure can all be used to influence the functions of nanofibers or nanofibrous membranes, which are based on their high specific surface area, high molecular orientation, and nanoscale size.

Electrospun fibres are characterized by high surface to volume ratio that found application in various fields, such as composites, healthcare, biotechnology, defense, protective clothing, and tissue engineering [2, 5, 6]. In the recent years, electrospinning process industrialized, especially the melt processing found interesting for bulk production of nanofibers [7]. Spinning of the ultra-high molecular weight polymers is very difficult because of extremely high melt viscosity.

Furthermore, because of the extremely high degree of molecular chain entanglement, it is only very possible to draw a melt-processed ultra-high molecular weight polymer. Although electrospinning of many polymers (more than 100) has been studied, the electrospinning of UHMWPP still has not been encountered due to challenges in the synthesis of polymer resin [8]. However, it has been reported that ultra-high molecular weight polypropylene (UHMWPP) fibres are fabricated by gel spinning process. Because of its incredibly long chains, UHMWPP is a particularly durable polymer with a high impact strength.

There are few challenges involved in electrospinning of UHMWPP. First, though melt elctrospinning of PP is being reported but because of very high molecular weight of UHMWPP, it causes very high melt viscosity to process as compared to conventional PP [9, 10]. Secondly, UHMWPP has poor solubility in conventional solvents used for electrospinning and not soluble in solvents at room temperature as well [1].

UHMWPP is analogous to UHMWPE which has extremely long molecular chains that sever effective transfer of load from polymer backbone causing outstanding physical and mechanical properties [10-12]. UHMWPE being a high-performance material well-known for various specialty applications, such as body armor [13, 14], biomedical applications [15, 16]. UHMWPP is advantageous over UHWMPE owing to its higher service temperature and stiffness causing UHMWPP to be more commercially important along with lighter material compared to UHMWPE [17, 18]. Therefore, the processing of UHMWPP material needs to be addressed.

The goal of this study is to comprehend the UHMWPP material's electrospinnability. The present study focuses on the generation of UHMWPP nanofibres using elctrospinning technique. Some modifications were made in the conventional setup to perform electrospinning. The conventional room temperature electrospinning machine was converted into high-temperature system by attaching IR heaters above the syringe. The setup consisted of syringe pump, IR heaters, collector drum, and a power source as shown in Figure 1. The heaters are movable and can be easily taken out of the system. This is advantageous over already existing high-temperature electrospinning machines where, the heating system fixed like jacketed heaters or silicone oil bath. Furthermore, the long conventional needles were made short of 0.5 cm in length. Since high viscous UHMWPP solutions tend to clog the long needle. Clogging problem was successfully encountered with short needle.

