Effect of nanoclay loading on zeta potential of polyester nanocomposite fibre

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Polyester (PET) nanocomposite fibres have been melt spun by adding master batches of linear low density polyethylene (LLDPE) loaded with organophilic nanoclay after compatibilizing the PET and LLDPE. The spun fibres show increased hydrophobicity which further increases progressively with the amount of nanoclay loaded into the fibre. The addition of this nanoclay also results in improved dyeability of the nanocomposite fibres with acid dyes due to the presence of quaternary ammonium organic substituent that is present in the nanoclay. There is slight decrease in tensile strength of the fibre accompanied by the decrease in elongation %, indicating that the addition of nanoclay makes the filaments stiffer. The onset of crystallization temperature occurs at higher temperature in case of composite fibres than in case of neat PET fibre because of nucleating effect of nanoclay.

Keywords: Nanoclay, Nanocomposite, Polyester, Polyethylene, Zeta potential

1 Introduction

The commercial textile poly (ethylene terephthalate) fibres are high oriented semicrystalline systems consisting of a spectrum of regions ranging from highly crystalline to virtually noncrystalline. They have closely packed fibre structure, high crystallinity and hydrophobic character.

The study of polymer clay nanocomposites has shown that the insertion of polymer chains into layered silicates dramatically modifies various physical properties, including thermal stability and fire resistance[1,2]. Natural clays are generally organophobic, and it is important to modify them, so that the miscibility between the clay and the polymer is enhanced. A cation exchange process achieves the organic modification of the clay; the inorganic cation (usually sodium) is replaced by an organic cation (typically ammonium and phosphonium), but other salts such as stibonium[3] and tropylium[4] have also been used. Various ammonium salts have been prepared and it is found that the substituent attached to these ammonium salts play a significant role in enhancing the nano-dispersion of the modified clay in the polymer. Clays containing oligomeric units[5,6] have also been used. In this paper, pyridine and quinoline-containing salts were also employed to modify montmorillonite. TGA analysis shows that the quinolinium modified clay has a higher thermal stability than the pyridinium modified clay[7].

Until recently[8] research on polyester nanocomposite fibres is focused on modulus and tenacity improvements with spinning speed[9] or spinning speeds in the form of draw down ratios[10-14]. McConnell[9] showed that increasing the spinning speed enhanced both modulus and tenacity of poly(ethylene terephthalate) (PET) fibres at a given nanoclay loading and with a specific surfactant type. Chang[10-14] examined several polyester nanocomposite systems at various draw down ratios from the spinneret. The as-spun nanocomposite and pure PET fibres showed very low elongations at break (3%) during loading at room temperature.

The electrical charge determines the zeta potential at the fibre liquid interface upon immersion of fibres in an aqueous solution. The zeta potential predicts the electrostatic interaction between individual fibres and the aqueous environment that is used for processing. Therefore, zeta potential characterization becomes very important. Several authors[9,15-19] have reported that nanoclay acts as nucleating agents in PET. But no study has been done on the effect of surface charge or zeta potential of nanocomposite fibres.

The basic theory about the electrokinetics as well as the employment of electrokinetic measurements for the characterisation of the reactivity of the polymer substances is well known[20].

In order to determine the changes in fibre surface charge, the zeta potential is measured through streaming potential measurements as a function of *p*H. These properties are generated by the

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electrochemical double layer (EDL), which exists at the phase boundary between a solid and a solution containing ionic moieties[21-23]. Three processes govern the net charge on the surface of a material in contact with a polar medium, namely (i) association /dissociation of surface chemical groups, (ii) adsorption of ionic species, and (iii) and dissolution of ions from the material into solution.

Variation in solution pH value and electrolyte content enables one to estimate the acidic/basic and polar/nonpolar character of the solid surface from zeta potential data. The pH dependence of the zeta potential at charged surfaces, dominated by dissociation events, gives information about the acidic or basic strength of the functional surface groups from the position of isoelectric points and zeta potential plateau ranges. The non-polar character of polyester fibres is responsible for the high degree of hydrophobicity reflected by a very high negative zeta potential. The fibres show negative surface charge most probably not because of different surface groups dissociation but due to the hydrophobic interactions between the fibre surfaces and the components of the electrolyte solutions.

