



Fabrication and optimization of processing parameters of 2D/3D arrays of composite PET electrospun nanofibrous webs

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Pristine and functional carbon nanofillers reinforced composite nanofibrous web of polyethylene terephthalate (PET) have been fabricated by the horizontal needle-based electrospinning technique. The nano materials are used to introduce the multi functionalities, like electrical conductivity, thermal stability and multiple adsorption sites. The nanocomposite nanofibrous webs are produced by mixing various weight percentages of 2D and 3D nanofillers in the matrix polymer solution. The micro structural morphologies, thermal stability, tensile strength of PET as well as the functional groups of nanofillers surface are optimized for making the 2D/3D assemblies multifunctional. The hybrid nanofibrous web is characterized by field emission scanning electron microscopy, thermal gravimetric analysis, universal testing machine, gel permeation chromatography and fourier transformed infrared spectrometer respectively. It has been found that the range of mean diameter of nanofibres lies between 165 nm and 272 nm due to the differential viscosity of nanofillers reinforced polymeric solution. The detailed structure-property studies are carried out on the reinforced functional PET nanofibres for various strategic applications.

Keywords: 2D polymeric nanofibres, Electrospinning, Mechanical properties, Nano fillers, Polyethylene terephthalate

1 Introduction

Electrospinning is a simple and very cost effective method which provides high surface area to volume ratio for producing very fine polymeric fibres with diameters ranging from few nanometers to micrometers¹⁻³. Freestanding electrospun polymeric nanofibrous membrane is also having good mechanical properties, high temperature and chemical resistant. Thus, they are used in tissue, air filtration, medical, water filtration applications, etc. The nano scale of polymer fibres may also offer advantages in inducing a specific kind of degradation.

Polyethylene terephthalate (PET) is a semi-crystalline polyester that, depending on the polymer grade, is frequently utilized to manufacture textiles and packaging. The molecular weight of PET polymer is important because it influences the polymer's physical properties, which can change its mechanical properties. When polymer's molecular weight increases, its strength, toughness, brittleness, melting temperature, and melting viscosity also increase, but its solubility decreases. The researchers used trifluoroacetic acid and dichloromethane to dissolve PET polymer and then

tested the produced fibres in air filtering applications⁴. PET plastic water bottle shreds were dissolved in HFIP (hexafluoroisopropanol) overnight at room temperature, and TBAC (tert-butyl acetate) was added to decrease the bead formation. The fabrication of polymeric nanofibres was used for water filtration⁵.

In recent years, different low-dimensional nanomaterials have been assembled together to generate new features, concurrently retaining the extraordinary properties of individual nano materials. Researcher⁶ found that the dispersion of carbonaceous nano materials in the polymer solution is very challenging due to strong inter-tube Vander wall forces that results in CNT bundles or aggregates in the polymer matrix during fibre mixing. The addition of nano material to a polymer matrix improves the mechanical strength and thermal stability of the polymeric nanofibrous webs^{7,8}. Researcher⁹ found that nano-hybrid shish-kebab-type microphase separation was observed in PAN/TPU with a 0.5 weight percentage of single-dimensional nanofillers. The researchers¹⁰ observed that adding 2 wt% of nanofillers to the polymeric nanofibre film results in the highest tensile strength (24.5%), which is 57–55% higher than that of pure PLA film. The functionality of the nanofibres is increased by the addition of nanofillers in

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the polymeric solution. Hence, functionalized nanofibres can be easily fabricated by the electrospinning process¹¹.

In this study, the nanofibrous web of PET and PET/fillers (2D & 3D) composite (free-standing) has been designed by the needle electrospinning technique. The influence of varying loading percentages of 2D and 3D nanofillers on the various functional properties, like surface characterization by field emission scanning electron microscopy (FESEM), fourier transform infrared (FTIR) as well as mechanical and thermal stability properties of nanofibrous free-standing webs has also been studied. This research can be further exploited in water filtration applications.