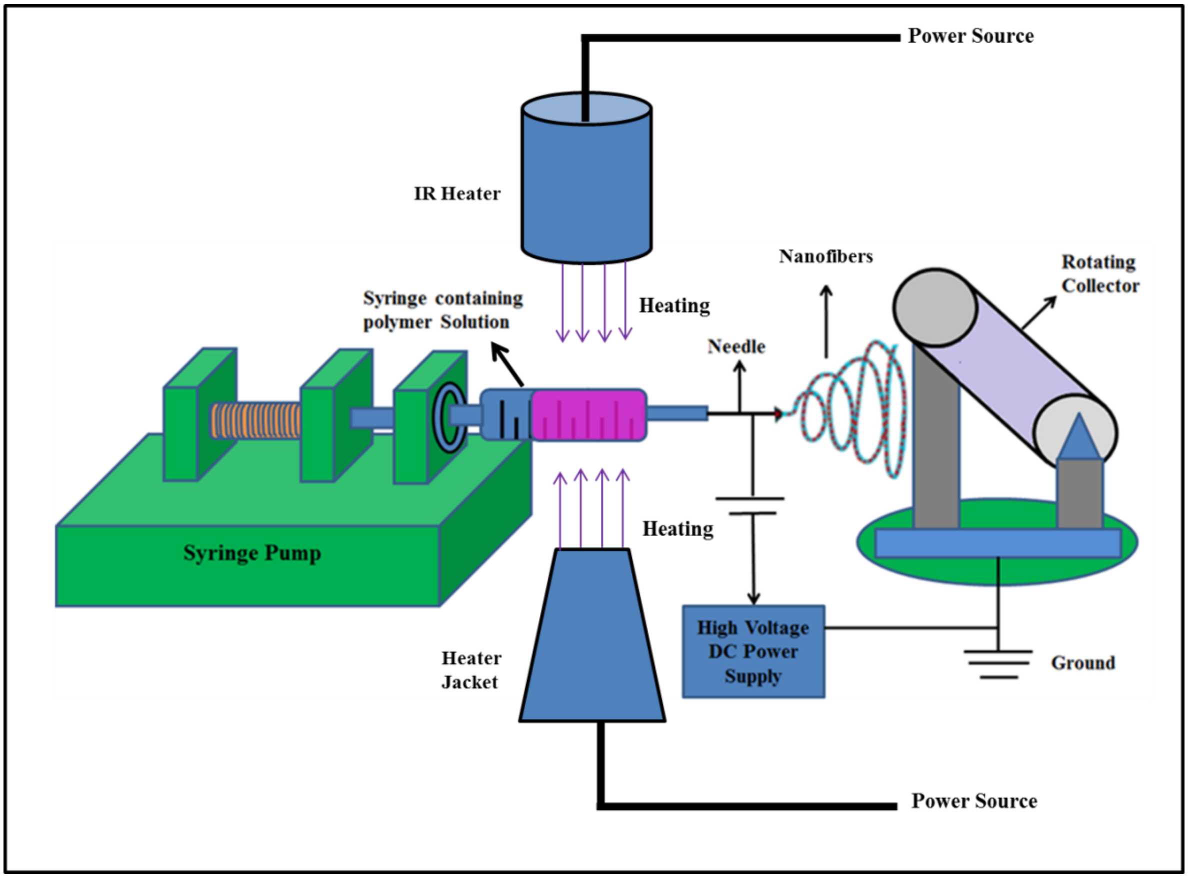

Figure 1: Schematic diagram of high-temperature electrospinning setup

EXPERIMENTAL

Materials

UHMWPP synthesized (molecular weight 1.2 X 105 g/mol) as procedure described in the reference [18]. The supplier of 1,2,3-Trichloropropane solvents, PET, was Sigma Aldrich. Decalin, Dichloromethane, Tetrafluroacetic acid were procured from Loba Chemicals. Polyethyeleneglycol400 (PEG) purchased from Merck Specialties, ethanol procured from fisher scientific and Ethylene-octene copolymer (ENGAGE 8100) obtained from Dow Chemicals. All the materials were used without any modifications.

Electrospinning processing

The electrospinning experiments are conducted on the E-SPIN Nanotech (Model: SUPER ES 2) machine. Prepared the UHMWPP polymer solution of different concentrations in decalin solvent at 140 ^{o}C. The prepared solutions were used for electrospinning process under specific conditions such as, syringe needle was maintained to 145 ^{o}C, the applied voltage of 7 kV, distance between needle and collector drum maintained 12 cm, solution flow rate of 3 µL/s and collector speed of 450 rpm. The. Glass syringe with 0.8 mm needle diameter was used.

Methods

Scanning electron microscopy (SEM, EVO 60/Zeiss, Germany) was used to analyze the morphologies of electrospun nanofibers at a 10 kV accelerating voltage. All samples were gold coated using a plasma gold sputter for 90 seconds prior to microscopy. The thermal analysis (DSC) performed using a TA instrument (Metter-Toledo-TA89E system) at 10 oC/min heating rate. DSC performed in the range of 30 oC to 300 oC temperature.

Fabrication of bilayer composite mat products

The fabrication of bilayer composite mat using two engineering polymers UHMWPP and PET to develop high performance materials. Bilayer composite mat was fabricated by depositing monolayer of electrospun UHMWPP fibers on top of monolayer electrospun PET fibers. 10 wt % PET solution was prepared by dissolving PET in 4:1 mixture of dichloromethane (DCM) and tetrafluroacetic acid (TFA) at room temperature. Electrospinning was conducted at 15 kV voltage at a flow rate of 1 µL/s at room temperature for 30 min with needle to collector distance of 15 cm and collector speed of 1000 rpm. Then 1 wt % UHMWPP solution in decalin was electrospun at 15 kV voltage with a flow rate of 3 µL/s at 160 °C for 1hr with needle to collector distance of 12 cm and collector speed of 1000 rpm.

