Polyester Nanocomposite fibers with Antibacterial Properties

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ABSTRACT

Antibacterial nanocomposite polyester (PET) fibres were melt spun by adding nano ZnO loaded Linear Low Density Polyethylene (LLDPE) master batch (MB) to the PET chips. The influence of content of nano ZnO on the antibacterial properties, crystallization behaviour and mechanical properties was studied. It was found that PET composite fibres having 1 % nano ZnO showed the optimum antibacterial activity. The presence of nano particles advanced the onset of crystallization temperature and also adversely affected the mechanical properties but well within acceptable limit.

Key words: Nanocomposite, Polyester, Antibacterial, Nano ZnO.

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INTRODUCTION

Composite materials may show enhancement in the mechanical, thermal, optical, and physicochemical properties when compared with the pure polymer. These enhancements attract the interest of many researchers because they lead to wider application of many polymers. Composite materials obtained using different polymer matrices have been reported [1]. Polyester (PET) is widely used to produce fibers, films, and packaging materials with high barrier properties [2–4]. It is also one of the versatile manmade fiber and finds its use in a variety of applications such as apparel, industrial fabrics. It is semi-crystalline, transparent and thermoplastic with high strength [5].

To date, many composite PET fibres have been researched to improve thermal and crystalline properties of PET fibers [6-8] or to introduce new functional properties such as electrical conductibility [9], antibacterial function [10] and flame-retardancy [11]. Among these functional materials, antibacterial materials have recently been in focus. When antibacterial materials are applied to PET fibres, the resultant self-sterilizing fabrics have the potential benefits of reduced disease transfer among hospital population, bio warfare protection, and other applications.

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The application of nanoparticles to textile materials has been the object of several studies aimed at producing finished fabrics with different performances. For example nano-Ag has been used for imparting antibacterial properties [12, 13], nano-TiO$_2$ for UV-blocking and self-cleaning properties [14-16] and ZnO nanoparticles for antibacterial and UV-blocking properties [17-20].

The use of nanotechnology in the textile industry has increased rapidly. This is mainly due to the fact that conventional methods used to impart different properties to fabrics often do not lead to permanent effects, and will lose their functions after laundering or wearing. Nanoparticles can provide high durability for treated fabrics, in comparison to conventional materials, because they possess large surface area and high surface energy that ensures better affinity for fabrics and leads to an increase in durability of the textile functions. Wash fastness is a particular requirement for textile and it is strongly correlated with the nanoparticles adhesion to the fibres. Therefore, antibacterial finishing has come up in a huge way [21-23].

Today biocides are important in textile finishing in the area of anti-microbial finishes. These include material protection (rot proofing and preservation), aesthetic (prevention of staining) and hygiene finishes (control of the development of odor and bacteria) [24].

Many antimicrobial products that were formerly used with textiles are now strictly regulated because of their toxicity and potential for environmental damage. Products such as copper naphthenate, copper-8-quinolinate, and numerous organo mercury compounds fall into this category [25-29]. Silver ions, for example, incorporated in glass ceramic, have a very low toxicity profile and excellent heat stability [30]. These principles are also used for fiber modification, an alternative to the antimicrobial finishes with high permanence [31-32].

Of the inorganic materials, metal oxides such as TiO$_2$, ZnO, MgO and CaO are of particular interest as they are not only stable under harsh process conditions but also generally regarded as safe materials to human beings and animals. Some of the metal oxides e.g. MgO and CaO are essential minerals for human. Other metal oxides such as TiO$_2$ and ZnO have been used extensively in the formulation of personal care products. Synthetic fibers can be treated with these metal oxides during production in order to make them anti-microbial.

Master batches are predispersed color / additives concentrates available in different thermoplastics base and in different concentration of colorants / additives as per the requirements and applications. Like colorants, many other types of additives / fillers can be perfectly added / dispersed to modify / reinforce certain properties of the fiber according to its applications and requirements. Suitability of base polymeric material depends upon the matrix and its processing methods. Careful selection of the proper carrier resin is vital. It should be the same as the matrix resin or so-called universal concentrates can also be used [33].