2 Materials and Methods

2.1 Materials

The thermoplastic recycled polyethylene terephthalate (PET) polymer chips of molecular weight 67427 g/mol were obtained from Reliance Industries Ltd., Mumbai. Trifluoroacetic acid (CF_3COOH , $M_w=114.03$) g/mol was purchased from Flucka Chemicals, Switzerland. Dichloromethane (CH_2Cl_2 , $M_w=84.93$) g/mol was purchased from Sigma Aldrich USA. Two dimensional filler (hydroxyl functionalized graphene) and 3-dimensional filler (hybrid functionalized carbon nanotube-graphene three-dimensional nanofillers) synthesized in DMSRDE, laboratory were used. The synthesis of multiwalled carbon nanotubes (MWCNTs) used for making 3D fillers was carried out by the catalytic chemical vapor deposition (CCVD) method using the bimetallic catalyst, where the MWCNTs are 99.9% pure with average 20 nm diameter. The few layers graphene flakes have been prepared by sonicating the oxygenated functionalized graphite in nitrogenous

solvent, where the edge functionalized graphene is of 20 μm flake size with a maximum of 15 graphitic layers. The mixture of functionalized nanotubes and graphene flakes was sonicated using an ultrasonic bath followed by centrifugation to collect the abundant amount of individual functionalized CNTs immobilized in functionalized few layers graphene flakes.

2.2 Preparation of Nanocomposite Solution

For the recycled PET nanofibres, the solution of PET polymer (12.5% conc.) was prepared in a 4:1 mixture of trifluoroacetic acid and dichloromethane at 30°C with continuous magnetic stirring at 300 rpm for 3 h. Different weight percentages of low dimensional carbon nanofillers (2D and 3D) were dispersed in 4:1 mixture of trifluoroacetic acid and dichloromethane by sonicating for 1 h at 30°C. The dispersed nanofillers solution was merged with 12.5% concentration PET polymer solution to make nanocomposite solution, where different low dimensional carbon nanofillers (2D and 3D) were maintained as 0.5, 1.0, and 2 wt%. After that the, highly dispersed nanofillers containing polymer solution was loaded into a 10 mL glass syringe to prepare for the nano fabrication by electrospinning.

2.3 Electrospinning of Pure and Nanocomposite Fibres

The polymer solution of nanocomposite was loaded in a 10 mL glass syringe to prepare the Taylor cone on the surface of a pendent drop for the electrospinning process (Fig. 1). The positive electrode of high voltage was connected to the steel needle tip and the grounded negative electrode was connected to a rotating cylinder covered with aluminium foil. The gap distance between the 0.83 mm stainless steel needle tip to the collector drum distance

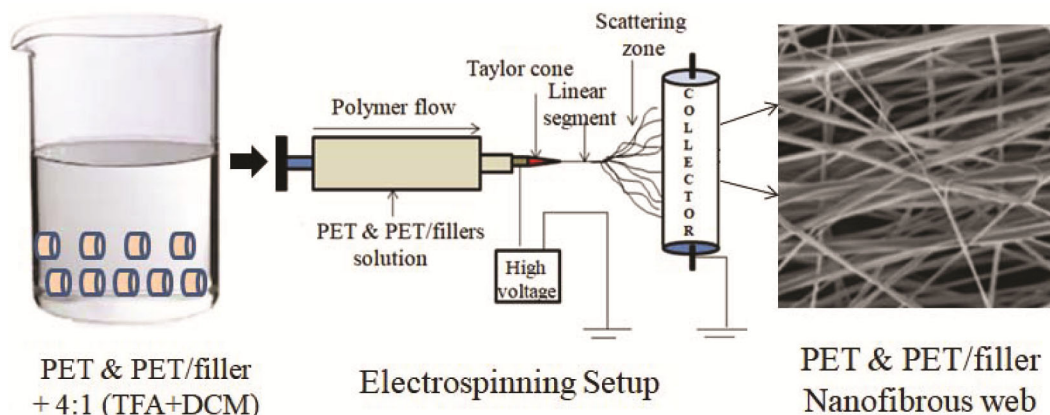


Fig. 1 — Schematic preparation and characterization of the nanofibrous web of pure PET and PET/2D and 3D nanofillers

was fixed at 15 cm for 18 kV electric field and 1 $\mu\text{L/s}$ flow rate. Fibres were vacuum dried overnight at 30°C before characterization. Spinning parameters for the fabrication of pristine and nanocomposite polymeric web were kept the same.