Polyester (PET) is mass coloured by different methods, such as master-batch addition method. In this case coloured chips containing a high percentage (10-50%) of a colorant are produced using a polymer such as polyethylene or low-melting polyester. Alternatively, the same PET may be used to prepare master batches of the colorant. The master batches of colored chips are blended together with the white chips in the desired proportion and are spun together to get a colored fibre[24].

Like colourants, many other types of additives / fillers can be perfectly added / dispersed to modify / reinforce certain properties of the plastic 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[25]. Linear low density polyethylene (LLDPE) is highly flexible with good elongation properties, good chemical resistance properties and tensile strength[26].

Although lot of literature is available on the nano composites based on nanoclay, no research work has been done so far to understand the effect of nano clay loading on zeta potential characteristic of the polyester. The nanoclay loading affects the surface characteristics of the fibre, which, in turn, affects the dyebility. Hence, in this study, PET nanocomposites have been prepared by incorporating organophilic nano clay by masterbatch addition technique, using LLDPE as base polymer. The characterization of nanocomposites was carried out for changes in zeta potential, thermal properties, mechanical performance and dyeing behaviour.

2 Materials and Methods
2.1 Materials
Polyester (PET) chips having IV 0.73 was supplied by Reliance Industries Ltd., Mumbai and LLDPE having melt flow index of 55 was supplied by Clariant Chemicals (India) Limited. Crysnano1010 an organophilic natural montmorillonite nanoclay, modified with a quaternary ammonium salt, was provided by Crystal Nanoclay Pvt. Ltd., Pune, (India). Optim GE-340 (GMA-LLDDPE) was used as compatibilizer for compatibilizing LLDPE and PET. This was obtained from Pluss polymers, New Delhi, India.

Commercial grades of dyes, chemicals and auxiliaries were used in the present study. Acid dye, Colocid Blue RL was obtained from Colourtex Pvt. Ltd., Mumbai

After optimizing the amount of compatibilizer to be added for compatibilizing the LLDPE and PET, master batches (MB) of organophilic nanoclay were prepared by compounding Crysnano1010 (with 30% loading) and optimized amount of compatibilizer (0.25%) with LLDPE in a twin screw extruder of MARIS-TS with different temperature range (100°, 120°, 130°, 150°, 165°, 175° and 180° for Z_1, Z_2, Z_3, Z_4, Z_5, Z_6 and Z_7 zone respectively and 100 rpm. Details of these MBs are shown in Table 1.

2.2 Methods
2.2.1 Melt Spinning
Before melt spinning the PET chips were dried in a vacuum dryer for 16 h at 150^{0}C to remove traces of moisture. The LLDPE MB was also dried in an oven at 60^{0}C for 4 h. The melt spinning of the PET chips

Table 1 — Details of amount of PET and nanoclay MB-Crysnano1010

Sample	PET, g	LLDPE loaded with 30% Crysnano1010, g
PET/0.5% Nanoclay	245.84	4.16
PET/1% Nanoclay	241.67	8.33
PET/2% Nanoclay	233.34	16.66

blended with nanoclay MB was carried out on Laboratory Melt Spinning M/c obtained from Fair Deal Associates, New Delhi, India.

The temperatures of the extruder zones maintained were 270, 285 and 290^0C for Z_1, Z_2, and Z_3 zones respectively, and they were distinctly above the melting point of the PET chips. In the extruder zone, there is a provision for supply of nitrogen gas to prevent oxidation of PET 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 m long quench duct. The filaments were guided to the godet roller via metered spin finish passage and then subsequently they were 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 package could be produced. The final speed of melt spinning was 107 m/min and denier per filament was 8.

2.2.2 Tests
Wide Angle X-Ray Diffraction (WAXD)
The finely cut fibre samples were gently pressed into a rectangular felt using an appropriate spacer. WAXD patterns were recorded for 2θ angle from 0^0 to 50^0 with Lab XRD – Ricaku, Japan.

Measurement of Zeta Potential
The surface characteristics of polyester fibres were analyzed by determination of zeta potential. This was carried out using the Electro Kinetic Analyzer (EKA), Anton Paar, Germany based on the streaming potential, Fairbrother and Mastin Method. One gram of finely cut polyester fibres was kept in the cylindrical sample cell which is equipped with silver electrodes coated with AgCl. The pressure was adjusted to 400 mbars at 35% pump speed. Zeta potential measurement was done at different pH in the range of 3 - 10 in a streaming solution of 10^{-3} mol/L KCl. Initially pH was adjusted to 9 using 0.1 N NaOH and then decreased stepwise by using 0.1 N HCl. The sample was dipped for 5 min into the streaming solution for swelling before putting into the measurement cell.

