

## Study on Morphology, Thermal and Physical Properties of Poly(trimethylene terephthalate)-Nano Silica Composite

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The morphology, thermal behaviour and melt viscoelastic properties of poly(trimethylene terephthalate)-nano silica containing 2, 4 and 8 % of nano silica were investigated. The blend samples were prepared by an internal mixer. The results obtained from DSC showed that the heat of crystallization ( $\Delta H_{\text{cry}}$ ) of poly(trimethylene terephthalate) matrix follows a decreasing trend with increasing the nano particle up to 8 % above which it begins to increase again. The decrease in  $\Delta H_{\text{cry}}$  of the poly(trimethylene terephthalate) can be related to strong interaction between PTT and nano particle surface. The crystallization temperatures ( $T_c$ ) of the poly(trimethylene terephthalate) matrix increase with the increasing nano particle concentration but it decrease with increase 8 % of nano silica. Cryogenically fractured surface of the samples examined by SEM. The results obtained from SEM showed the samples containing 8 % of nano particle showed a great extent of agglomeration formed between the nano particles. The melt flow behaviour and viscoelastic properties were studied by using a rheometre mechanical spectrometer (RMS). The results obtained from RMS showed viscoelastic properties for poly(trimethylene terephthalate) and the samples containing 2 and 4 % of nano particle are almost similar while the sample containing 8 % of nano particle exhibits a pronounced viscosity upturn with high and nonterminal storage modulus at low frequency range.

**Key Words:** Nano silica, Morphology, Poly(trimethylene terephthalate), Nano composite.

### INTRODUCTION

Thermoplastic and thermosetting polymers are filled with particulate reinforcements to augment various mechanical, thermal and chemical properties, such as tensile strength and fracture toughness, barrier to diffusion of solvents and chemicals and dimensional stability against thermal fluctuations at high temperatures. Nano size particulate reinforcements are particularly attractive as the properties of filled polymers can be taken much beyond their intrinsic values<sup>1-5</sup>.

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Poly(trimethylene terephthalate) (PTT), which was recently commercialized<sup>6</sup> has molecular weight similar to that of other polyesters. It can be formed into fibers and films<sup>7-9</sup>. The characteristic properties for PTT are a flexible trimethylene repeated group in the polymer chain, lower melting temperature (238 °C) and glass transition (*ca.* 58 °C) and lower water absorption relative to PET<sup>7</sup>. Poly(trimethylene terephthalate) fibers display superior elasticity and recovery properties relative to PET<sup>6-9</sup>. Poly(trimethylene terephthalate) has properties between those of PET and PBT, by taking an unusual combination of the outstanding properties of PET and processing characteristics of PBT. These characteristics make PTT highly suitable for uses in fiber, film and engineering thermoplastics applications.

Fumed silica is a very useful reinforcement of thermoplastic and thermosetting polymers and finds usage as component material for dental filling<sup>10</sup>, electronic packaging<sup>11</sup>, thickeners of paints and coatings<sup>12</sup>, reinforcement of silicones, PVC and acrylics for various sealing and structural applications<sup>13-17</sup> and reinforcement of vulcanized rubbers<sup>18</sup>. Fumed silica is available as individual articles ranging from 10 -20 nm and, if dispersed well to the scale of 10 -50 nm in matrix polymers. It has the potential to improve heat deflection temperature (HDT) and barrier to diffusion of solvents apart from increasing the modulus. Fumed silica nano particles manufactured by high temperature hydrolysis of silicon tetrachloride in a flame have extremely large surface areas and smooth non-porous surfaces<sup>19</sup>, which could promote strong physical contact between the filler and the polymer matrix. Sumita *et al.*<sup>20</sup> pointed out earlier, the benefits of replacing silica micro particles by nano particles. Silica nano particles provide high rigidity, which has actually been demonstrated for almost all composite systems and increased the yield strength and elongation at break of the nano particle-filled polymers compared to the values for pristine nylon 6<sup>21,22</sup>, poly(ethylene terephthalate)<sup>23</sup>, polypropylene<sup>24</sup> and polyimide<sup>25</sup>. The yield strength of the silica nano particle filled composites increased with filler content and decreased with filler size<sup>20</sup>. Silica nano particles have a prominent reinforcing effect on the elastic properties of the polymers when uniaxially oriented by cold drawing, because the diameters of the silica nano particles are comparable to the sizes of crystalline regions in a polymer<sup>15</sup>. The purpose of the present work is to study effect of silica nano particles on morphology, melt rheology and thermal behaviour of poly(trimethylene terephthalate) (PTT).