RESULTS AND DISCUSSION

The morphology and diameter of electrospun fibre is determined by various parameters. This includes solution, process and ambient parameters. Proper control over these parameters gives electrospun fibre with desired morphology and diameter. An optimum solution concentration is required to produce continuous fibres [4]. At low concentrations beaded structure is formed because of breaking of fibre into beads before reaching the collector and higher concentrations leads to high viscosity making difficult to control flow rate through the syringe that prohibits the formation of continuous fibres. The amount of polymeric chain entanglements in a solution, and consequently the viscosity of the solution, is indicated by the polymer molecular weight. The molecular weight has great influence on rheological properties such as viscosity, surface tension and electric properties like conductivity and dielectric properties. This has been found that too low molecular weight forms beads instead of fibres [2]. Too much high molecular weight creates problem in processing such as clogging of needle. When spinning polymeric fibers, solution viscosity has a significant impact on the fiber's size and shape [6]. Continuous fiber processing is impossible at very low viscosities, and ejecting jets from polymer solutions becomes challenging at very high viscosities. Surface tension governed by the type of solvent from which solution made, and different solvents contribute different surface tension. Fibres without beads can be obtained by reducing the surface tension. In addition, lower surface tension of solution help to carry out electrospinning at lower applied voltage. In general, at high surface tension of solution lead to the jet instability and generate droplets which inhibit electrospinning process. Conductivity of solution contributed by type of solvents, polymers and ionizable salts. As electrical conductivity of solutions increases fibre diameter decreases. Hayati et al. demonstrated that extremely high conductive solutions were unstable in strong electric fields, which leads to a dramatic bending instability also a broad diameter distribution [7]. At lower solution conductivity, the insufficient elongation of jet by electric field lead to the formation of beads instead of uniform fibre.

Applied voltage is one of the crucial parameters in the electrospinning process. Only after threshold voltage, fibre formation takes place, this introduces the necessary charges in the solution that initiates electrospinning process. Generally, higher the applied voltage contributes higher columbic forces causing greater extent of stretching of solution and lead the reduction of fibre diameter. At very high voltage bead formation takes place as well.

The conventional room temperature electrospinning machine was converted into high temperature system by attaching IR heaters. The schematic diagram is shown in Figure 1. The heaters are movable and can be easily taken out from system. This is advantageous over already existing high temperature electrospinning machines where heating system is fixed like jacketed heaters or silicone oil bath. The syringes were made of glass to withstand at high temperature. The other modification in needle design where the long conventional needles were cut into the needle length of 0.5 cm in since high viscous UHMWPP solutions tends to clog the long needle. With short needle, the clogging problem was successfully encountered.

The important aspect of electrospinning process is to produce nanofibers which has high surface to volume ratio and significant role in introducing UHMWPP is due to its superior mechanical properties with being light weight material. This is an important criterion when one is fabricating the polymer composite with higher mechanical properties. We fabricated polymeric composite by using ethylene-octene copolymer (ENGAGE) as a matrix and bilayer composite mat of UHMWPP and PET as a reinforcement. The process of fabrication of sandwiched composite was completed in two steps. In the first step, two sheets of 1 mm thickness of ethylene octane copolymer were made by compression molding at molding temperature of 85 °C and pressure of 10000 lb for 10 min. In second step, the bilayer composite electrospun mat of UHMWPP with PET was sandwiched separately between two sheets of ethylene-octene copolymer at 3000 lb pressure and 80 °C for 7 min.

Because of their distinct rheological responses, shear thickening fluids exhibit certain mechanical qualities that make them unique for particular applications. In protective gear like sports gear and liquid armor, they serve as shock absorbers and impact-resistant materials for dampening and shielding. One of the most significant upcoming uses in the liquid armor manufacturing industry. Since, the use of fluids instead of layered conventional armors will make them light weight, cost effective, flexible and wearable so that much beneficial.