SEM and DSC Studies
The surface morphology of nanocomposite fibres was characterized using scanning electron microscopy JEOL JSM 6380LA, JEOL Ltd. Japan.

Thermal properties of nanocomposites were analyzed in a nitrogen atmosphere (flow rate 20mL/min) by differential scanning calorimetry (Shimadzu, Japan)[27]. 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 15 readings was noted and expressed in terms of kg. Testing was carried out as per the test method ISO 5079 (2006) for breaking strength of fibre.

2.2.3 Dyeing of Nanocomposite Fibres
Dyeing with Disperse Dye
The spun filaments from the package were cut into fine fibres, thoroughly mixed and then dyed using standard method of dyeing of PET fibres 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 to reduction clearing treatment for 20 min at 70^OC with 2 g/L of caustic soda and 2 g/L of sodium hydrosulphite (hydrose). All fibre samples were then thoroughly washed at room temperature followed by neutralization with 1 g/L acetic acid solution. The fibre samples were finally washed in water and air dried.

Dyeing with Acid Dye
The spun filaments from the package were cut into fine fibres, thoroughly mixed and then dyed using an Acid dye at 100^OC in acidic pH using 3% H_2SO_4. After dyeing the fibre samples were thoroughly washed with cold water.

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[28].

2.2.4 Evaluation of Fastness
The dyed samples were then subjected to wash fastness evaluation using ISO 105-C06 (2006) in a Launder-O-meter for 20 min at 60 ^{O}C, using 2 g/L non-ionic soap (Auxipon NP) and 2 g/l soda ash at a liquor ratio of 50:1[28].

For determination of light fastness [ISO 105-A02], dyed fibre samples were stuck on a cardboard paper and their half portions were covered by a black sheet. The remaining portion was exposed to light continuously for 17 h. After that the fading of exposed samples was compared with Blue Wool Standards, which were also exposed simultaneously.

3 Results and Discussion

3.1 Wide Angle X-Ray Diffraction Analysis

The wide angle X-ray diffraction (WXRD) spectra of the series of PET nanocomposite fibres are shown in Fig. 1. The intense diffraction peak of nanoclay appears at $2\theta = 1.8^0$. But for the PET nanocomposites, the WAXD peaks of the nanoclay almost disappear even though the amount of nanoclay loading is increased from 0.5% to 2%. It indicates that these silicate layers could be completely exfoliated and dispersed in the PET matrix forming a nanometer scale uniform composite.
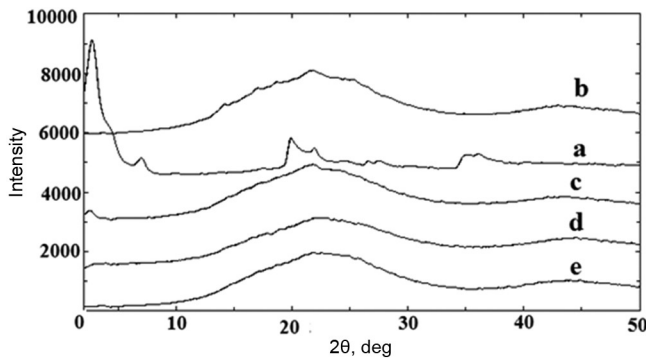

Fig. 1 — XRD spectra of PET and its nano composite fibres (a) nanoclay, (b) PET, (c) PET/0.5% nanoclay, (d) PET/1% nanoclay, and (e) PET/2% nanoclay
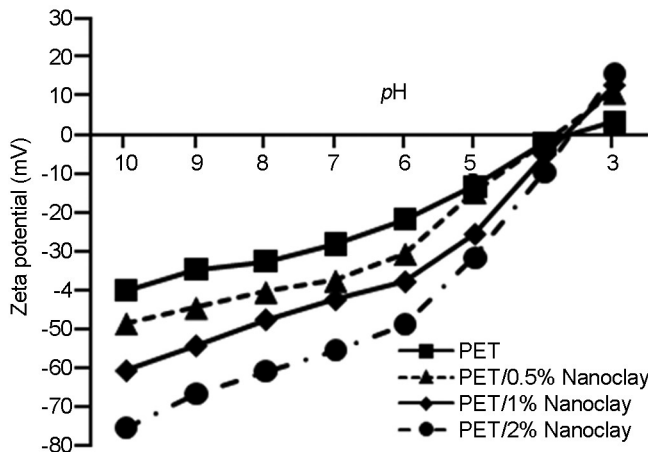