## EXPERIMENTAL

Poly(trimethylene terephthalate) (PTT) with an Intrinsic viscosity of 0.92 dL/g was supplied by Zimmer Co and Fumed nano silica (Aerosil 200) was provided by Degussa Ag. The hydrophilic nature of the nano silica powder was caused by the presence of silanol groups on its surface. The particle has a spherical surface and is also free of pores. The specifications of the nano silica Aerosil 200 are shown in Table-1.

TABLE-1  
SPECIFICATION OF THE NANO SILICA AEROSIL 200

Surface	BET surface area (m/g)	Primary particle size (nm)	Ignition loss (%)	pH in 4 % aqueous solution	Purity (% of nano silica)
Hydrophilic	200±25	12	< 1	3.6-4.3	99.8

**Sample preparation:** Poly(trimethylene terephthalate), fumed silica and the blend samples were dried for 24 h at 100 °C in vacuum to ensure low moisture levels. The blend samples containing 2, 4 and 8 % of nano particle were prepared by an internal mixer. The melt compounding was performed at 260 °C and rotor speed was 60 rpm. The blending composition and sample codes are shown in Table-2.

TABLE-2  
BLENDING COMPOSITION AND SAMPLE CODES

Sample No.	PTT (%)	NANO (%)
PTN0	100	0
PTN2	98	2
PTN4	96	4
PTN6	94	6
PTN8	92	8

The melt flow behaviour and viscoelastic properties of the neat polymers and blend samples were studied by using a rheometric mechanical spectrometer (RMS), equipped with parallel plate geometry. Morphology of the blend samples were studied with the scanning electron microscopy (SEM). The SEM micrographs was taken from cryogenically fractured surfaces of blend specimens. Thermal analysis was performed on neat PTT as well as nano composite samples using DSC method.

## RESULTS AND DISCUSSION

**Thermal behaviour:** DSC measurements were made on the PTT/silica blends containing 0 % (neat PTT), 2, 4 and 8 % (by weight silica). The results of heat of fusion ( $\Delta H_f$ ), heat of crystallization ( $\Delta H_{cry}$ ) and crystallization temperature ( $T_c$ ) measured for the samples varying in nano particle concentration are given in Table-3.

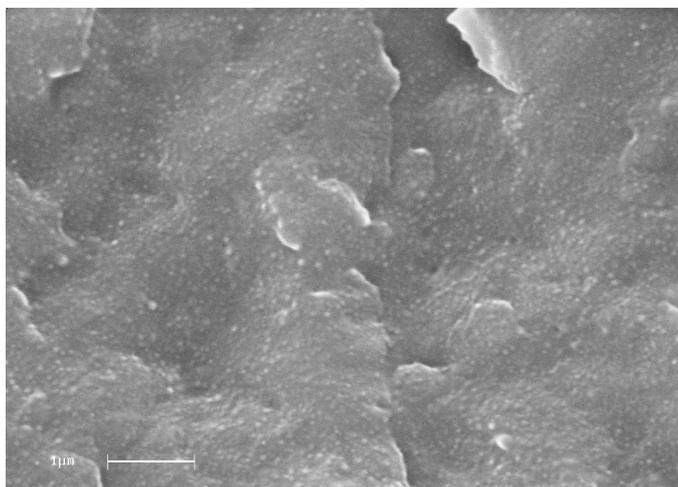
TABLE-3  
RESULTS OF HEAT FLOW FOR PTT AND THE BLEND SAMPLES

Sample No.	$T_c$ (°C)	$T_m$ (°C)	$\Delta H_{cry}$ (J/g)	$\Delta H_f$ (J/g)
PTN0	199.56	229.74	83.99	75.91
PTN2	196.35	228.78	54.30	51.70
PTN6	195.75	228.19	42.11	41.11
PTN8	195.69	228.23	49.84	46.64