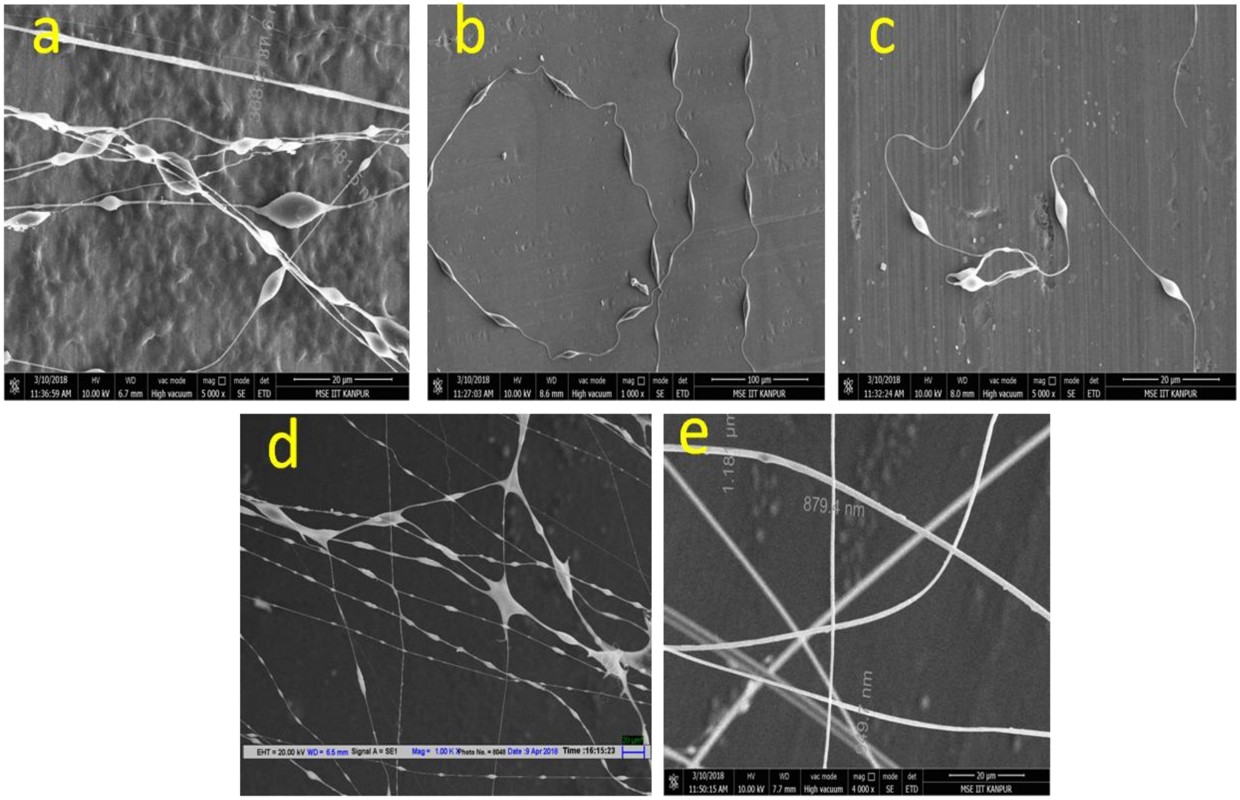

Figure 2. SEM micrographs of the electrospun fibres from solutions of UHMWPP in decalin for various concentrations (a) 0.3 wt.% (b) 0.5 wt.% (c) 0.7 wt.% (d) 0.85 wt.% (e) 1 wt.% at temperature of 160 ^{o}C, applied voltage of 15 kV, flow rate of 3 μL/s.

SEM images as shown in Figure 2 indicate that at low solution concentrations fibres did not form. At 0.1 wt.% concentration viscosity was too low and not able to deposit material on collector drum and hence, no fibre formation occurred. As we increased the concentration to 0.3 wt.%, nanofibres were formed with bead formation in between. We further increased the solution concentration from 0.3 wt.% to 0.85 wt.% and observed that the extent of bead formation reduced relatively. Again, we increased the solution concentration to 1 wt.% to optimize the solution concentration. Finally, the nanofiber formed without beads at 1 wt.% concentration. We also made 1.5 wt.% the solution became too viscous that jet couldn’t reach to collector due to gravity and immediately felled down. Thus, it was found that as viscosity increase the extent of bead formation gets reduced and at 1 wt.% UHMWPP in decalin gives uniform fibres and considered as the optimum concentration.