2.4 Determination of Molecular Weight

Molecular weight distribution of recycled PET polymer was measured by the Gel Permeation Chromatography (GPC) Agilent 1260 Multidetector system using the Plgel Mixed-C Column at a 1 mL/min flow rate and 2 mg/mL sample solution concentration by using trichloromethane + hexafluoroisopropanol ($\text{CHCl}_3 + \text{HFIP}$) as a solvent. A UV detector at 280 nm is used. Standard used PS STD -900000, 170000, 90000, 47500, 23000, 8000, 4000 & 800. The sample was injected at 30°C in a 10 μL .

2.5 Characterization of Nanofibrous Webs

The surface characterizations of the neat PET and PET/2D and 3D fillers nano webs were measured by using field emission scanning electron microscopy (FESEM) (TESCAN, model MIRA 3, with an accelerated voltage of 10 kV).

2.6 Thermal Analysis

The thermal stability of PET nanofibrous web samples was investigated by thermogravimetric method (TGA) using Perkin Elmer TGA-4000. The temperature range of 30-600°C was used with a heating rate of 10°C/min in presence of nitrogen gas.

2.7 Chemical Analysis

Chemical structure analysis of the neat PET and PET/2D and 3D fillers electrospun nanofibrous membranes was performed by fourier transforms

infrared spectrometer (FTIR), and spectra of web were recorded in a bruker (model alpha ECO-ATR).

2.8 Tensile Properties

Tensile strength was determined using an instron universal testing machine at an extension rate of 10 mm/min at 30°C with a specified size (length 20 mm and width 10 mm). In order to prevent slippage from the grips, the direct contact with the fibre layers was avoided. A double-sided cushion sticky paper tape was used for this purpose¹². Three random samples are tested and their mean values are reported.

3 Results and Discussion

3.1 Molecular Weight Distribution

The molecular weight distribution of 0.82 intrinsic viscosity PET polymer chips is determined using high temperature GPC. The molecular weight distribution of PET is determined using trichloromethane + hexafluoroisopropanol ($\text{CHCl}_3 + \text{HFIP}$) as a solvent. Detection limit of the method is checked by analyzing the samples (2 mg/mL) with 1 mL/min flow rate. A measurable peak is observed with this concentration (Fig. 2). Intrinsic viscosity and molecular weight are important parameters to evaluate the effective action of chain extenders on recycled PET. The intrinsic viscosity $[\eta]$, molecular number (M_n), molecular weight (M_w), polydispersity (M_w/M_n), and viscosimetric molecular weight (M_v) of PET polymer are 0.82, 22474, 67427, 3 and 114346 respectively.

3.2 Characterization of Nanofibres

The morphological structures of pure PET and PET/2D filler are shown in Fig. 3. Before the characterization, polymeric nanofibrous webs are

