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Morphology and Properties of Nanostructured Materials Based on Poly(trimethylene terephthalate) Fiber and Organoclay

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Nanostructured materials based on organically modified montmorillonite (OMMT) and poly (trimethylene terephthalate) fiber were prepared *via* melt-mixing of poly(trimethylene terephthalate) and organically modified nano clay in a twin screw extruder followed by fiber spinning. Rigid inorganic filler has been longtime used as a reinforcement agent for polymer materials. Recently, more work is focused on the possibility that using nano filler like organoclay for improving properties of fibers *via* melt intercalation. In this article, we reported our efforts on the change of morphology and properties of poly(trimethylene terephthalate)/nanoclay nanocomposite fibers. The effects of filler content and post processes on the morphology, crystallization behaviour, thermal stability and mechanical properties were investigated by SEM, DSC, TGA and mechanical test. A correlation was established between the changes in the nanostructure and mechanical properties. Exfoliated clay morphology was realized using a wide angle X-ray diffraction technique when both requirements of selecting an organic modifier that was thermodynamically compatible with polymer matrix and applying sufficient degree of shear stress were fulfilled.

Key Words: Poly(trimethylene terephthalate), Organoclay, Melt-intercalation, Nanostructure, Nanocomposite fiber.

INTRODUCTION

Poly(trimethylene terephthalate) (PTT) belongs to a series of engineering thermoplastic aromatic polyesters including poly(ethylene terephthalate) (PET) and poly(butylenes terephthalate) (PBT). Although the synthesis of poly(trimethylene terephthalate) using a poly condensation of terephthalic acid and 1,3-propanediol (trimethylene glycol) was reported. A recent new development in the synthesis of the monomer 1,3-propanediol using hydroformylation of ethylene oxide has been the key to launching a successful commercialization. Mechanical properties of poly(trimethylene terephthalate) are roughly between those of poly(ethylene terephthalate) and poly(butylenes terephthalate) and it can be melt processed using a variety of processing methods to produce fibers, films and molded pars[1,2].

The thermodynamic properties of poly(trimethylene terephthalate) included heat capacities in both solid and liquid states, the amorphous glass transition temperature (T_g) at 37-42 ºC with a heat capacity increase at T_g of 94 j/kmol and the typical melting temperature in the region of 207-232 ºC were reported[3].

The equilibrium melting temperature (T_m) was assumed to be 237 ºC; the heat of fusion (ΔH_f) of 30 kj/mol and the entropy of fusion of 58.8 j/kmol were calculated based on the measured head capacity data[4,5].

A variety of inorganic materials, such as glass fibers, talc, calcium carbonate and clay minerals, have been successfully used as additives or reinforcement to improve the stiffness and strength of polymers. The extent of property enhancement depends on many factors including the aspect ratio of the filler, its degree of dispersion and orientation in the matrix interface. Generally, in organic materials has neither good dispersion nor adequate adhesion, as a result, surface treatments are common. Mica-type silicates like montmorillonite, hectorite and saponite have received a great deal of attention as reinforcing materials for polymers owing to their potentially high aspect ratio ad unique intercalation/exfoliation characteristics[6-8]. Such clay minerals have a layer structure (typically 1 nm in thickness) which if property exfoliated can lead to platelets (approaching 1 μm in lateral dimensions) with high stiffness and strength dispersed in the polymer matrix. To achieve a better interaction with organic polymers, the cations (typically sodium) present on the surface of montmorillonite to balance the net negative charge of aluminum/magnesium silicate layer are exchanged with organic molecules with a cation group, *e.g.*, alkyl ammonium ions to produce an organoclay[9]. The degree of exfoliation and intercalation the clay platelets in the polymer matrix, as