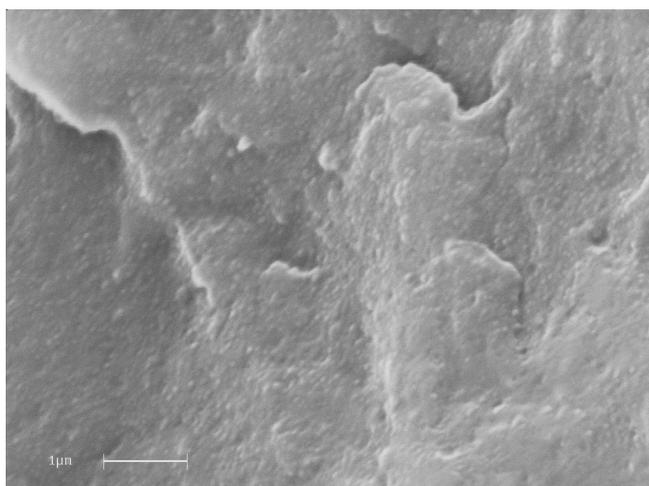
It can be seen that, the  $\Delta H_{\text{cry}}$  and  $\Delta H_{\text{f}}$  of the PTT matrix follow the decreasing trend with increasing the nano particle, up to 8 % above which it begins to increase again. The decrease in  $\Delta H_{\text{cry}}$  of the PTT can be related to strong interfacial interaction between PTT and nano particle surface. The greater  $\Delta H_{\text{cry}}$  of the sample containing 8 % of nano particle compared to the other samples is due to the agglomeration between the nano particles.

The increase in crystallization temperature ( $T_c$ ) of the poly(trimethylene terephthalate) with increasing nano particle concentration shown in Table-2 could be related to the nucleating effect of the nano particles.

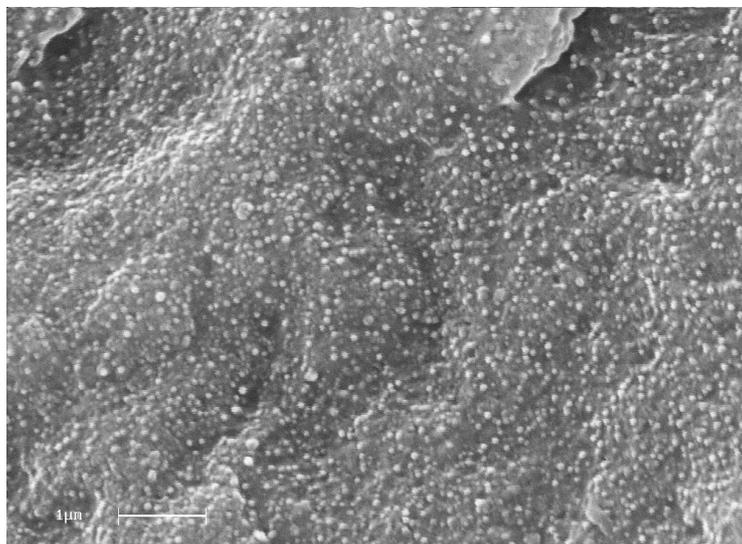
**Morphology:** The SEM cross-sectional micrographs of three nano composite samples containing 2, 4 and 8 % of Fumed Silica Nano particle (Aerosil 200) are shown in Fig. 1.



(a)



(b)



(c)

Fig. 1. SEM micrograph of the nano composite sample containing a) 2 %, b) 4 % and c) 8 %

As it can clearly be seen, for the samples containing 2 and 4 % of nano particle no agglomeration is observed and the nano particles are finely dispersed in the PTT matrix, while the SEM of sample containing 8 % of nano particle show a great extent of agglomeration formed between the nano particles.

