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Morphology Development and Melt Viscoelastic Properties of PTT/PET/TLCP Ternary Blend

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The morphology development and melt linear viscoelastic properties of PTT/PET/TLCP ternary blends were studied and results were compared with PET/TLCP and PTT/TLCP binary blends. The blend samples were prepared by melt mixing of the blends component both in an internal mixture and a modular twin screw extruder. The morphological studies were perform on cryogenically fracture samples using SEM. The melt-state linear viscoelastic properties of samples were studied by using a rheometric mechanical spectrometer (RMS). Differential scanning calorimeter was employed to examine the crystallinety of the sample. The SEM results showed a matrix disperses type morphology in which thermotropic liquid crystalline polymers (TLCP) phase was uniformly dispersed in polymer matrix. The average diameter of the TLCP particle in PET/TLCP blend was found to be comparable with that in ternary blends but smaller compared to PTT/TLCP blend. For all the blends, the average TLCP diameter was smaller for the samples prepared by extruder compared to those produced by internal mixer. These results suggested lower compatibility between PTT and TLCP phase compared to that between PET and TLCP. The melt viscoelastic properties of the PTT/PET binary blend seemed to obey the additive rule suggesting that the PET and PTT melts are miscible. It was also shown that the viscoelastic properties of ternary blends was predominately controlled by matrix components and indicating that TLCP phase remains as dispersed droplets in the matrix. The results obtained of DSC showed a single crystallization temperature peak (Tc ≈ 155 ºC) for PET/PTT binary and PET/PTT/TLCP ternary blends; the results which could support the SEM and viscoelastic results.

Key Words: Ternary blend, Morphology, PTT/PET/TLCP, Rheology.

INTRODUCTION

In recent years, melt blending of thermotropic liquid crystalline polymers (TLCPs) with conventional thermoplastics has attracted great attention because of the improvement of the strength and modulus of polymer composites[1-9]. Thermotropic

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liquid crystalline polymers (TLCPs) have been used for high performance engineering plastics due to their high strength and modulus, excellent thermal endurance and chemical stability[10-13]. They consist of rigid molecular chains and exist as ordered domains in LC state. Thermotropic liquid crystalline polymers (TLCPs) that have a relatively low melt viscosity can be oriented to form fibrils under elongational flow in melt processing and the oriented fibrous structures are developed in the extruded TLCPs. Due to the rigid rod-like mole-cules of TLCPs, they exhibit the high strength and stiffness, which develop into the highly ordered structures and result in self reinforcing characteristics[14,15]. Blending of poly(trimethylene terephthalate) (PTT) with poly(ethylene terephthalate) (PET) has attracted increasing interest from industrial fields to scientific, because of the improved properties that combines the excellent properties of PTT with the economical efficiency of PET[16-23]. Transesterification reactions occurred between PTT and PET during melt blending, leading to the formation of block copolymers first and then of random copolymers, which enhances the miscibility of the blend systems too. This result has been observed in several other systems[20-24]. The structure and properties of ternary blend sample were analyzed by using scanning electron microscopy (SEM), rheometric mechanical spectrometer (RMS) and differential scanning calorimetry (DSC). The main objective of the present work is to study properties and morphology of PTT/PET/TLCP ternary blend.

EXPERIMENTAL

Poly(trimethylene terephthalate) (PTT) with an intrinsic viscosity of 0.92 dL/g supplied by Zimmer and poly(ethylene terephthalate)(PET) with an intrinsic viscosity of 0.67 dL/g were supplied by Polyester Cheeps Yazd Co., Iran. The thermotropic liquid crystalline polymer (TLCP) used in this research was Vectra A950 was purchased from Ticona Co.

All the materials were dried at 120 ºC in vacuum for at least 12 h to minimize the effect of moisture before being used. PTT/PET/TLCP ternary blends were prepared by a modular twin screw extruder. The blending composition and sample codes are shown in Table-1.