well as the orientation of the clay particles, have been found to have important implications for the final property of nano-composite for instance, polymers which contain exfoliated clay particles have better mechanical properties than those which have intercalated clay structures[10]. Furthermore, as the bending modulus of clay is much less than the elastic modulus, the polymers also exhibit anisotropic mechanical properties[11,12]. From the tribological view point, the major benefit of these polymer nanocomposites relative to those micro size particle composites is that the material removal is expected to be less as the nano additives has similar size to the segments of the surrounding polymer chains[13-15]. This is possible owing to the much greater surface area to volume ratio of nano additives, which may be important for bonding of the particle to the polymer matrix. In addition to the influence on the tribological performance of the composites, the nano additives also change the crystallinity, microstructure, physical and mechanical properties of the polymer matrix[16]. Considering the dimension of polymers chains and their crystalline assemblies, it can be said that all polymers have structure on the nanometer size scale and further, the mechanical properties of polymers are governed by the interactions of these nanostructures with one another. Therefore, to influence the interactions that govern the mechanical properties of polymer, specific nano scale reinforcement is efficient and beneficial. Montmorillonite clay provides such reinforcement through the interaction of poly-(trimethylene terephthalate) polymer chains with the charged surfaces of clay lamellae[17]. The incorporation of organoclays into thermoplastic matrix by conventional polymer melt comp-ounding processes is a promising new approach for forming nanocomposites that would greatly expand the commercial opportunities for this technology. If technically possible, melt compounding would be significantly more economical and simple than *in situ* polymerization processes. This approach would allow nanocomposites to be formulated directly using ordinary compounding devices such as extruders or other mixers according to need without he necessary involvement of resin producers. However, there are few studies on formation of nanocomposites by direct melt compounding[18,19] and therefore, the corresponding knowledge about this process and what can and cannot be accomplished is still incomplete. In this process, the theological and thermodynamic character of the materials can be important parameters that affect the degree of exfoliation and properties of the final nanocomposites. The dispersion of filler agglomerates can be achieved when the cohesive forces of the agglomerates are exceeded by the hydrodynamic separa-ting forces applied by the matrix fluid[20].

Poly(trimethylene terephthalate) offers several advanta-geous properties, including good tensile behaviour, resilience, outstanding elastic recovery and dye ability. Moreover, poly-(trimethylene terephthalate) fibers have the resiliency and softness of nylon fibers, as well as the chemical stability and stain resis-tance of the poly(ethylene terephthalate) counterparts, making them ideal candidates for use in applications such as carpets and other textile fibers[20-22]. In the preparation process of poly(trimethylene terephthalate) nano composites, elevated temperatures greater than 250 ºC are required for successful in melt blending process. If the processing temperature is higher than the thermal stability of the organoclay, then decomposition occurs and the interface of the nano filler and the matrix polymer are not effectively altered[23,24].

The purpose of the present work is to evaluate the effect of nanoclay in poly(trimethylene terephthalate) nanocomposite fibers, both direct and masterbatch systems. A thermally stable organoclay was used in order to prevent thermal degradation of the nanocomposite fibers. In this study, we describe a method for preparation poly(trimethylene terephthalate) nanocomposites *via* melt blending. We finally report on the mechanical properties of poly(trimethylene terephthalate)/ nanocomposites fibers for different organoclay contents, systems of adding nano filler and draw ratios.

EXPERIMENTAL

Fiber grade poly(trimethylene terephthalate) was produced by shell chemical company with trade name of CORTERRA9240. The organically modified montmorillonite nanoclay (Cloisite 15A) supplied by southern clay products Inc, were used as received for melt blending.

Methods

Specimen preparation: Poly(trimethylene terephthalate) and organoclay were dried in vacuum oven for 24 h at 80 ºC. To obtain enough materials for mechanical properties test, melt compounding was also conduced by using a co rotating twin screw extruder (Zsky). Masterbatch with ratio poly(trimethylene terephthalate)/nanoclay: 2/1 was prepared by melt mixing in a Haake Rheocord 90 internal batch mixer at 240 with a rotor speed of 60 rpm. The extrusion zone temperature ranged from 220-250 and a screw speed of 100 rpm was used (the mixing time is less than 4 min). The extradites were pelletized with Haake pelletizer. The sample compositions are given in Table-1.