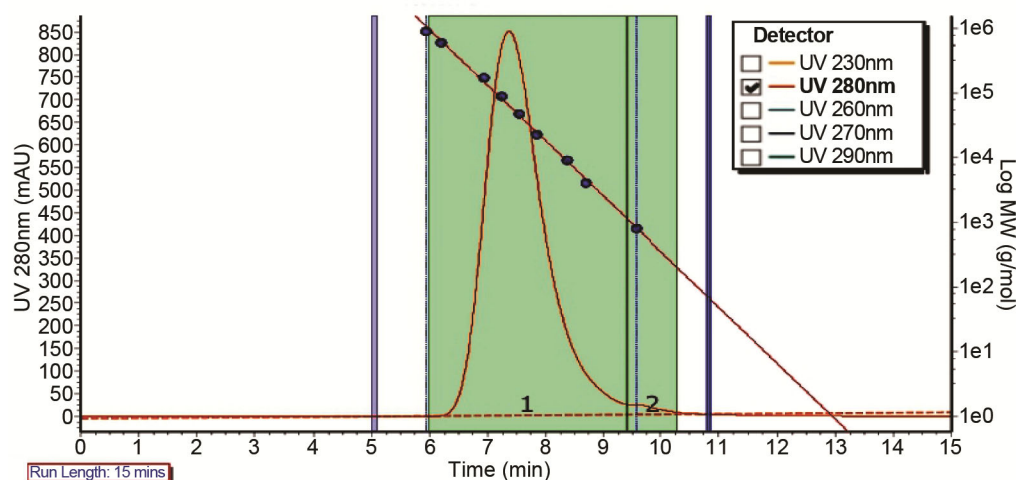


Fig. 2 — Gel permeation chromatogram of 0.82 intrinsic viscosity PET polymer

vacuum dried overnight and after that sputter is coated with a gold thin coating. Figure 3(b2) shows the pure PET nanofibrous web of the optimized 12.5% concentration. The continuous fibre formation is observed during the electrospinning process with an average 165 nm fibre mean diameter. Figure 3(e1)-(e3) show the morphologies of different loading weight percentages of 2D filler (0.5, 1.0 and 2.0%) respectively, continuous formation of nanofibres is observed. It is observed that the mean fibres diameter ranges from 165 nm to 272 nm. The solvents have an important role in determining the fibre diameter and morphology structure during spinning of polymer nanofibres, because these affect the polymer solution directly. The effect of addition of functionalized carbon nanotube to enhance the stability of electrospun PET 2D flexible sheet has been investigated as a function of loading percentage of nanofillers. The further increase in the mean fibre diameter of the nanotube reinforced PET is observed and can be explained by the enhanced viscosity of the polymeric solution for the introduction of functional nanofillers [Figs (3) & (4)]⁹. The higher diameter distribution in the cases of increased

nanofillers loading can be explained by the agglomeration of nano materials at higher weight fractions. The fibre diameter dependent modulus and tensile properties have been reported for electrospun polymeric fibres where the lower diameters are found to have higher mechanical strength due to the higher crystallinity and molecular orientations¹³. The mean fibre diameter is measured by using image analysis software (Image J software program). The diameter distribution histogram is plotted by the Origin Pro software.

Figure 4 shows the morphology images of different loading weight percentages of 3D hierarchical nanofillers of CNT-graphene in polymer matrix (0.5, 1.0, and 2.0%) respectively. Figure 4 [d1 (a)] shows the cross-sectional micrographs of nanofibrous membrane, and Figs 4 (b) & (c) show the higher resolution of the cross-section view of the nanofibrous membrane. The cross-section of polymeric nanofibrous membrane shows a thickness of 89 μm . We observe that on increasing the weight percentage of 3D filler in the polymeric solution, the fibre diameter also increases due to the increase in solution viscosity¹⁰.