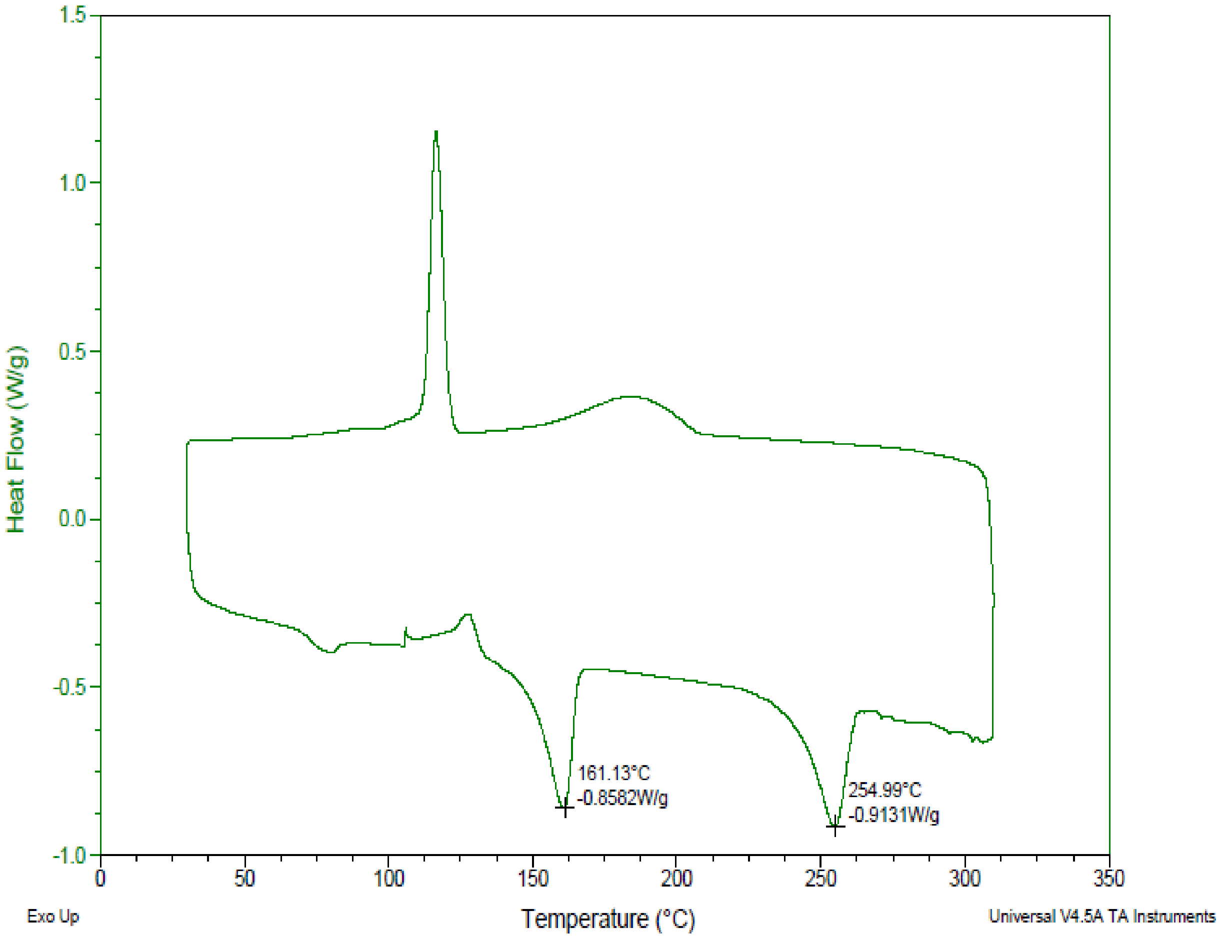

Figure 3. DSC thremogram of bilayer composite mat of UHMWPP with PET.

DSC analysis of developed UHMWPP/PET composite mat product observed two distinct melting points at 161.1 °C and 254.9 °C (as shown in Figure 3), which is due to UHMWPP and PET polymeric materials, respectively.