Linear Low Density Polyethylene (LLDPE) is highly flexible with good elongation properties, good chemical resistance properties and tensile strength [34].

This research paper describes the work in which nanocomposite antibacterial PET fibres were prepared using antibacterial masterbatch and pure PET resin by melt-spinning method. Results of

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the investigation on the performance properties of composite PET fibres, i.e., antibacterial, mechanical properties, and the crystallization characteristic are described.

MATERIALS AND METHODS

Materials
Commercial grades of Polymers, Dyes, Chemicals and Auxiliaries were used in the present study. Polyester (PET) chips having IV 0.73 supplied by Reliance Industries Ltd., Mumbai and Linear Low Density Polyethylene (LLDPE) having Melt Flow Index of 55 supplied by Clariant India Ltd were used.

MA-g-LLDDPE was used as compatibilizer for compatibilizing LLDPE and PET and it was obtained from Pluss polymers, New Delhi, India. *Escherichia coli* (*E. coli*) (ATCC 10140) and *Staphylococcus aureus* (*S. aureus*) (NCTC-3750) were provided by Hafkin Institute, Mumbai.
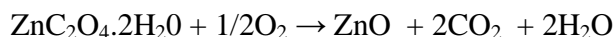
Nano ZnO used in the project was synthesized by the following method [35].
In one flask, Zinc Acetate dihydrate (10.98 gm) was stirred in 300 ml of ethanol at 60°C for 30 minutes to dissolve it completely. Oxalic acid dihydrate (12.6 gm) was dissolved in 200 ml of ethanol at 50°C for 30 minutes in another flask. The oxalic acid solution was then added slowly to the warm ethanolic solution of zinc acetate with continuous stirring. A thick white gel was formed, which was kept for drying at 80°C for 20 hours in the oven. The white powder so obtained was calcined at 600°C for 2 hours to yield ZnO nanoparticles.

Formation of Zinc Oxalate:
$$Zn(CH_3COO)_2.2H_2O + H_2C_2O_4.2H_2O \rightarrow ZnC_2O_4.2H_2O + 2CH_3COOH + 2H_2O$$
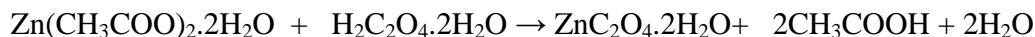
Calcination of Zinc Oxalate:
$$ZnC_2O_4.2H_2O + 1/2O_2 \rightarrow ZnO + 2CO_2 + 2H_2O$$

Preparation of Master batches (MBs)
After optimizing the amount of compatibilizer to be added for compatibilizing the LLDPE and PET, MB of nano ZnO was prepared by compounding nano ZnO (with 20% loading) and optimized amount of compatibilizer (0.25%) with LLDPE in a twin screw extruder of MARIS-TS with temperature range and rpm as shown in Table 1.

Table 1: Temperature in different zones of Twin Screw Extruder

Zone	Temperature (^{0}C)
Z_1	100
Z_2	120
Z_3	130
Z_4	150
Z_5	165
Z_6	175
Z_7	180
RPM	100

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Melt Spinning

Before Melt spinning the PET chips were dried in a vacuum dryer for 16 hours at 150^0C to remove traces of moisture. The LLDPE MB was also dried in an oven at 60^0C for 4 hours. The exact amounts of PET and nano ZnO loaded LLDPE is shown in Table 2.

Table 2: Details of amount of PET and nano ZnO loaded MB

Samples	PET(gm)	LLDPE loaded with 30% nano ZnO (gm)
PET/0.5% Nano ZnO	245	5
PET/1% Nano ZnO	240	10
PET/1.5% Nano ZnO	235	15

The melt spinning of the PET chips blended with nano ZnO MB was carried out on Laboratory Melt Spinning M/c. obtained from Fair Deal Associates, New Delhi, India.