**Rheology:** The results of complex viscosity and storage modulus of the neat PTT and nano composites samples measured at 260 °C are shown in Fig. 2. These results clearly show almost similar viscoelastic properties for PTT and the sample containing 4 % of nano particle while the sample containing 8 % of nano particle exhibits a pronounced viscosity upturn with high and nonterminal storage modulus at low frequency range. Such viscoelastic behaviour observed for sample containing 8 % can be explained in terms of three dimensional agglomerate formed between the nano particles.

### Conclusion

Nano composites based on poly(trimethylene terephthalate) (PTT) fumed silica nano particles produced by melt mixing showed particulate type morphology upto the 4 % of nano particle in which nano particles were uniformly dispersed in PTT matrix, while in samples containing 8 % of nano particles a pronounced agglomeration was formed between the nano particles. The results of melt viscoelastic measurements were found to be in agreement with the morphology results. The results of thermal analyses showed strong interfacial interaction between two phases and nano particles was found to act as nucleating agent.

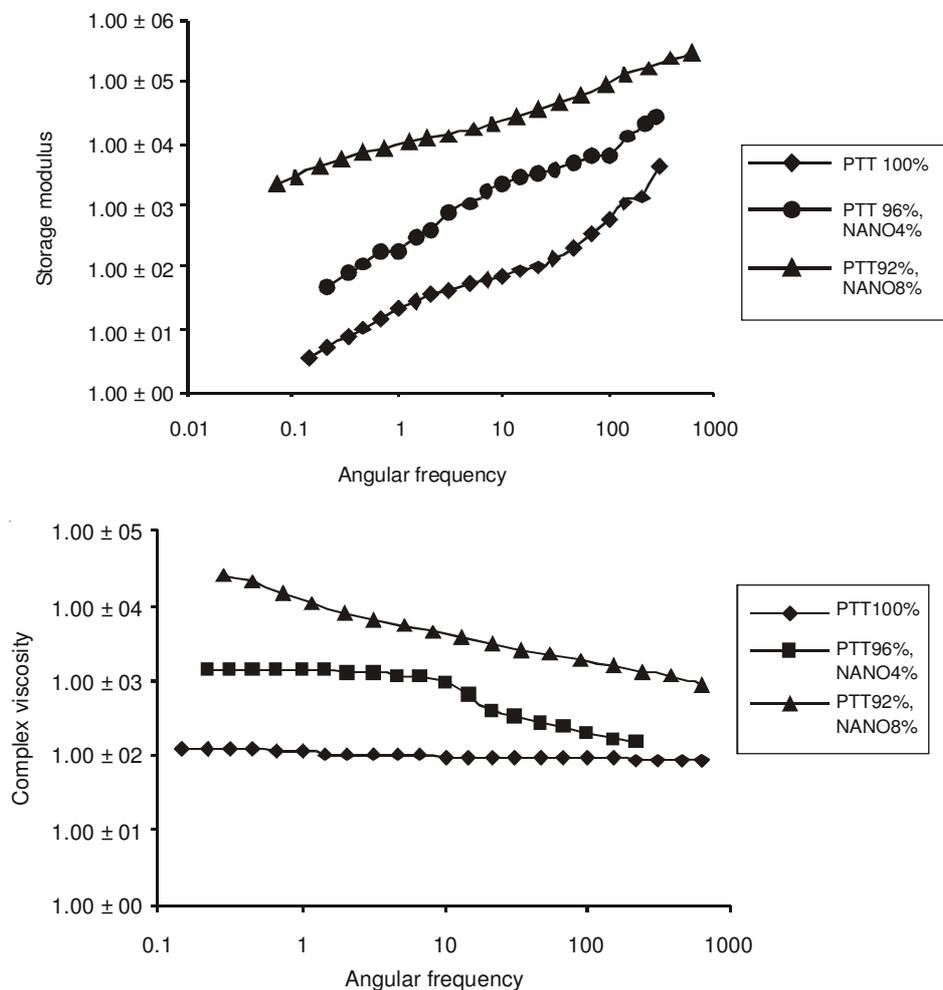


Fig. 2. Results of melt viscoelastic measurements

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