TABLE-1
BLENDING COMPOSITION AND SAMPLE CODES

Sample No	PTT (%)	PET (%)	TLCP (%)
PTE	50.0	50.0	0
PTEL5	47.5	47.5	5
PTEL10	45.0	45.0	10
PTEL15	42.5	42.5	15
PTT	100.0	0.0	0
PET	0.0	100.0	0

The temperatures of heating zones from hopper to die were set to 270, 285, 285 and 275 ºC, respectively and screw speed was fixed at 50 rpm. For thermal analysis experiments, differential scanning calorimeter (DSC) was used. The samples were first heated from room temperature to 290 ºC at 5 ºC/min, held for 5 min to remove the thermal history and quenched to room temperature. The morphologies of the blend samples were observed with a scanning electron microscope (SEM). The measured blend samples were broken in liquid nitrogen and then the fracture surfaces were sputter-coated in vacuum with gold before scanning to prevent charging in the electron beam. The melt flow behaviour and viscoelastic properties were studied by using a rheometric mechanical spectrometer (RMS). Pure PTT, PET, TLCP and blend samples melt -pressed into circular disks of 1 mm in thickness and 25 mm in diameter. Before each measurement the measuring chamber was heated to 290 ºC.

RESULTS AND DISCUSSION

Thermal behaviour: The heat of fusion and the crystallinity of the PTT/PET/TLCP blends were measured by DSC. Table-2 gives the relevant numerical data. The heat of fusion and crystallization for the PTT/PET/TLCP blends have been normalized with respect to TLCP content. Fig. 1 shows the heat of fusion as a function of TLCP content for PTT/PET/TLCP blends. The heat of fusion showed a maximum at about 10 wt % of TLCP and it was decreased with increasing TLCP content. That is the 10 wt % system had a heat of fusion of (based on the mass of PTT/PET in the blends) 45.80 J/g compared to 42.61 J/g for the PTT/PET control. This initial increase of heat of fusion may be indirect evidence of an increase in per cent crystallinity of the blends. Further, it indicates that the addition of small amounts of TLCP enhanced the formation of crystallites or the crystallization process[25,26]. Fig. 2 shows the crystallinity as a function of TLCP content for PTT/PET/TLCP blends. The crystallinity of PTT/PET/TLCP blends Xc showed a maximum at 10 wt % of TLCP and then decreased at higher TLCP content. The addition of small amounts of TLCP enhanced the formation of crystallites. The values of Xc can be calculated from $Xc = \Delta Hm/\Delta$, where (PTT/PET) = 76.24 J/g is the heat of fusion calculated for 100 % crystalline PTT/PET. It should be noted that the crystallinity calculated by this method is an apparent value. It can be considered only as a measure of the amount of crystalline phase and not necessarily a description and regularity of the lamellas[25]. The cold crystallization temperatures as a function of TLCP content for PTT/PET/TLCP blends are shown in Table-2. The PTT/PET sample blend was not showed a cold crystallization temperature peak and heat of cold crystallization. But ternary blend sample with 5 % TLCP content showed a cold crystallization temperature peak at 120.50 ºC which indicates that it is an efficient nucleating agent for PTT/PET matrix. The ability for TLCP to perform as nucleating agents has been observed in several other systems too[27]. This result showed no significant melt depuration while the heat of crystallization (ΔHc) of the blends was found to be slightly lower than those predicted form additive rule indicating small compatibility between PTT/PET and TLCP phases.

TABLE-2
THERMAL PROPERTIES OF PTT/PET/TLCP BLENDS

Sample	T_g (ºC)	T_m (ºC)		T_c (ºC)	ΔH_m (J/g)	$\Delta H'_m$ (J/g)	ΔH_c (J/g)	$\Delta H'_c$ (J/g)
		T_{mPTT} (ºC)	T_{mPET} (ºC)					
PTE	62.74	223.80	251.68	–	42.61	76.24	–	67.26
PTEL 5	62.21	223.96	249.89	120.50	43.87	72.42	23.09	63.89
PTEL 10	65.23	221.16	244.23	124.67	45.80	68.61	31.10	60.53
PTEL 15	65.15	222.67	249.34	124.95	41.04	64.80	23.03	57.17
PET	80.66	260.13	202.31	71.11	–	65.07	–	
PTT	59.76	230.84	183.94	81.36	–	69.37	–	
TLCP	–	286.21	–	–	–	–	–	

T_g = Glass transition temperature; T_c = Cold crystallization temperature; ΔH_c = Heat of cold crystallization of the blends; $\Delta H'_c$ = Heat of cold crystallization based on the mass of PTT/PET in the blends; T_m = Melting temperature; ΔH_m = Heat of fusion of the blends; $\Delta H'_m$ = Heat of fusion based on the mass of PTT/PET in the blend0.