The temperatures of the these extruder zones maintained were 270^0C, 285^0C and 290^0C for Zone-I, Zone-II and Zone III, respectively, and they were distinctly above the melting point of the PET chips. In the extruder zone there is a provision for Nitrogen gas to prevent oxidation of PET and the chips melt to form a molten mass, which moves further to metering pump and then to Die head zone. The filaments extruded from the spinnerets were cooled down by blowing cool air in 1.5 meter long quench duct. The filaments were guided to the godet roller via metered spin finish passage and then subsequently it was taken over to the draw rollers. The drawing was carried out by two stage drawing method at previously optimized draw ratio of 3. The filaments were finally fed to the take up winder machine over the condenser arm wheel, which applies tension to the yarn and controls the speed of the spindle, ensuring that consistent, well-formed package could be produced. The dpf was 8 and final speed of spinning was 107 m/min, and denier per filament was 8.

Evaluation of Antimicrobacterial Activity

The antimicrobial efficacy of a compound will vary as per its presence in solution or on the textile substrate. Quantitative assessment of antibacterial activity exhibited on polyester spun filaments was carried out by AATCC Test 100-2004 (AATCC 2007) and the colony-forming units (CFUs) were enumerated using Lapiz Coloney Counter (Medica Instrument Mfg.Co., Mumbai, India). The filaments were introduced in the 100 ml nutrient broth inoculated with the *S. aureus* and *E. coli* microbe and incubated at 37^oC for overnight (24hours). Microbial inhibition was determined by the reduction in number of bacterial colonies formed with respect to the untreated control sample using following equations:

$$R = \frac{B - A}{B} \times 100$$

(1)

Where

    R = percent reduction in bacteria

    A = CFU for treated test specimen swatches in the jar incubated for 24h contact period,

    B = CFU for untreated control test specimen swatches in the jar immediately after inoculation (at "0" contact time).

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Dyeing of Nanocomposite fibers

The spun filaments from the package were cut into fine fibers, thoroughly mixed and then dyed using standard method of dyeing of PET fibers in high temperature / high pressure (HTHP) beaker dyeing machine, with Disperse Yellow Brown F2GL (Disperse Orange 30), for 1% shade. The dyed samples were then subjected for reduction clearing treatment for 20 minutes at 70^OC with 2gpl of caustic soda and 2gpl sodium hydrosulphite. All fiber samples were then thoroughly washed at room temperature followed by neutralization with 1 gpl acetic acid solution. The fiber samples were finally washed in water and air dried.

Evaluation of Wash Fastness

The dyed samples were then subjected for washing fastness [ISO 3] in a Launder-O-meter for 20 min. at 60 ^{O}C, using 2 gpl non-ionic soap (Auxipon NP) and 2gpl soda ash at a liquor ratio of 50:1 [36].

Evaluation of Light Fastness

For determination of light Fastness **[ISO 105-A02]**, dyed fiber samples were stuck on a cardboard paper and its half portion was covered by a black sheet and remaining portion was exposed to light continuously for 17 hours. After that the fading of exposed samples was compared with that of the Blue Wool Standards, which were also exposed for the same time, simultaneously.

Evaluation of Color Strength

The samples were evaluated for color depth in terms of Kubelka Munk function (K/S) using a Spectra Flash® SF 300, Computer Color Matching System supplied by Data color International, U.S.A [37]. Kubelka Munk K/S function is given by:

$$\frac{K}{S} = \frac{(1 - R)^2}{2R}$$

(2)

Where,

      "R" is the reflectance at complete opacity,

      "K" is the absorption coefficient,

      "S" is the scattering coefficient.

Characterization of Nano ZnO

XRD patterns of nano ZnO was obtained using XRD machine Miniflex, Rigaku, Japan. Shape and size of nano ZnO were characterized using Transmission Electron Microscope of PHILIPS, Model: CM200S.