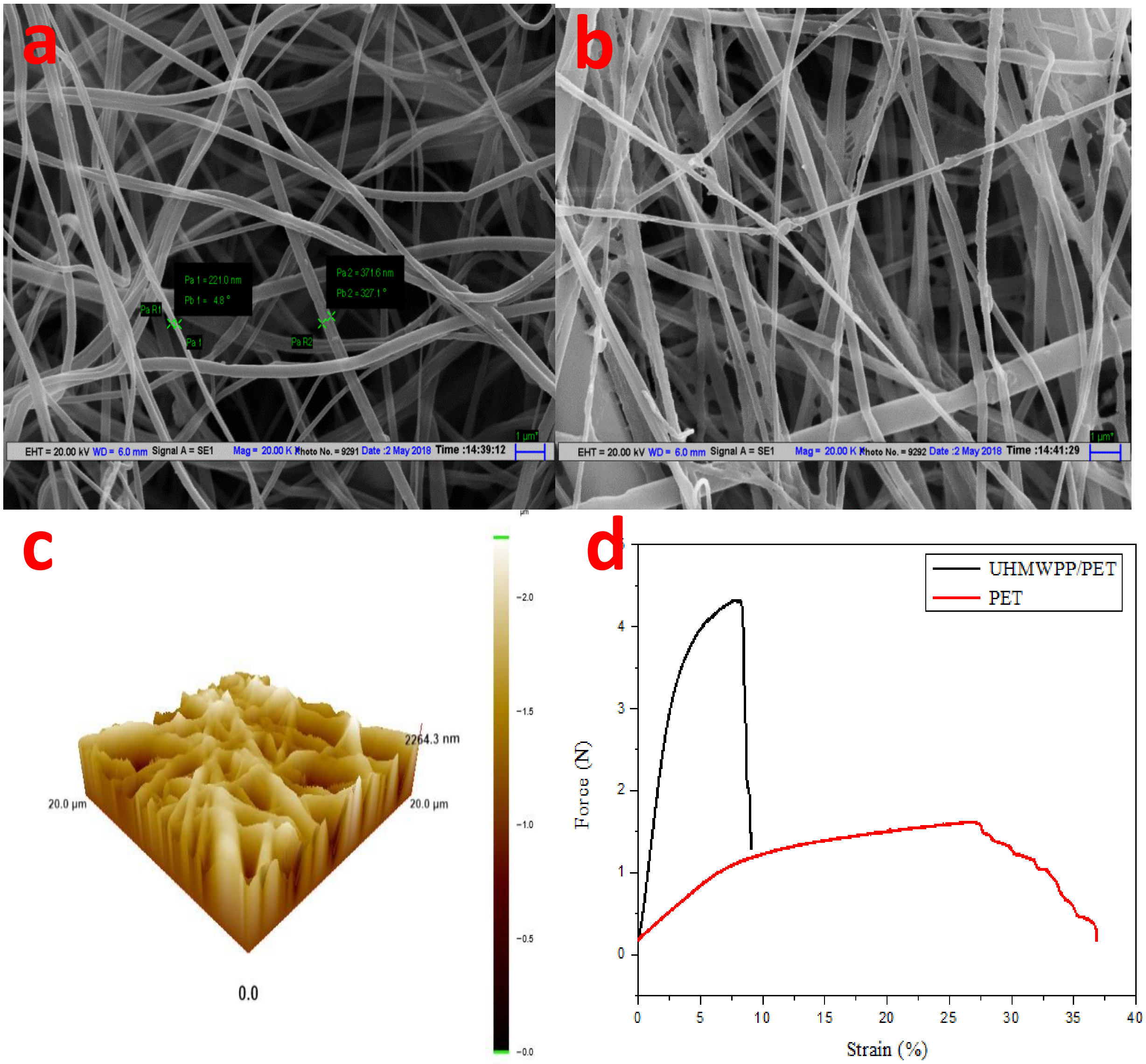

Figure 4. (a) SEM of PET mat (b) SEM of bilayer composite mat of UHMWPP with PET (c) AFM of bilayer composite mat made from UHMWPP and PET (d) Force vs strain graph of PET and bilayer composite mat of UHMWPP and PET.

SEM analysis shows (Figure 4(a,b)) that electrospun PET fibers are ~200nm diameter and electrospun fibers of bilayer composite mat of UHMWPP with PET have a diameter in the range from ~200 to 900nm. Thus, fibers having ~ 200 nm diameter are of electrospun PET fibers and electrospun UHMWPP fibers are of diameter ~900nm. The mat products were also characterized by AFM which confirms the presence of fibres as shown in Figure 4(c).