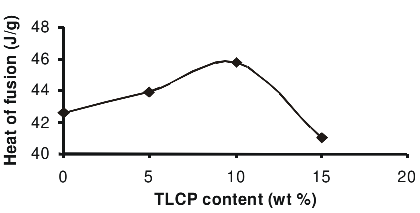

Fig. 1. Heat of fusion of PTT/PET/TLCP ternary blends as a function of TLCP content; based on the mass of PTT/PET in the blend

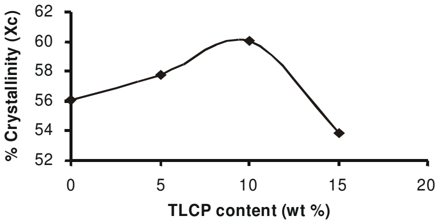

Fig. 2. % Crystallinity of PTT/PET/TLCP blends as a function of TLCP content; based on the mass of PTT/PET in the blend

Rheological properties: Results of melt viscoelastic measurements prepared on the blend components and the ternary blend samples are shown in Fig. 3. These results showed an almost similar pseudo plastic type behaviour with nearly equal viscosity for PTT and PET neat polymers in whole range of frequency (Shear rate) (0.1-1000 1/s) while the TLCP exhibited a pronounced viscosity upturn and nonterminal behaviour for storage modulus (G´) at low frequency range.

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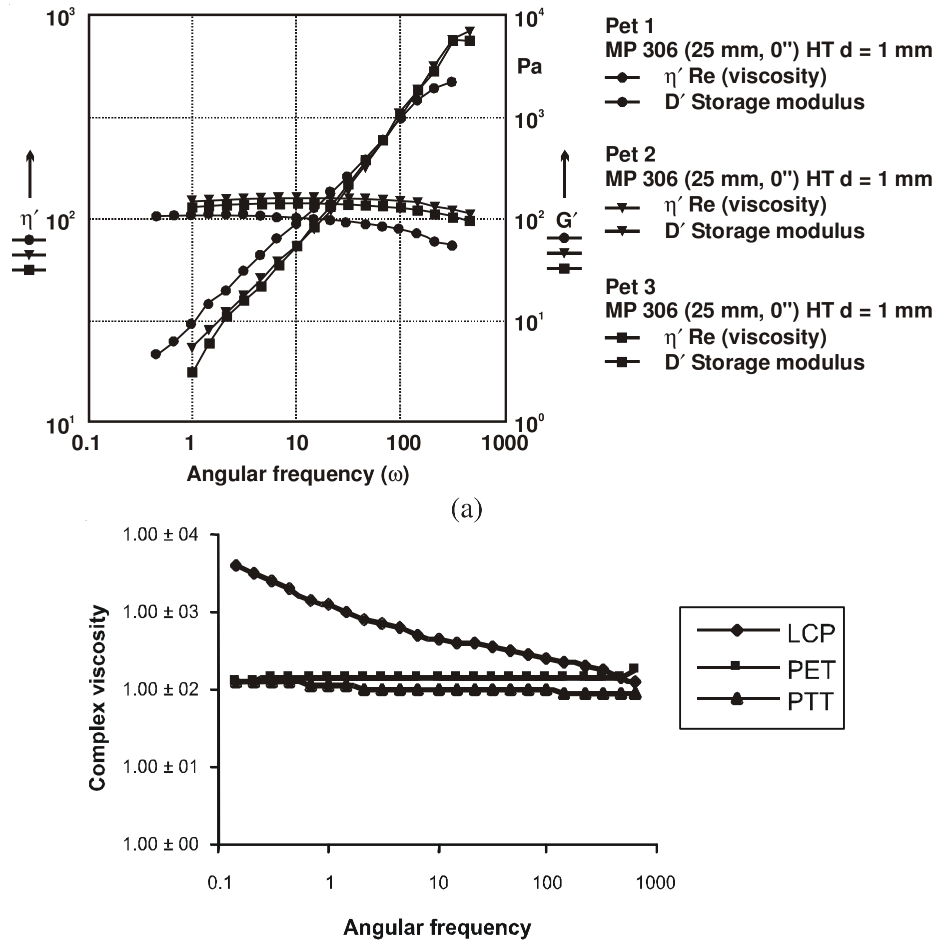
Morphology: The results of DSC and SEM micrographs showed that PTT and PET are almost miscible. A typical SEM morphology obtained for PTT/PET