Characterization of Composite fibers
Wide Angle X-Ray Diffraction (WAXD)

The finely cut fiber samples were gently pressed into a rectangular felt using appropriate spacer. WAXD patterns were recorded for 2θ angle from 0^0 to 60^0 with Lab XRD – Ricaku, Japan**.**

Scanning Electron Microscope

Surface morphology of nanocomposite fibers was characterized using SEM JEOL JSM 6380LA, JEOL ltd. Japan

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Differential Scanning Calorimetry (DSC)

Thermal properties of nanocomposites were analyzed in a nitrogen atmosphere (flow rate 20ml/min) by differential scanning Calorimetry (Shimadzu, Japan [38]. To remove previous thermal history, all samples were first heated at 290^0C for 5 min and then quenched to 50^0C. The heating and cooling rates were set at 20^0C/min. The second scanning of heating and cooling was then performed under the same conditions and these values are reported.

Tensile Strength and Elongation at Break

The tensile strength and elongation at break of PET filaments were measured on 'Tinius Olsen' M/c supplied by Aimil Ltd. A single filament of test length 10 cm was used at an extension rate 50mm/min. An average of 5 readings was noted and expressed in terms of Kg. Testing was carried out as per the test method ISO 5079 for breaking strength of fibers [39].

RESULTS AND DISCUSSION

Characterization of nano ZnO
X-Ray Diffraction Analysis
Figure 1 shows the X-ray diffraction patterns of nano ZnO. No peaks due to impurity were observed, which suggests that high purity ZnO was obtained. In addition, the peak was widened implying that the particle size is very small. The broadening of peaks was observed mainly due to the nano size effect [40].
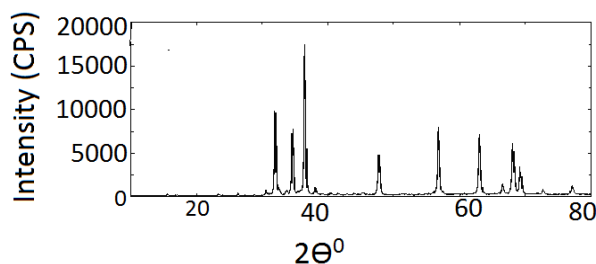

Figure 1: XRD peaks of nano ZnO

TEM Analysis
The particle size of the ZnO as determined from TEM is shown in Figure 2. It shows regular and spherical like morphology. The ZnO powder prepared by the method mentioned earlier gave a particle size in the range of 20-40nm.
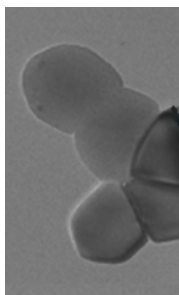

Figure 2: TEM image of nano ZnO

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Characterization of Antibacterial fibers
X-Ray Diffraction Analysis
The wide angle X-ray diffraction (XRD) spectra of the series of PET nanocomposite fibers are shown in Figure. 3. The intense diffraction peak of nano ZnO appears at $2\theta = 38^0$. But for the PET/nano ZnO nanocomposites, the WAXD peaks of the nano ZnO almost disappeared even though the amount of Nanoparticles loading was increased from 0.5% to 1.5% .It indicates that these nanoparticles could be completely exfoliated and dispersed in the PET matrix forming a nanometer scale composite.
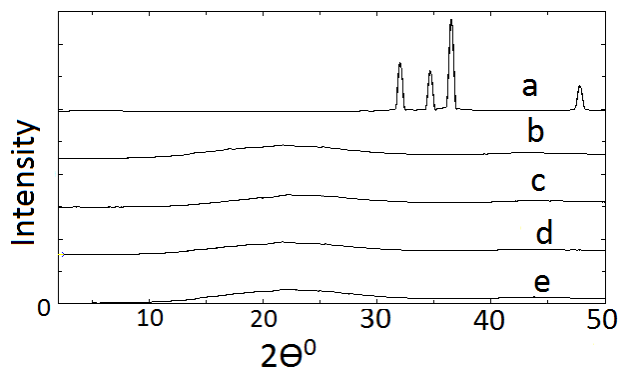