Table 1. Tensile testing of electrospun mat.

Sample	**F_{break} (N)**	**F_{max} (N)**
PET	0.17	1.62
UHMWPP/PET	1.30	4.32
% increase	166%	30%

The mechanical properties of electrospun mats, in particular tensile properties were studied and the results of stress as a function of strain as showed in Figure 4(c) and (d). From the Table 1, the breaking force for neat PET mat was 0.17 N and for UHMWPP with PET composite mat 1.30 N observed. The maximum force taken by PET mat was 1.62 N whereas the composite mat found 4.32 N force. Thus, the breaking force was increased by 30% and maximum force taken by 166% when PET mat was deposited with UHWMPP nanofibres on it. This clearly indicated the improved nanofiber fabrication from the UHMWPP and PET composite materials. Furthermore, the modulus of ethylene/1-octene copolymer sheet, electrospun PET in ethylene/1-octene copolymer matrix and electrospun UHMWPP/PET mat sandwiched in ethylene/1-octene copolymer matrix is shown in Figure 5. The results showed improvement in the modulus 6 MPa to 15.1 MPa for UHMWPP/PET mat incorporated in copolymer matrix, which was almost 155% increase modulus. When PET was incorporated the modulus increased to 9.3 MPa (i.e. 55% increase compared to plain ethylene/1-octene sheet). The tensile strength and percentage elongation values were not obtained due to elastomeric nature the samples became thin and slip from grip.

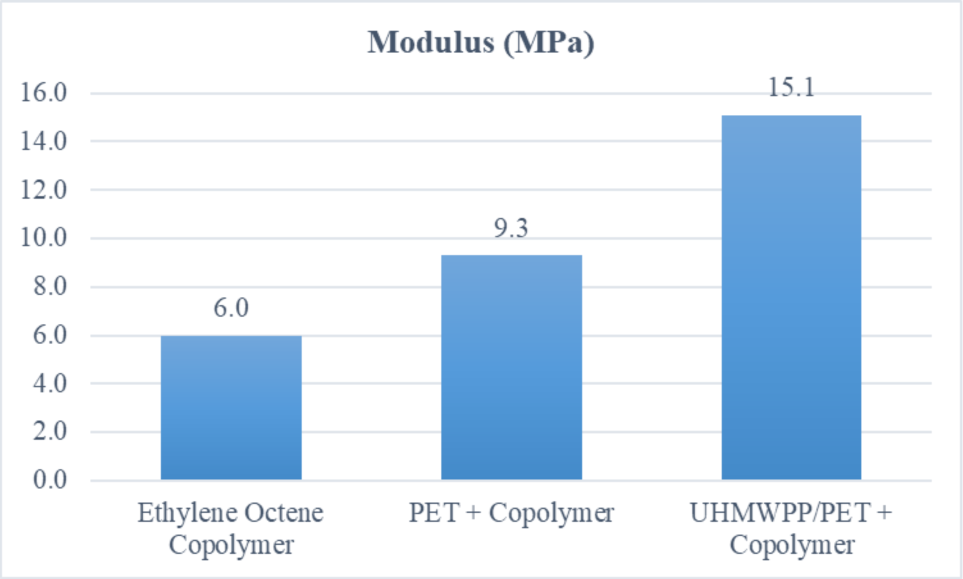

Figure. 5. Modulus results of different nanofibers.

CONCLUSIONS

In summary, we reported the electro-spinnability of ultra-high molecular weight PP (UHMWPP) polymer composites. The uniform naofibers of the UHMWPP/PET composites can be obtained using decalin solvent at 140 ^{o}C with 1% solution concentration. The high tensile bilayer composite mat of UHMWPP with PET was successfully fabricated. These mat when used as reinforcement in polymer matrix demonstrated that the final composite has higher modulus (~155% increase) in modulus compared to neat mat developed from ethylene/1-octene copolymer product. Thus, high modulus composites can be fabricated using these bilayers mats and that can open a wide area in the field of high-performance materials.

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CONFLICTS OF INTEREST STATEMENT

The authors declare that they have no conflicts of interest.