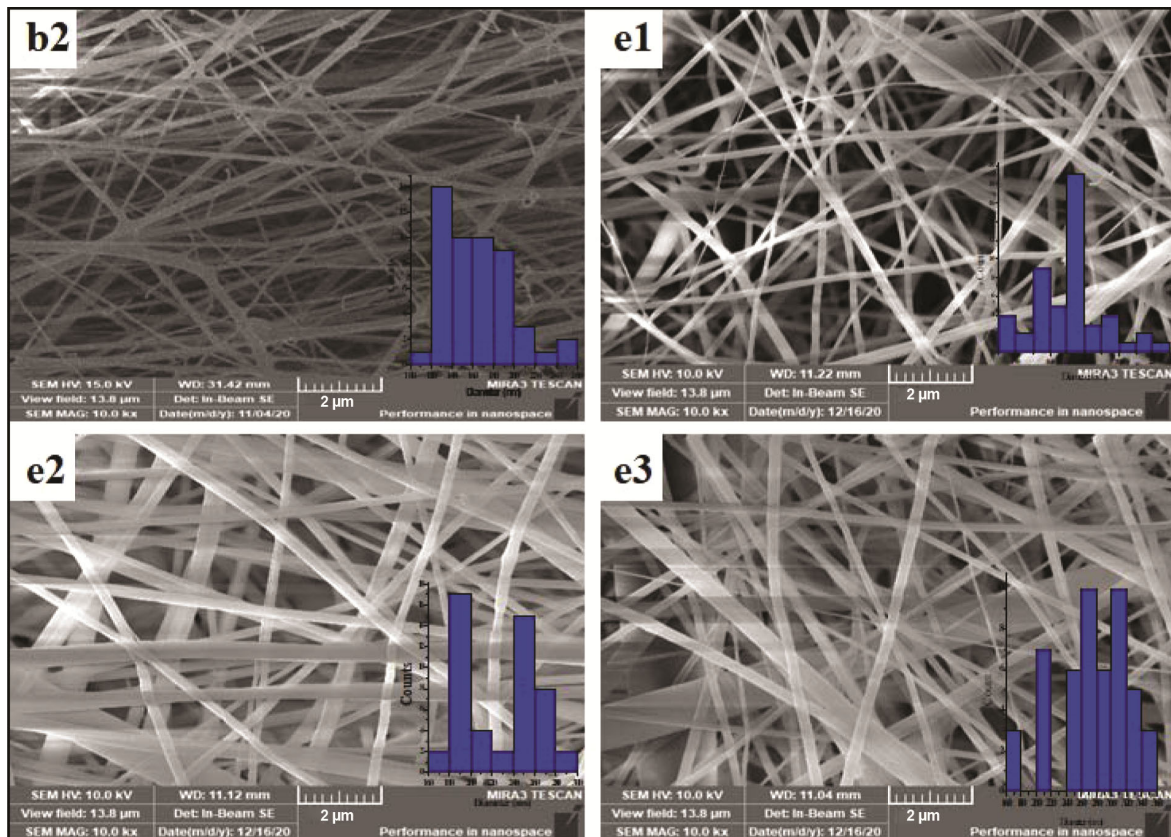


Fig. 3 — FESEM micrographs and diameter distribution histograms of the PET and PET/2D filler samples [(b2) PET with 12.5% concentration; and PET/2D with (e1) 0.5, (e2) 1.0 and (e3) 2.0 weight percentage of 2D filler]

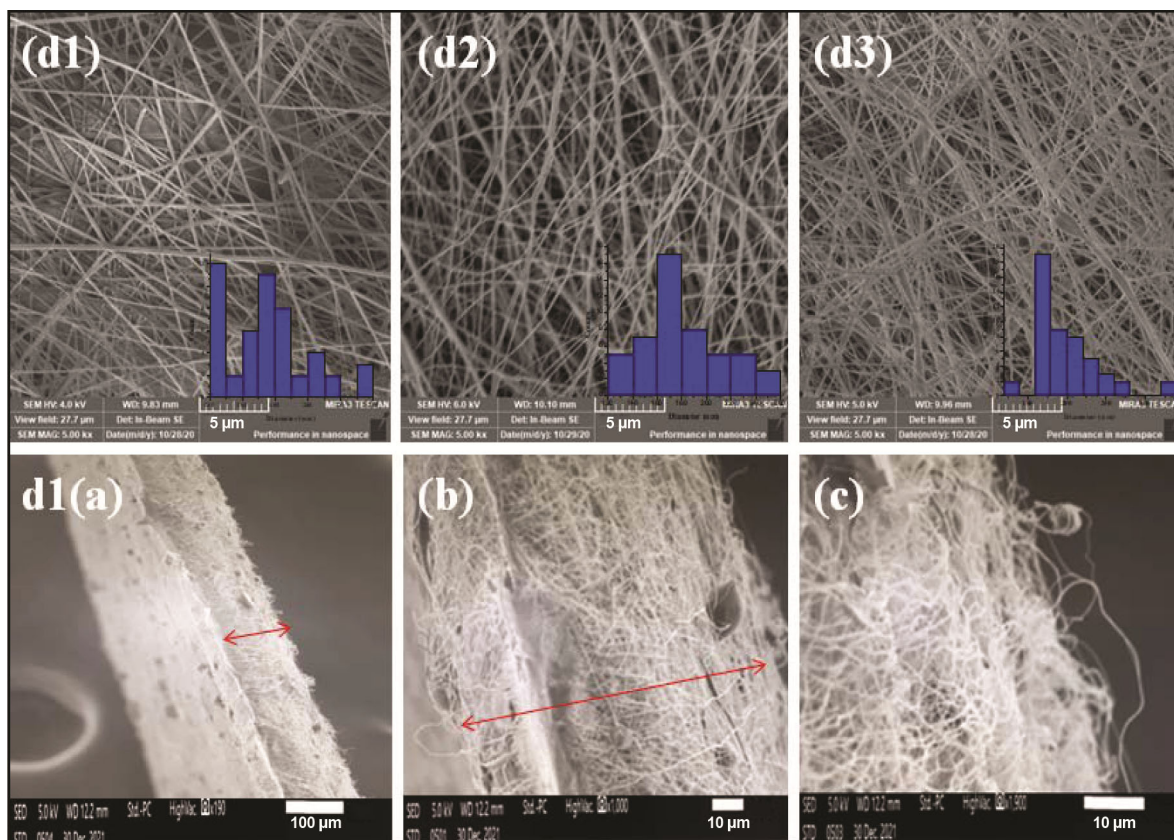


Fig. 4 — FESEM micrographs and diameter distribution histograms of PET/3D filler samples with (d1) 0.5%, (d2) 1.0% & (d3) 2.0% weight percentage of 3D filler; and d1 (a) 100 μ m, (b) 10 μ m & (c) 10 μ m scale cross-sectional views of polymeric web