Figure 3: XRD Spectra of PET and Its Nano Composite fibers a) Nano ZnO b) PET/0.5% Nano ZnO c)

PET/1% Nano ZnO d) PET/1.5% Nano ZnO e) PET
Figure 4 is the SEM image of the antibacterial nano composite PET fibers in which 1% nano ZnO was added. In this we can see many little particles on the polyester fibre surface, and these particles are relatively homogeneous, without formation of any agglomerates.
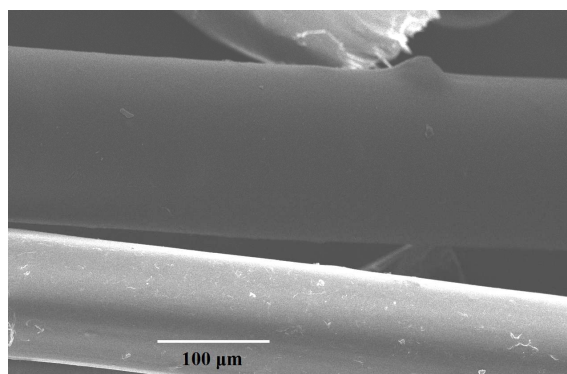

Figure 4: SEM micrograph Extruded Polyester fibre loaded with 1% Nano ZnO

Antibacterial Properties
The finely cut nanocomposite fibers were eveluted quantitaively using AATCC Test 100-2004 (AATCC 2007) for the antimicrobial test and the results for percent reduction of colonies against *S.aureus* are shown in Table 3. The results indicate that all the nano composite fibers showed a good colony reduction and it increased with increase in loading of nano ZnO, indicating progressive increase in antibacterial activity.

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Table 3: Antibacterial Activity Results for NCTC 3570 *S.aureus* (Gram Positive)

Samples	No of Colonies at '0' Time Contact	No of Colonies after '24' hours Time Contact	Activity (%)
PET	86	137	NA
PET /MB	90	141	-63.95
PET/0.5% Nano ZnO	56	23	73.26
PET/1% Nano ZnO	49	15	82.56
PET/1.5% Nano ZnO	46	9	89.53

The results for reduction of *E. coli* shown in Table 4. also indicate that the increase in nano ZnO in composite fiber, antimicrobial property was progressively enhanced.

Table 4: Antibacterial Activity Results for *E. coli* strain AATCC 10148 (Gram Negative)

Samples	No of Colonies at '0' Time Contact	No of Colonies after '24' hours Time Contact	Activity (%)
PET	55	175	NA
PET /MB	48	210	-144.19
PET/0.5% Nano ZnO	50	24	72.09
PET/1% Nano ZnO	46	21	75.58
PET/1.5% Nano ZnO	23	3	96.51

Results in Tables 5 & 6 show that antibacterial activity of the composite fiber didn't show any significant reduction in the efficiency even after dyeing indicating that the ZnO nanoparticles are well embedded inside the polymer matrix. Thus such a finishing effect is going to be of permanent nature.

Table 5: Antibacterial Activity Results for NCTC 3570 *S. aureus* (Gram Positive) After Dyeing

Samples	No of Colonies at '0' Time Contact	No of Colonies after '24' hours Time Contact	Activity (%)
PET	86	137	NA
PET /MB	90	141	-63.95
PET/0.5% Nano ZnO	145	24	72.09
PET/1% Nano ZnO	68	17	80.23
PET/1.5% Nano ZnO	63	12	86.05

Table 6: Antibacterial Activity Results for *E. coli* strain AATCC 10148 (Gram Negative) After Dyeing

Samples	No of Colonies at '0' Time Contact	No of Colonies after '24' hours Time Contact	Activity (%)
PET	55	175	NA
PET /MB	48	210	-144.19
PET/0.5% Nano ZnO	60	25	70.93
PET/1% Nano ZnO	49	23	73.26
PET/1.5% Nano ZnO	38	6	93.02

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In both the cases i.e. for *S.aureus* and *E. coli* the antibacterial efficiency was up to 80% for 1% and 1.5% loading of nano ZnO, before as well as after dyeing. These values were enough to qualify the material as antibacterial textiles.