TABLE-1 NANO COMPOSITE COMPOSITIONS			
Sample code	Poly(trimethylene terephthalate) (w %)	Nano clay (wt %)	Master batch (wt %)
NC1	99	1	–
NC2	97	3	–
NC3	95	5	–
NC4	97	–	3
NC5	91	–	9
NC6	85	–	15

Before melt spinning, the polymer blends were dried in a vacuum oven for 24 h at 30 ºC. Melt spinning process was performed on a single screw (L/D = 26) Brabender melt extruder with a spinneret containing 20 orifices, each of 0.1 mm diameter.

The extruder was set with fine different temperature zones, 210, 210, 220, 230, 240 and 250 ºC, respectively; at the feed metering, die and spinneret section. The screw was run at 60 rpm.

The drawing of nanocomposite fibers was carried out with a heat stretching machine and total draw ratio of 1, 3 and 7 by using three step stretching. The stretching temperature for every step was 100, 125 and 145 ºC, respectively.

Scanning electron microscopy (SEM): SEM images were taken to study the morphology of poly(trimethylene terephthalate)/nanoclay nanocomposite fibers. SEM micro-graphs were taken from cryogenically fractured surface of

samples after submersion in liquid nitrogen for 1 h. The surface was then sputter coated with a layer of gold-palladium before viewing. The fractured surfaces of the fibers were investigated in a SEM instrument, LEO 440, operating at 20 KV.

Thermal analysis (DSC and TGA): Differential scanning calorimetry (DSC) spectra were recorded on a Perkin-Elmer DSC Pyris-I. Differential scanning calorimeter calibrated the temperature with indium and the crystallization behaviour can be obtained. All DSC were performed under nitrogen atmosphere. In this experiment, about 5 mg of dried sample was first hold in 50 ºC for 0.5 min, then heated quickly from 50-400 ºC at 20 ºC/min and hold for 5 min after reached the 200 ºC in order to eliminate the influence of thermal history after that, the samples were cooled from 400 ºC at-5 ºC/min. Thermo gravimetry analysis was performed with a Perkin-Elmer TGA7 thermal analysis system. The TGA scan was recorded at 10 ºC/min under a nitrogen atmosphere from 50-700 ºC.

X-Ray diffraction analysis (XRD): A siemens X-ray diffraction unit operated at 30 KV and 20 mA, with Cu element and Ni filter was used to find the changes in dispersion of nanoclay in matrix.

Mechanical testing: The tensile properties of the as produced poly(trimethylene terephthalate)/nanoclay nanocomposite fibers were determined at room temperature using an Instron mechanical tester, with a crosshead speed of 20 mm/min.

The experimental uncertainties in the tensile strength and modulus were averaged over 10 different determinations to give values of ± 1 MPa and ± 0.05 GPa, respectively.

RESULTS AND DISCUSSION

Morphology: A comparative study of fracture surface morphologies of the poly(trimethylene terephthalate), NC1 and NC3 sample fibers were given in Fig. 1.
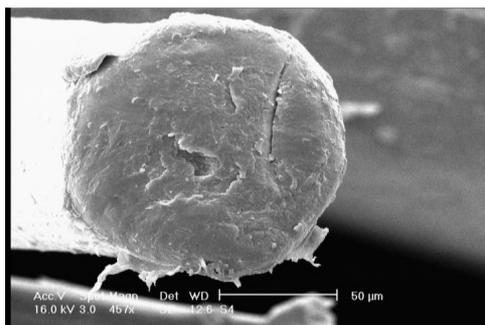
(a)
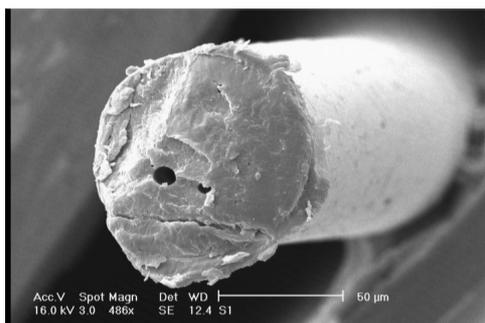
(b)
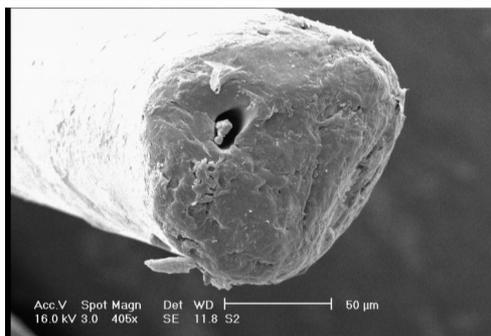
(c)