Fig. 2 — Graph of *p*H *vs* zeta potential of PET and its nanocomposite fibres

3.2 Zeta Potential Analysis

Figure 2 shows the plot of zeta potential (ζ) of PET and its nanocomposite fibre over a *p*H range of 3-10. As can be seen, as the nanoclay loading is increased the ζ value also increases making the fibre more hydrophobic at the surface. However, the charge reversal of all the fibres takes place at the same *p*H, indicating that there is no change in the inherent structure of the fibre, except for the fact that the amount of cationic sites is more. The zeta potential (ζ) in the plateau region of unmodified fibres is –39 mV. The incorporation of nanoclay increases the negative zeta potential of the nanocomposite fibres to –75 mV. It is to be noted that organophilic nanoclay containing long chain quarternary ammonium compound does increase negative value of ζ, due to increase in loading. However, as the *p*H of the streaming solution is decreased from alkaline side to the neurtal one, or as the H$^+$ ions go on adding in the streaming solution the increase in positively charged ions on the surface decrease ζ and finally it becomes almost zero or gives isoelectric point at *p*H 4. Beyond this *p*H when the concentration of acid is increased, the whole fibre surface changes its charge and becomes positively charged. Hence at *p*H 3, the positive ζ potential is observed. It could be possible that at this *p*H, dyeability with acid dyes may result to support the theory. The isoelectric points are not affected by the presence of quaternary ammonium nanoclay at any condition. The reason for the ζ increase for all the nanocomposite fibres could be because of organophilic nanoclay that is present not only in the fibre matrix but also on the fibre surface as can be seen in the Fig. 3.
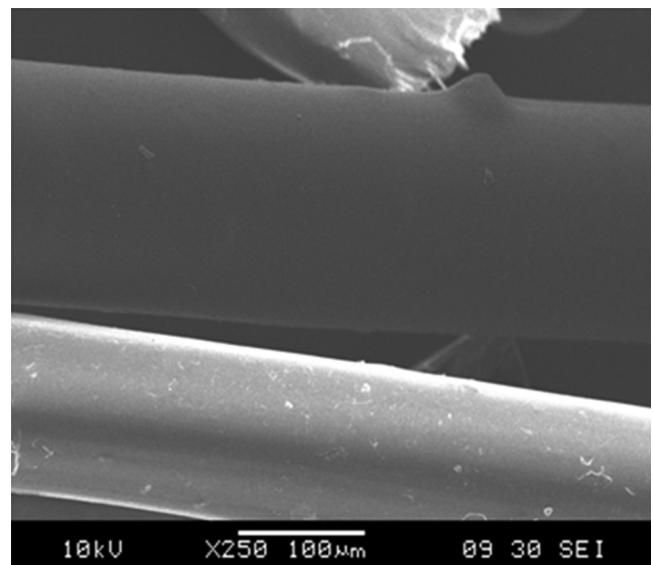

Fig. 3 — SEM photograph of PET/2% nanoclay

Table 2 — Acid dyeability of PET with Colocid Blue RL for 1% shade				
Sample	*K*/*S*	% Increase in *K*/*S*	Wash fastness	Light fastness
PET	0.21	-	1	6
PET /MB	0.22	4.76	1	6
PET/0.5% Nanoclay	0.66	214.29	3-4	7-8
PET/1% Nanoclay	0.78	271.43	3-4	7-8
PET/2% Nanoclay	0.85	304.76	3-4	7-8

Table 3 — Rate of decrease in ζ w.r.t. per unit decrease in *p*H from 10 to 4

Sample	Rate of decrease in ζ	
	From *p*H 10 to 7 (CV%)	From *p*H 7 to 4 (CV%)
ET	-11.79 (1.40)	-26.059 (1.67)
PET/0.5% Nanoclay	-10.94 (1.75)	-35.187 (1.54)
PET/1% Nanoclay	-18.15 (1.44)	-36.921 (1.65)
PET/2% Nanoclay	-19.79 (1.80)	-45.816 (1.81)

3.3 Dyeing with Acid Dye

It was expected that if nanoclay having a quarternary ammonium salt is present in the fibre structure then it should have an affinity for acid dye. Hence, polyester and its nanocomposite fibres were dyed with Colocid Blue RL and results are shown in Table 2. It can be seen that the nanocomposite fibres indeed get dyed with acid dye although lighter in shade. An increase in depth of dyeing up to 300% is observed as the amount of nanoclay is increased in the fibre. Thus, there is a possibility of using the affinity of the acid dyes to estimate the amount of quarternized ammonium nanoclay present in the fibre. These results also support changes in the ζ of the fibre as the content of nanoclay varies in the fibre.