(a)

(b)

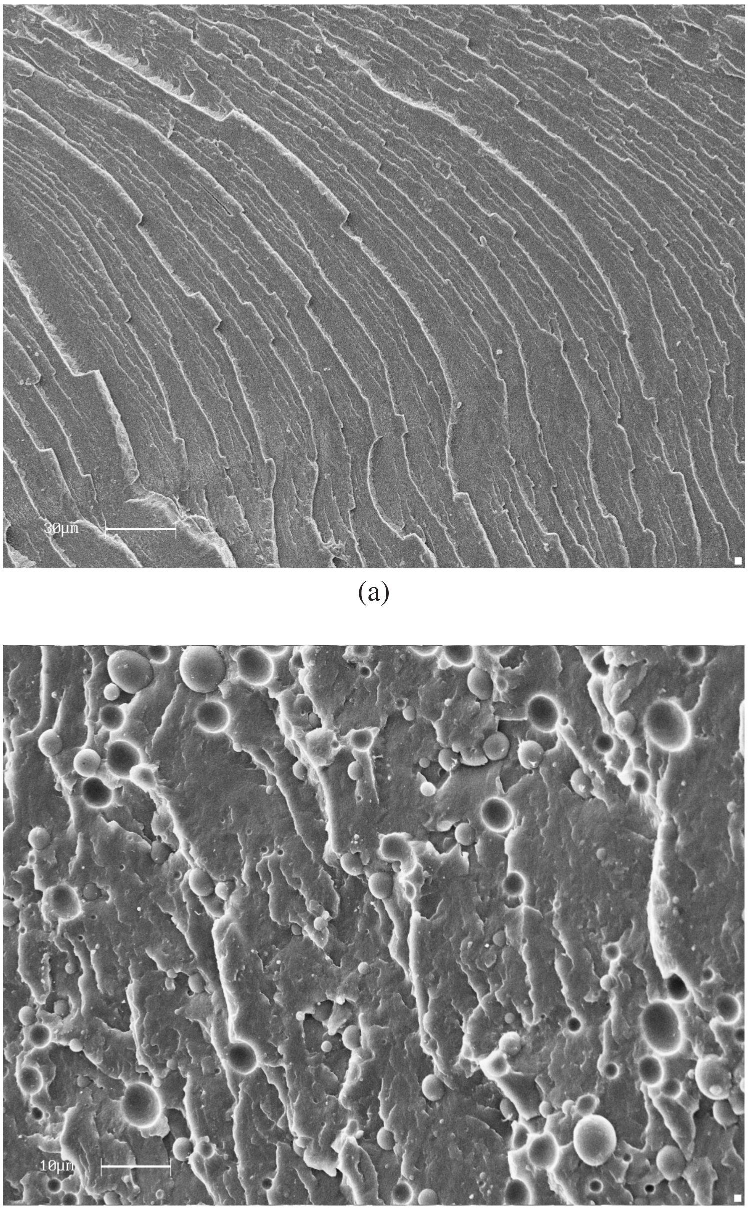
Fig. 3. Results of melt viscoelastic measurements

binary blend and PTT/PET/TLCP ternary blend samples is shown in Fig. 4. In all blend samples, the TLCP phase was uniformly dispersed in the PTT/PET matrix.

The TLCP average diameter in ternary samples prepared by twin screw extruder was found to be smaller than those produced in internal mixer.

Conclusion

The SEM results showed a matrix disperses type morphology in which TLCP phase was uniformly dispersed in polymer matrix. The viscoelastic properties of ternary blends was predominately controlled by matrix components and indicating that TLCP phase remains as dispersed droplets in the matrix. This result showed no significant melt depuration while the heat of crystallization (ΔHc) of the blends was found to be slightly lower than those predicted form additive rule indicating small compatibility between PTT/PET and TLCP phases.



(a)

(b)

Fig. 4. SEM micrographs of (a) PTT/PET binary blend (b) PTT/PET/TLCP ternary blend

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