Fig. 1.   SEM micrograph of cryogenically fractured surface of fibers (a) poly(trimethylene terephthalate) fiber, (b) NC1 fiber and (c) NC3 fiber

The SEM cross sectional micrographs of three nanocomposite samples containing 1, 3 and 5 % of nanoclay are shown in Fig. 2.
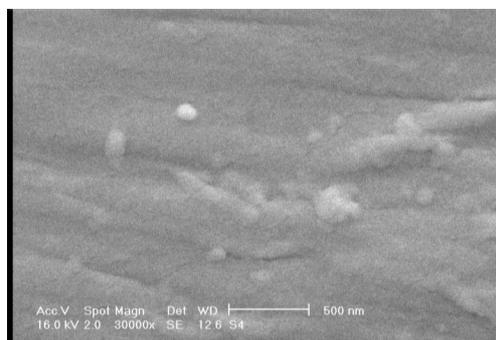
(a)
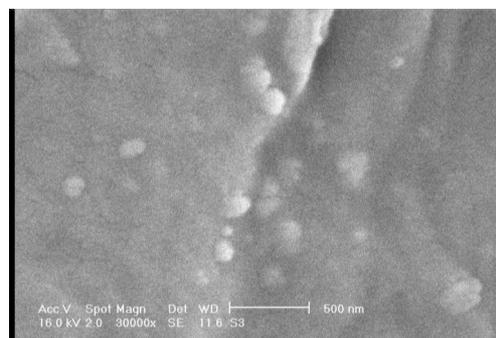
(b)
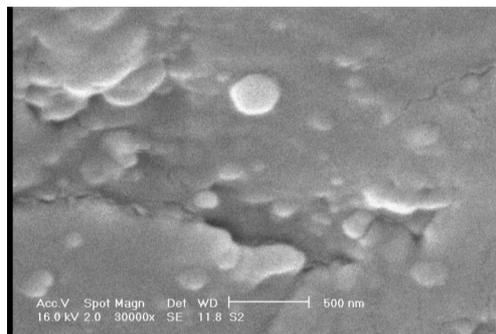
(c)

Fig. 2.   SEM micrograph of nanocomposite fiber sample containing (a) 1 %, (b) 3 % and (c) 5 %

As it can clearly be seen, for the samples containing 1 % of nanoclay no agglomeration is observed and the nanoparticles are finely disperad in the poly(trimethylene terephthalate) matrix, while the SEM of samples containing 3 and 5 % of nanoclay show agglomeration formed between the nanoparticles *via* nano size characterization. By using masterbatch the dispersion of nanoclay was improved. As it was clear in micrograph (Fig. 3), even for sample containing 5 % nanoclay fine dispersion was obtained.
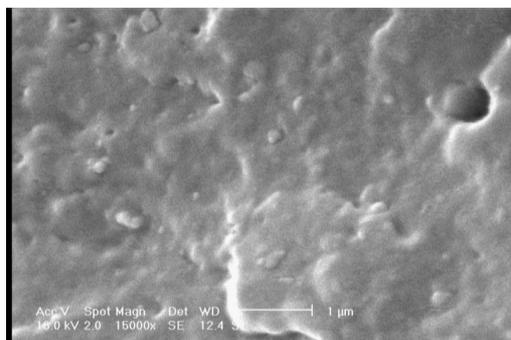
Fig. 3. SEM micrograph of 5 % nanoclay in poly(trimethylene terephthalate) nanocomposite fiber by using masterbatch