3.4 Dyeing with Disperse Dye

On dyeing with disperse dyes, not much difference in *K*/*S* values of the dyed PET and PET nanocomposite fibres is achieved. The *K*/*S* values for PET, PET/MB, PET/ 0.5% nanoclay, and PET/ 1.0 % nanoclay, and PET/ 2.0 % nanoclay are found to be 19.35, 18.93, 18.91, 18.98 and 18.34 respectively. The wash and light fastness of the nanocomposite dyed samples are also exactly same as that of the virgin PET fibre, i.e. 5 and 7 respectively. In other words, the amorphous content which is responsible for dyeing seems to have no significant impact.

As the % of nanoclay increases the rate of fall in -ζ from 10 to 7 is increased, indicating the increased N^+ content in the nanoclay itself (Table 3). As the *p*H is further decreased from 7 to 4, this rate shows more clear trend and influence of N^+ moieties and their influence in changing the fibre characteristic. While on one hand, this hydrophobicity may have increased due to overall increase in content of organophilic nanoclay, it is to be noted that the surface properties further get influenced.

3.5 Thermal Behaviour

Table 4 and Fig. 4 show the results relating to thermal behaviour of PET nanocomposite, heated at the rate of 20^0C/min in DSC analysis. The presence of nanoclay shows an increase in the onset of crystallization and peak crystallization temperature relative to virgin PET. The onset of crystallization from the melt is increased by 7^oC at 0.5 % and at 2 % loading; the temperature is increased by 11^0C. The nano particles themselves act as nucleating agents as cited by many authors[29-32]. It should also be noted that the curve for PET/MB is very much similar to that of the PET [Figs 2 (a) & (b)]. In the nanoclay filled cases, cold crystallization progresses faster than the pure PET sample. Therefore, the crystal growth rate is accelerated by the presence of nanoclay and shifted to towards the higher temperature. The addition of nanoclay has no effect on the melting temperature of the nanocomposite as the melting peaks (*Tm*) of all nanocomposites at the second heating are almost same as virgin PET. But, the degree of super cooling (ΔT) decreases with increasing filler content in all nanocomposites, indicating that the nanoclay act as nucleating agents in polymer matrix and accelerates the crystallization rate[33]. It is also interesting to note that the addition of nanoclay shows no significant effect on the glass transition temperature, (T_g) of PET, which is about 75^0C.

Results in Table 4 also show that the nanocomposite fibres have a lower degree of crystallinity than the pure PET fibre. During melt spinning, the presence of the nanoclays alters the chain conformation of the PET chains either through particle– matrix interactions or through winding speed suppression due to the nanoclays' ability to dissipate some of the deformational energy in the spin-line. From the melt, the nanoclay particles form a temporary network structure with the PET chains preventing the development of crystalline order and amorphous orientation[34].

3.6 Tensile Strength and Elongation

The presence of LLDPE causes decrease in tensile strength obviously due to decrease in crystallinity. The tensile strength of the PET composite decreases further as the nanoclay content is increased (Table 5). The decrease in tensile strength is also accompanied by decrease in the elongation %, which indicates that the filaments have become stiffer.

Table 4 — DSC data of PET and its nanocomposites

Sample	T_g, ^{0}C	T_c Peak, ^{0}C	T_m Peak, ^{0}C	ΔH_f, J/g	ΔT, ^{0}C	Cyrstallinity from XRD, % (CV%)
PET	76.28	193.62	251.41	42.16	57.79	22.12 (1.21)
PET /MB	74.96	193.38	252.93	40.6	59.55	21.7 (1.46)
PET/0.5% Nanoclay	77.99	200.83	252.02	41.02	51.19	20.68 (1.77)
PET/1% Nanoclay	76.19	203.83	252.84	39.89	49.01	20.35 (1.05)
PET/2% Nanoclay	77.10	205.48	253.54	32.53	48.06	19.82 (1.44)