Polymer concentration, applied voltage and feed rate were kept constant at 12.5%, 18 kV and 1.0 μ L/s respectively. Continuous fibre of average diameter 165, 170, 227, and 272 nm were found after adding 2D nano filler 0, 0.5, 1.0, and 2.0 wt. % respectively. Similarly, continuous fibre of average diameter 176, 180, and 202 nm were found after adding 3D nano filler 0.5, 1.0, and 2.0 wt. % respectively.

3.3 Chemical Analysis

Fourier transform infrared spectroscopy (FTIR) is used to observe the functional groups, and the effect of crosslinking agent on the chemical structure of PET electrospun nanofibrous membrane. The non-crosslinked and crosslinked webs of pure PET and PET/2D filler are shown in Fig. 5. It is observed that the higher peak of pure PET web is at 1699 cm^{-1} , and the higher peak of PET/2D filler (0.5 wt.%) is at 1716 cm^{-1} , indicating the very strong presence of the carboxyl C=O group. In the finger print region, the peak at around 1242 cm^{-1} is due to the C-C-O stretching vibration of the ester linkage and therefore confirms the formation of the ester product. The ester groups contain one C=O bond and

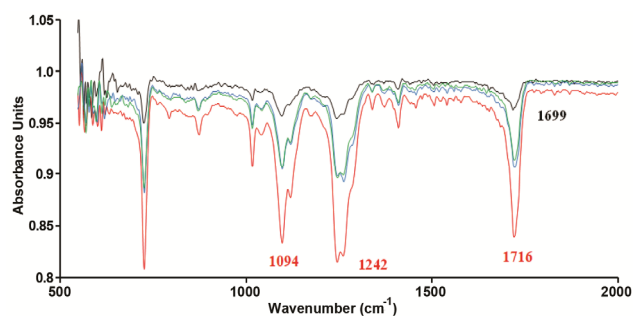


Fig. 5 — FTIR spectra of the carbonyl region [PET/2D filler nanofibrous webs of 12.5% concentration at different wt.% of 2D filler, black 0%, red 0.5%, blue 1.0% and green 2%]

two C-O bonds. The peak at around 1094 cm^{-1} is due to O-C-O stretching. The systematic increase in the carbonyl stretching vibrational frequencies of PET is found by the addition of higher amount of carboxylated nanotubes for better electrostatic force of attraction.

3.4 Tensile Strength

The mechanical properties of pure PET and PET/2D filler with a different weight percentage of 2D filler are selected for mechanical testing. 2D filler

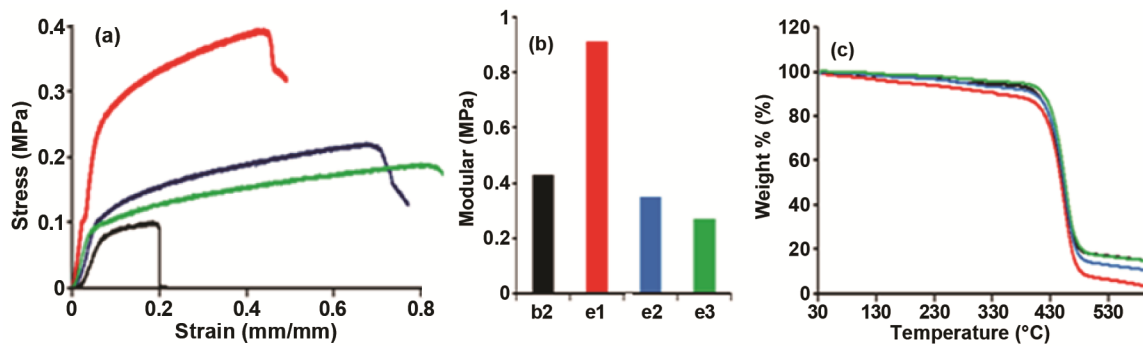


Fig. 6 — (a) Stress-strain curve, (b) Young modulus values and (c) TGA thermogram of different weight percentages of 2D filler [black (b2) 0%, red (e1) 0.5%, blue (e2) 1.0% and green (e3) 2%]