Thermal analysis: Fig. 4 presents the thermal behaviours of poly(trimethylene terephthalate)/nanoclay nanocomposite and nanocomposite fiber obtained by melt blending. The endothermic peaks of the samples appear around 230 ºC and correspond to the melting transition temperature (T_m). Compared with pure poly(trimethylene terephthalate), the maximum transition peaks of poly(trimethylene terephthalate) nanocomposite and nanocomposite fiber were virtually unchanged in the DSC thermograms regardless of the effect of spinning process. The heat of fusion (ΔH_m) also changed by adding nanoclay that it shows nanoclay hindered chain motion to the crystal cell.

A thermo gravimetric analysis (TGA) of poly(trimethylene terephthalate) nanocomposite containing 3 % nanoclay is shown in Fig. 5. The observed weight losses due to the decomposition of poly(trimethylene terephthalate) and its hybrid were found to be similar below 350 ºC. However, beyond his temperature, the initial thermal degradation temperature was notably influenced by the organoclay loading within the poly(trimethylene terephthalate) hybrid. The weight of the final residue at 600 ºC was found to increase by 3 % nanoclay, in accordance by adding mineral materials.

X-Ray diffraction: Table-2 lists the wide angle X-ray diffraction of poly(trimethylene terephthalate)/nanoclay nanocomposite and its fiber. The d001 reflection for the Na^+-MMT was found at 20 = 8.60 ºC, which corresponds to an interlayer distance of 11.99 Å, The XRD peak for the surface-modified clay was found corresponding to an interlayer distance of 18.6 Å. For poly(trimethylene terephthalate) containing a 3 % organoclay content, only slight peak at d = 14.34 Å existed in the XRD results for the nanocomposite and at 23.77 Å for nanocomposite fiber. A substantial increase in the distance between layers was observed by forming to fiber, which suggests that the dispersion is better at fiber because of elongational force in melt spinning.

(a)

(b)
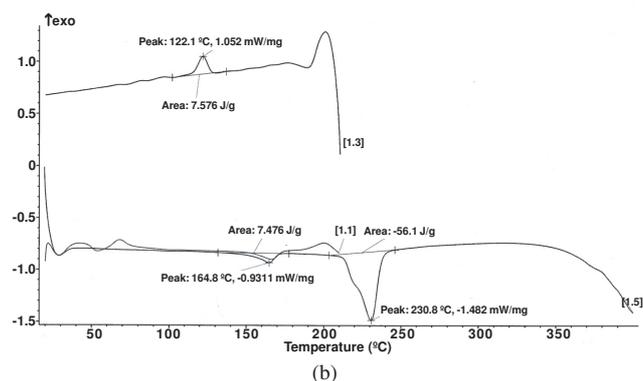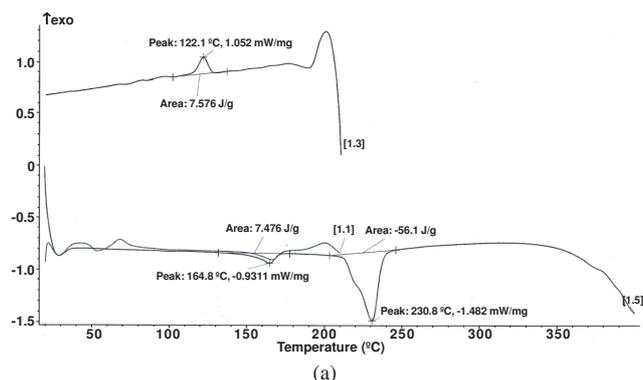
Fig. 4. DSC thermograms of (a) poly(trimethylene terephthalate)/nanoclay nanocomposite (b) poly(trimethylene terephthalate)/nanoclay nanocomposite fiber containing 3 % nanoclay
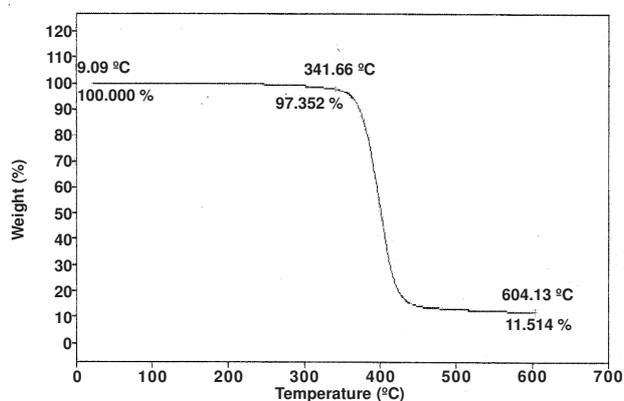
Fig. 5. TGA thermo gram of poly(trimethylene terephthalate) nanocomposite fiber with 3 % nanoclay