Table 5 — Effect of nanoclay on tensile strength and elongation of PET and its nanocomposites

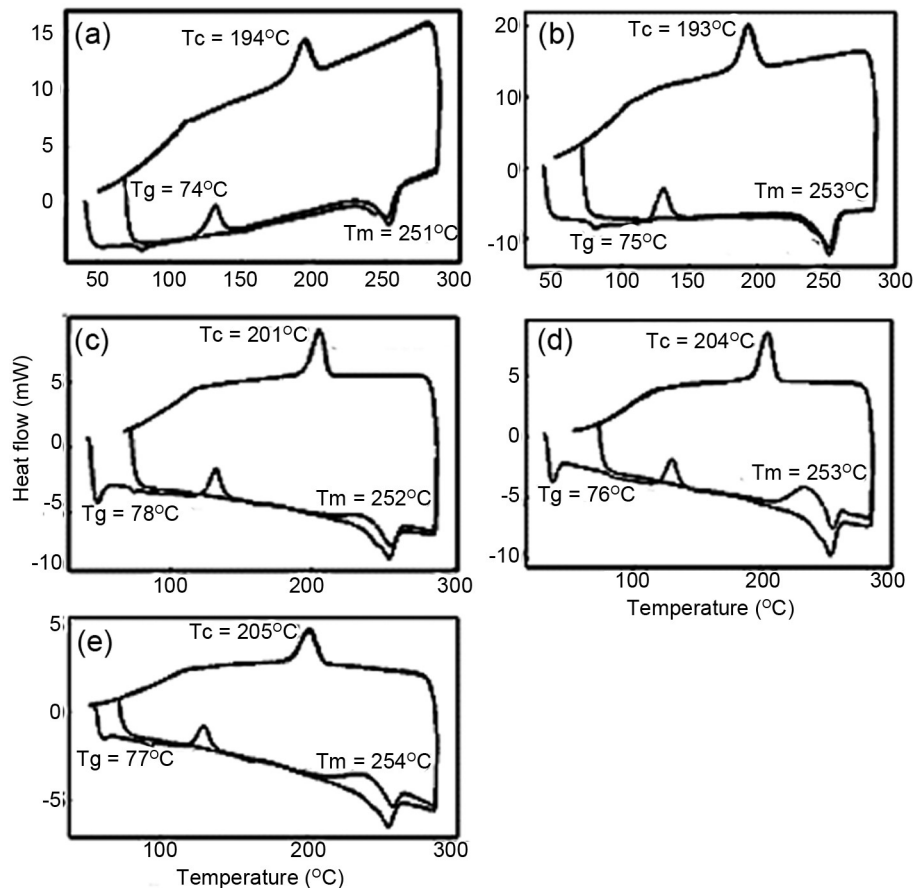| Sample	Tensiles strength MPa (CV%)	Elongation at break, % (CV%)	Loss in tensile strength, %	Cyrstallinity from XRD, % (CV%)
PET	5.29 (2.01)	82.60 (1.65)	–	22.12 (1.66)
PET /MB	4.80 (1.32)	90.40 (1.32)	9.26	21.7 (1.32)
PET/0.5% Nanoclay	5.00 (1.54)	42.26 (1.43)	5.56	20.68 (1.38)
PET/1% Nanoclay	4.80 (1.07)	35.17 (1.22)	9.26	20.35 (1.11)
PET/2% Nanoclay	4.50 (1.76)	22.85 (1.66)	14.81	19.82 (1.65)

Fig. 4 — DSC scan of PET and its nanocomposites (a) nanoclay, (b) PET, (c) PET/0.5% nanoclay, (d) PET/1% nanoclay, and (e) PET/2%

4 Conclusion

Oragonophilic nanoclay loaded into the PET causes PET nanocomposite fibre more hydrophobic as reflected by the increase in negative ζ of the fibre. However, the charge reversal for virgin as well as nanocomposite fibres occurs at the same *p*H, indicating that there is no change in the inherent structure of the fibre. Addition of nanoclay causes loss in strength but within the acceptable limit with no adverse effect on the dyeability. These nanocomposites obtained by adding MBs of organophilic nanoclay imparts the nanocomposite fibres dyeability with acid dyes to a great extent due to the cationic nature of the organophilic nanoclay.

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