Mechanical Properties

Table 7 shows the results of loss in tensile strength, elongation at break and % crystallinity for PET and its composite fibers. The crystallinity % has a direct relation with tensile strength and extensibility of the fiber. It can be seen that both the tensile strength and elongation %, decreased with increasing content of nano ZnO. The phenomenon is associated with the decrease of PET macromolecule arrangement along the fibre axis because of the antibacterial materials added in the structure.

Table 7: Tensile Strength, Elongation and Crystallinity of PET and Its Nanocomposite fibers

Samples	Tensile Strength (MPa X 10^{-2})	Elongation at Break (%)	Loss in Tensile Strength (%)	Cyrstallinity from XRD (%)
PET	5.29	82.6	--	22.12
PET /MB	4.80	90.4	9.26	21.7
PET/0.5% Nano ZnO	4.75	60.15	10.19	18.49
PET/1% Nano ZnO	4.56	41.28	13.89	17.45
PET/1.5% Nano ZnO	4.26	29.36	19.44	15.28

The values for loss in tensile strength % are 10.19%, 13.89% and 19.44% for 0.5%, 1% and 1.5% of nano ZnO fiber. Thus the antibacterial activity of these fibers was at the expense of the loss in tensile strength which is more pronounced in case of 1.5% loading. Therefore it is recommended that the nano ZnO loading should not be more that 1% for making antibacterial nano composite PET fibers, as the loss in tensile strength in this case is well wihin the acceptable limit.

Differential Scanning Calorimetry (DSC)

By comparing DSC curves in Table 8 and Figure 5 it is seen that the Peak cooling crystallization temperature (T_c) was shifted to higher temperature (from 194^0C for virgin PET to 208^0C for 1.5% nano ZnO loading) with the increasing content of nano ZnO. This is because the nano ZnO plays the role of a heterogeneous nucleation agent when the composite antibacterial fibres are cooled. So, the crystallization temperature (T_c) is increased.

It should also be noted that the curves for PET and PET nano composites are very much similar and have little impact on the glass transition temperature of the fibers (Figures 5 a,b,c,d and e).