Mechanical properties: The tensile mechanical properties of pure poly(trimethylene terephthalate) and poly(trimethylene terephthalate)/nanoclay hybrid fibers are listed in Table-3. The tensile mechanical properties of the hybrid fibers were found to increase with increasing organoclay content (draw ratio = 1), where increase in content from 0 to 5 wt %, resulted in linear improvement in the tensile strength. Similar behaviour was also observed for the initial modulus of the poly(trimethylene terephthalate) hybrid fiber containing 1 % organoclay (2.83 GPa), which is about much more than the modulus of pure poly(trimethylene terephthalate).

The increase in the tensile modulus of the poly(trimethylene terephthalate) nanocomposite fibers are thought to the dependent on the interactions between the poly(trimethylene terephthalate)

TABLE-2
DATA OF X-RAY DIFFRACTION PEAK OF POLY(TRIMETHYLENE TEREPHTHALATE)
NANO COMPOSITE AND ITS FIBER CONTAINING 3 % NANO CLAY

Angle (2θ, °)	d value (Å)	Intensity (count)	Intensity (%)	Angle (2θ, °)	d value (Å)	Intensity (count)	Intensity (%)
2.18	40.49216	209	5	2.16	40.86704	141	8.2
2.74	32.21752	1200	28.8	2.236	39.47532	210	12.1
2.98	29.62333	1511	36.3	2.38	37.08844	391	22.6
3.04	29.0388	1600	38.4	2.48	35.59455	528	30.6
3.14	28.11421	1906	45.8	2.564	34.42425	679	39.3
3.44	25.66304	2281	54.8	2.675	32.99602	896	51.9
3.68	23.98988	2587	62.1	2.828	31.21357	1075	62.3
3.957	22.30915	3012	72.3	2.94	30.02628	1215	70.3
4.144	21.30252	3123	75	3.08	28.66176	1316	76.2
4.473	19.73822	3287	78.9	3.217	27.44117	1402	81.2
4.76	18.54894	3529	84.7	3.293	26.80995	1452	84.1
5.02	17.58881	3490	83.8	3.4	25.96486	1639	94.9
5.08	17.3812	3700	88.8	3.459	25.52381	1556	90.1
5.24	16.85083	3776	90.7	3.568	24.74605	1680	97.3
5.575	15.83789	3705	89	3.713	23.77937	1727	100
5.88	15.01808	3877	93.1	3.907	22.59443	1610	93.2
6.156	14.34532	4165	100	4.12	21.42879	1556	90.1
6.589	13.40381	4005	96.1	4.193	21.0565	1662	96.2
6.747	13.08933	4046	97.1	4.32	20.43715	1558	90.2
6.82	12.9501	3988	95.7	4.44	19.88506	1562	90.5
7.219	12.23575	3817	91.6	4.6	19.19376	1360	78.8
7.36	12.00113	3726	89.4	4.697	18.79571	1367	79.2
7.44	11.87226	3688	88.5	4.84	18.24253	1286	74.4
7.66	11.53177	3463	83.1	4.98	17.73	1252	72.5
7.98	11.07005	3327	79.9	5.243	16.84177	1149	66.5
8.28	10.66962	3199	76.8	5.42	16.29161	993	57.5
8.58	10.29722	2718	65.2	5.5	16.05482	953	55.2
8.76	10.08603	2602	62.5	5.6	15.76929	895	51.8
9.1	9.70994	2359	56.6	5.688	15.52491	919	53.2
9.42	9.38079	2106	50.6	5.84	15.12037	828	47.9
9.52	9.28248	1993	47.8	6	14.71799	749	43.3
9.78	9.03628	1715	41.2	6.068	14.55398	706	40.9
10.08	8.76801	1348	32.4	6.158	14.34009	678	39.3
–	–	–	–	6.266	14.09378	745	43.1
–	–	–	–	6.503	13.58095	668	38.7
–	–	–	–	6.68	13.2212	632	36.6
–	–	–	–	6.76	13.06491	522	30.2
–	–	–	–	6.857	12.88022	615	35.6
–	–	–	–	6.98	12.65361	467	27
–	–	–	–	7.14	12.37041	520	30.1
–	–	–	–	7.2	12.26746	514	29.7
–	–	–	–	7.34	12.03378	471	27.3
–	–	–	–	7.486	11.79908	477	27.6
–	–	–	–	7.564	11.67722	415	24