Table 1 — Tensile strength of pure PET and PET/2D filler nanofibrous web

Sample No.	Concentration %	Nanofiller wt%	Modulus MPa	Tensile extension at break, mm	Elongation-at-break, %	Tensile strength, MPa
b2	12.5	0	0.43	5.91	29.55	0.0960
e1	12.5	0.5	0.91	14.55	72.75	0.4310
e2	12.5	1.0	0.35	17.48	87.40	0.2229
e3	12.5	2.0	0.27	18.37	91.85	0.2227

presents the best morphology with an average diameter ranging from 165 nm to 272 nm and easily peels off free standing polymeric nanofibrous web as compared to 3D filler. Different fragments of sample with 2D filler are mounted on the Instron, to determine the elastic modulus and elongation-at-break. These properties are tested by analysing five samples; the results are presented in Table 1. Figure 6(a) represents the typical stress-strain curve of PET and with different weight fractions of nanofillers, showing the initial increase in stiffness and tensile strength from the pristine PET samples and Figure 6(b) represents the modulus. The average values found for Young's modulus of pure PET nanofibrous web are 0.096 MPa and for elongation-at-break 29.55%.

The addition of various weight fractions of nanofillers demonstrate the initial increase in stiffness and tensile strength of pristine PET samples. Table 1 shows that the 2D filler improves the modulus and tensile strength of the nanofibrous web up to a loading percentage of 0.5. The average value found for Young's modulus of 0.5 wt% of PET/2D nanofibrous web is 0.43 MPa and the elongation-at-break is 72.75%. It has been found that increasing the filler weight percentage increases the extension-at-break. The fibre diameter dependent modulus and tensile properties have been reported for electrospun polymeric fibres, where the lower diameters are found to have higher mechanical strength due to the higher crystallinity and molecular orientations¹³. The

Table 2 — TGA results of pure PET and PET/2D filler polymeric nanofibrous webs

Temperature, °C	Weight loss, %			
	b2	e1	e2	e3
50	0.77	1.51	0.62	0.16
100	1.41	2.75	1.72	0.57
200	3.01	5.69	3.17	1.88
300	5.35	8.68	5.98	3.79
400	8.49	13.52	9.7	6.47
450	46.94	51.71	45.36	39.44
500	82.07	92.93	85.91	82.12
600	85.27	96.96	89.58	85.28

improvement in tensile strength and modulus is likely related to very good dispersion and orientation of the 2D filler in the TFA+DCM solvent, within the polymer matrix and strong interfacial interactions with functional nano materials.

3.5 Thermal Stability

The percentage change in weight loss against the temperature of pristine PET and PET/2D filler webs is depicted in Fig. 6(c). The values of weight loss at different temperatures of the polymeric nanofibrous webs are also illustrated in Table 2. The range of mass decomposition temperatures of the main constituents is 400–500°C. Initial low temperature weight loss of the films starts at around 30°C and goes to 100°C, due to the evaporation of moisture absorbed by the polymeric webs. The incorporation of nanomaterials into polymer matrices improves the mechanical strength of polymeric webs^{7, 8}. From Fig. 6(c), it is

observed that when increasing the temperature above 400°C, a sudden drop in weight can be seen due to the decomposition of PET nanofibrous webs.

4 Conclusion

Pristine PET and PET/2D filler and PET/3D filler have been prepared by the electrospinning technique using trifluoroacetic acid and dichloromethane, which is a good solvent to obtain pure PET and nanocomposite electrospun nanofibres and a homogenous dispersion of nanofiller. It is found that free-standing nanofibres diameter increases while increasing the weight percentage of nano fillers. The diameter is increased due to a change in solution viscosity. The composite nanofibrous webs of PET/2D filler (0.5%) are well dispersed and hence they enhance the tensile properties by 0.096-0.4310 MPa and elongation-at-break from 29.55% to 72.75% as compared to pure PET nanofibrous web.

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