Table 8: DSC Data of PET and Its Nanocomposite fibers

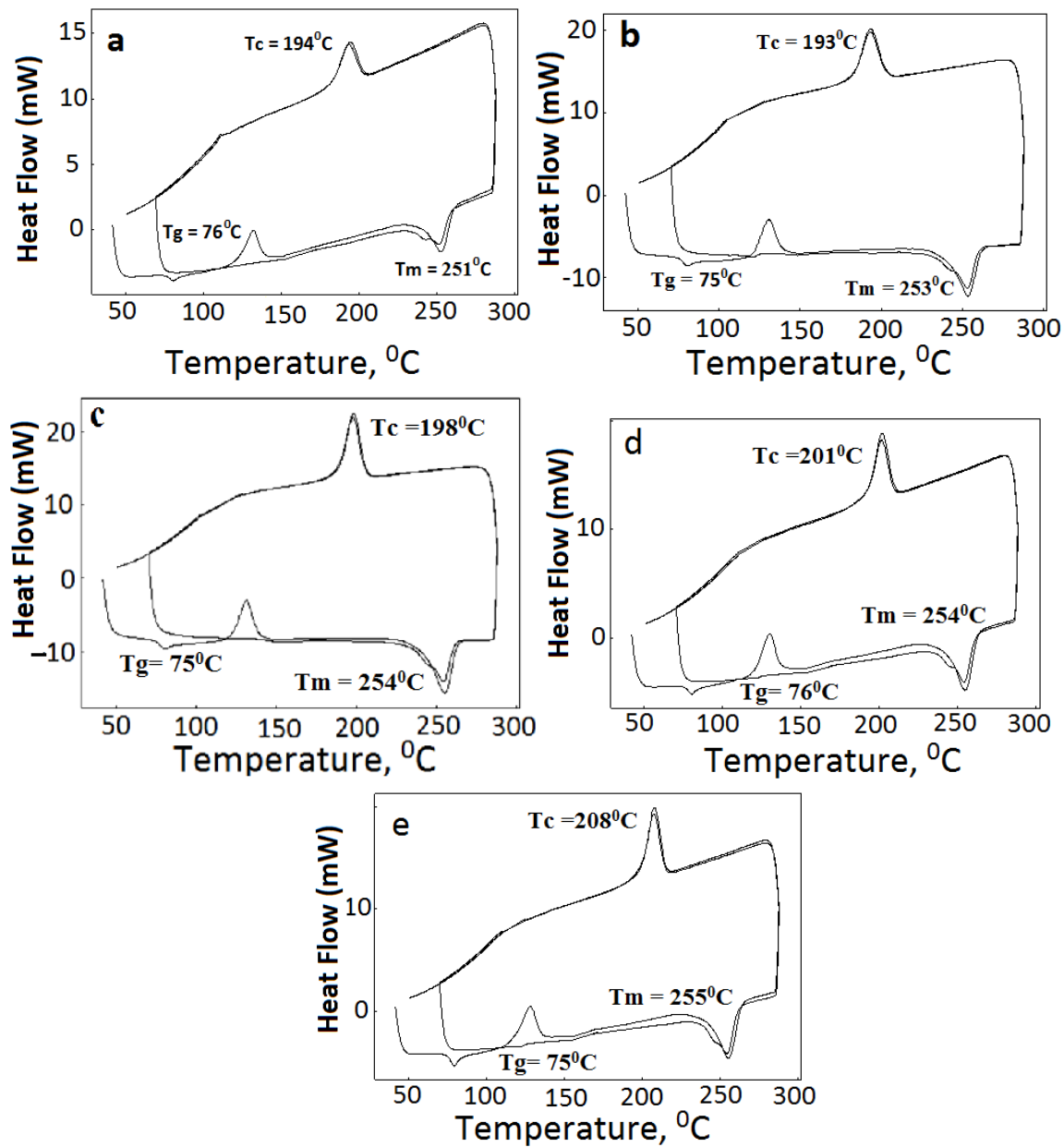| Samples	$T_g(^0C)$	T_c Peak(^0C)	T_m Peak(^0C)	$\Delta H_f(J/g)$	$\Delta T (^0C)$
PET	76	194	251	42	58
PET /MB	75	193	253	41	60
PET/0.5% Nano ZnO	75	198	254	44	56
PET/1% Nano ZnO	76	201	254	46	52
PET/1.5% Nano ZnO	75	208	255	49	47

$$\Delta T (^0C) = T_m - T_c$$

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Figure 5: PET and Its Nanocomposite fibers a) PET b)PET /MB c)PET/0.5% Nano ZnO d) PET/1% Nano

Dyeing

As can be seen from Table 9, there is not much difference in K/S values of the PET and PET nanocomposite fibers. The wash and light fastness of the nanocomposite dyed fiber samples is also exactly same as the virgin PET fiber. In other words the amorphous content which is responsible for dyeing seemed to have no significant impact.

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Table 9: Effect of Nano ZnO on Depth of Shade, (K/S) and Washing fastness
Dye Used: Disperse Yellow Brown F2GL, Wavelength max. abs.: 450nm
Shade Dyed: 1%

Samples	K/S value	Wash Fastness	Light Fastness
PET	17.36	5	8
PET /MB	16.125	5	8
PET/0.5% Nano ZnO	16.578	5	8
PET/1% Nano ZnO	16.693	5	8
PET/1.5% Nano ZnO	16.651	5	8

CONCLUSION

Permanent antibacterial PET fibers can be developed using nano ZnO during spinning of PET composite fibers. It also results in reduction in mechanical properties although they are within acceptable limit. As the amount of nano ZnO in the fiber goes on increasing antibacterial activity is also found to be progressively enhanced. The addition of nanoparticles causes early onset of crystallization.

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