chains and the layered nanoclays, as well as on the rigidity of the clay layers are themselves.

An increase in mechanical tensile strength with increasing draw ration is commonly observed in engineering plastics, as well as in flexible coil like polymers. The system of mixing by altering the dispersion of nanoclay in the matrix improve the mechanical properties, fine dispersion of nanoclay in samples manufactured by masterbatch have led to nanostructure without any defect.

Conclusion

In this study the effect of added of organically modified nanoclay, draw ratio, nanoclay content and the system of mixing on the morphology and properties of poly(trimethylene terephthalate) nanocomposite fibers were investigated. The presence of nanoclay within the poly(trimethylene terephthalate) matrix was observed to have a reinforcing effect, as seen in the properties and morphologies of the poly(trimethylene terephthalate)/nanoclay nanocomposite fibers. Compounding methods included direct and masterbatch mixing in the melt state using a twin extruder were conducted. poly(trimethylene terephthalate)/nanoclay nanocomposite were then melt spun into fibers using conventional fiber spinning conditions. Morphology and mechanical properties of these nanocomposite fibers have been studied and show that nanoclay can be incorporated into poly(trimethylene terephthalate) matrix with good dispersion in masterbatch system. On the basis of the preceding results, it is concluded that the state and the degree of loading of the nanoclay layers in the matrix polymers affect both the thermal behaviour and the tensile mechanical properties of each poly(trimethylene terephthalate)/nanoclay hybrid fibers.

TABLE-3
TENSILE PROPERTIES OF POLY(TRIMETHYLENE TEREPHTHALATE)/NANO CLAY NANO COMPOSITE FIBERS

Organoclay (wt %)	Draw ratio	Ult. Str. (MPa)	Ini. Mod. (GPa)	Elongation present a break	System of mixing
0	1	30	1.82	2	–
	3	34	1.9	2	–
	7	36	1.93	2	–
1	1	33	2.65	2	Direct
	3	36	2.86	3	Direct
	7	39	2.90	3	Direct
	1	33	2.7	2	Master batch
	3	36	2.83	2	Master batch
	7	38	2.91	2	Master batch
3	1	34	2.63	2	Direct
	3	36	2.79	3	Direct
	7	37	2.96	3	Direct
	1	35	2.74	2	Master batch
	3	39	2.89	2	Master batch
	7	42	3.1	2	Master batch
5	1	39	2.73	3	Direct
	3	45	2.77	3	Direct
	7	47	2.93	3	Direct
	1	33	3.1	2	Master batch
	3	36	3.2	2	Master batch
	7	37	3.4	2	Master batch

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